



# Novel group of negative photochromes containing a nitrile-rich acceptor: synthesis and photochromic properties

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## Abstract

An approach to the synthesis of novel group of negative photochromes has been developed based on the interaction of the tricyanofuran TCF or hydroxytricyanopyrrole HTCP acceptors with methoxy-substituted 2-hydroxybenzaldehydes in ethanol in the presence of ammonium acetate. An essential part of the obtained photochromes is a combination of a phenol fragment and a butadienetricarbonitrile BDTC acceptor connected via a vinylene bridge. The synthesized compounds are sensitive to visible light T-type photochromes. A transformation degree of the initial form, as well as the rate of the reverse dark reaction, can be varied by changing both the position of a methoxy group at aromatic ring and the type of the heterocycle with the BDTC fragment.

**Keywords** Negative photochromism · Tricyanofuran TCF · Hydroxytricyanopyrrole HTCP · Butadienetricarbonitrile fragment BDTC · Cyano groups · Donor–acceptor chromophores

## Introduction

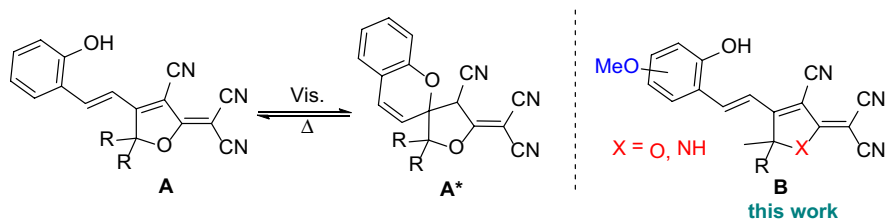
Photochromic compounds are intensively studied objects because of the great opportunities for their use as photo-switching components for biological research [1–5], various materials [6–8], nanosystems [9] and supramolecular chemistry [10, 11]. Most of the works in this field of research are related to positive photochromism. This is the phenomenon when the photo-induced form of a molecule has a deeper color than the original one. The reverse (negative) photochromism, when the colored

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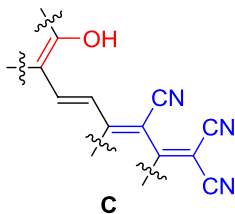
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**Fig. 1** Known representatives of TCF photochromes **A** and **B** compounds studied in this work

**Fig. 2** The general formula of a new group of negative photochromes containing a nitrile-rich acceptor and a 2-vinylphenol fragment



initial form of a molecule reversibly becomes less colored under the action of irradiation (mostly by visible light), is much less studied.

An obvious advantage for the practical use of negative photochromes is the possibility to use visible light, which is less destructive for organic compounds and living systems than ultraviolet radiation. In this regard, research on new groups of reverse photochromes with widely varying practically significant properties is an important task.

There are several known groups of negative photochromes such as spiropyrans [12–15], 1,1'-binaphthyl-bridged imidazole dimers [16–18], dihydropyrenes [19–21] and Stenhouse adducts [22–25]. Results of the research on the reverse photochromes from all over the world have been recently summarized and collected in two review articles in 2017 and 2018 [26, 27]. However, there is only a little information about a new type of reverse photochrome **A**, which consists of a tricyanofuran (TCF) moiety (Fig. 1).

Only two examples of compounds **A** have been described, and an interaction of 2-(3-cyano-4-methylfuran-2(5*H*)-ylidene)malononitriles (TCF) with salicylic aldehyde was used for the synthesis [28, 29]. During the photochromic transformation, a colored form, **A**, becomes colorless under the action of visible light due to the formation of a spiro derivative **A\***, which is able to thermally transform back into the original form **A**. Based on these single data, it can be assumed that a system **C** consisting of a butadienetricarbonitrile (BDTC) acceptor and a phenolic fragment, bridged by a double bond, is necessary for photochromic transformations (Fig. 2).

We believe that an investigation of compound **C** is promising for discovering of a new wide group of negative photochromes, due to a variety of substituents being possible in the phenolic fragment. The literature on the chemistry of photochromes of this series does not reveal the effect of the substituent at the aryl moiety on the photochromic behavior and other physicochemical properties of compound **A**, since

only unsubstituted salicylic aldehyde was used. It is also important that only the TCF fragment is reported as the BDTC acceptor, and there is no information about the use of other acceptors in structures of type **C**.

In this regard, the purpose of this work is to show the possibility of varying the position of the substituent at the aryl ring, as well as changing the nitrile-rich acceptor, to synthesize novel negative photochromes with easily adjustable physicochemical characteristics.

## Experimental

### Materials and methods

The progress of the reactions and the purity of the 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 a FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO- $d_6$  on a Bruker DRX-500 spectrometer using tetramethylsilane as an internal reference. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The mass spectra were obtained on a gas chromatograph mass spectrometer (Shimadzu GCMS-QP2010S). The UV spectra were recorded on an Agilent Cary 60 UV-Vis Spectrophotometer. Melting points were determined on an OptiMelt MPA100 device.

### Synthesis and spectral data

**Typical procedure for the preparation of methoxy substituted (E)-2-(3-cyano-4-(2-hydroxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitriles 2a–d.** To a suspension of 0.199 g (1 mmol) of TCF acceptor **1a** in 2 mL of 96% ethanol 1.05 mmol of an appropriate methoxy substituted 2-hydroxybenzaldehyde and 0.077 g (1 mmol) of dry ammonium acetate were added. The resulting mixture was stirred at 40–50 °C for 10 min, then for 1–2 h at room temperature (TLC controlled). After the reaction completion, the mixture was cooled to 0–5 °C then the precipitated product was filtered, washed with cold ethanol and dried in a vacuum desiccator over CaCl<sub>2</sub> to constant weight.

**(E)-2-(3-cyano-4-(2-hydroxy-3-methoxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile 2a.** Mp 244–245 °C (dec.). <sup>1</sup>H NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.76 (6H, s, 2CH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 6.89 (1H, t,  $J$ =8.0 Hz, C<sub>6</sub>H<sub>3</sub>), 7.12 (1H, dd,  $J$ =8.0, 1.2 Hz, C<sub>6</sub>H<sub>3</sub>), 7.33 (1H, d,  $J$ =16.5 Hz, CH=), 7.45–7.48 (1H, m, C<sub>6</sub>H<sub>3</sub>), 8.27 (1H, d,  $J$ =16.5 Hz, CH=), 10.04 (1H, s, OH). <sup>13</sup>C NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  25.09, 53.88, 56.19, 97.31, 99.22, 111.36, 112.01, 112.88, 115.09, 115.38, 119.52, 121.02, 121.50, 143.49, 147.92, 148.15, 176.07, 177.45. MS, (EI, 70 eV):  $m/z$  (%) 333 [M]<sup>+</sup> (100), 318 [M–Me]<sup>+</sup> (17), 248 (76). IR (mineral oil, cm<sup>-1</sup>): 3224 (OH),

2228 (CN). 1631 (C=C). Anal. Calcd for  $C_{19}H_{15}N_3O_3$ : C, 68.46; H, 4.54; N, 12.61. Found: C, 68.32; H, 4.59; N, 12.75.

**(E)-2-(3-cyano-4-(2-hydroxy-4-methoxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile 2b.** Mp 234–235 °C (dec.).  $^1H$  NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.75 (6H, s, 2CH<sub>3</sub>), 3.81 (3H, s, OCH<sub>3</sub>), 6.48 (1H, d,  $J$ =2.4 Hz, C<sub>6</sub>H<sub>3</sub>), 6.57 (1H, dd,  $J$ =8.9, 2.5 Hz, C<sub>6</sub>H<sub>3</sub>), 7.27 (1H, d,  $J$ =16.3 Hz, CH=), 7.83 (1H, d,  $J$ =8.9 Hz, C<sub>6</sub>H<sub>3</sub>), 8.16 (1H, d,  $J$ =16.3 Hz, CH=), 11.07 (1H, s, OH).  $^{13}C$  NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  25.34, 52.54, 55.47, 94.72, 98.53, 100.86, 107.64, 111.47, 112.02, 112.11, 112.97, 115.07, 132.48, 144.54, 160.81, 164.72, 176.62, 177.28. MS, (EI, 70 eV):  $m/z$  (%) 333 [M]<sup>+</sup> (100), 318 [M–Me]<sup>+</sup> (23), 248 (100). IR (mineral oil, cm<sup>-1</sup>): 3246 (OH), 2226 (CN). 1624 (C=C). Anal. Calcd for  $C_{19}H_{15}N_3O_3$ : C, 68.46; H, 4.54; N, 12.61. Found: C, 68.39; H, 4.62; N, 12.70.

**(E)-2-(3-cyano-4-(2-hydroxy-5-methoxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile 2c.** Mp 258–259 °C (dec.).  $^1H$  NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.77 (6H, s, 2CH<sub>3</sub>), 3.76 (3H, s, OCH<sub>3</sub>), 6.98 (1H, d,  $J$ =8.9 Hz, C<sub>6</sub>H<sub>3</sub>), 7.01 (1H, dd,  $J$ =8.9, 3.1 Hz, C<sub>6</sub>H<sub>3</sub>), 7.39 (1H, d,  $J$ =3.1 Hz, C<sub>6</sub>H<sub>3</sub>), 7.43 (1H, d,  $J$ =16.4 Hz, CH=), 8.18 (1H, d,  $J$ =16.4 Hz, CH=), 10.42 (1H, s, OH).  $^{13}C$  NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  25.20, 53.74, 55.74, 97.24, 99.16, 111.34, 112.04, 112.91, 113.08, 115.26, 117.57, 121.40, 121.67, 143.96, 152.45, 153.04, 176.28, 177.41. MS, (EI, 70 eV):  $m/z$  (%) 333 [M]<sup>+</sup> (72), 318 [M–Me]<sup>+</sup> (18), 248 (100). IR (mineral oil, cm<sup>-1</sup>): 3290 (OH), 2222 (CN). 1607 (C=C). Anal. Calcd for  $C_{19}H_{15}N_3O_3$ : C, 68.46; H, 4.54; N, 12.61. Found: C, 68.30; H, 4.64; N, 12.77.

**(E)-2-(3-cyano-4-(2-hydroxy-6-methoxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile 2d.** Mp 282–283 °C (dec.).  $^1H$  NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.76 (6H, s, 2CH<sub>3</sub>), 3.89 (3H, s, OCH<sub>3</sub>), 6.57–6.60 (2H, m, C<sub>6</sub>H<sub>3</sub>), 7.33 (1H, t,  $J$ =8.3 Hz, C<sub>6</sub>H<sub>3</sub>), 7.63 (1H, d,  $J$ =16.5 Hz, CH=), 8.15 (1H, d,  $J$ =16.5 Hz, CH=), 11.04 (1H, s, OH).  $^{13}C$  NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  25.87, 53.48, 56.29, 97.23, 98.48, 102.43, 108.88, 110.77, 111.18, 112.11, 112.93, 116.60, 134.92, 140.09, 159.98, 160.62, 177.22, 177.28. MS, (EI, 70 eV):  $m/z$  (%) 333 [M]<sup>+</sup> (93), 318 [M–Me]<sup>+</sup> (20), 248 (100). IR (mineral oil, cm<sup>-1</sup>): 3226 (OH), 2231 (CN). 1611 (C=C). Anal. Calcd for  $C_{19}H_{15}N_3O_3$ : C, 68.46; H, 4.54; N, 12.61. Found: C, 68.42; H, 4.62; N, 12.73.

**Typical procedure for the preparation of methoxy substituted (E)-2-(3-cyano-5-hydroxy-4-(2-hydroxystyryl)-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitriles 2e–h.** To a suspension of 0.2 g (1 mmol) of 2-(3-cyano-5-hydroxy-4,5-dimethyl-1H-pyrrol-2(5H)-ylidene)malononitrile **1b** HTCP in 2 mL of 96% ethanol 1.05 mmol of an appropriate methoxy substituted 2-hydroxybenzaldehyde and 0.077 g (1 mmol) of dry ammonium acetate were added. The resulting mixture was stirred at room temperature for 4–8 h (TLC controlled). After the reaction completion, the mixture was cooled to 0–5 °C then precipitated product was filtered, washed with cold ethanol and dried in a vacuum desiccator over CaCl<sub>2</sub> to constant weight.

**(E)-2-(3-cyano-5-hydroxy-4-(2-hydroxy-3-methoxystyryl))-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitrile 2e.** Mp 171–172 °C (dec.).  $^1\text{H}$  NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.67 (3H, s, CH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 6.87 (1H, t,  $J=8.0$  Hz, C<sub>6</sub>H<sub>3</sub>), 7.09 (1H, dd,  $J=8.0$ , 1.2 Hz, C<sub>6</sub>H<sub>3</sub>), 7.19 (1H, s, OH pyrrol), 7.23 (1H, d,  $J=16.4$  Hz, CH=), 7.28–7.31 (1H, m, C<sub>6</sub>H<sub>3</sub>), 8.17 (1H, d,  $J=16.4$  Hz, CH=), 9.80 (1H, s, OH), 10.53 (1H, s, NH).  $^{13}\text{C}$  NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  25.90, 44.17, 56.13, 93.61, 99.06, 111.92, 114.13, 114.58, 115.34, 115.96, 119.61, 120.02, 121.75, 141.69, 147.21, 148.12, 160.40, 171.27. MS, (EI, 70 eV):  $m/z$  (%) 334 [M]<sup>+</sup> (4), 318 (100), 316 [M-H<sub>2</sub>O]<sup>+</sup> (81). IR (mineral oil, cm<sup>-1</sup>): 3350–3220 (OH, NH), 2223 (CN). 1593 (C=C). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 64.66; H, 4.22; N, 16.76. Found: C, 64.50; H, 4.31; N, 16.55.

**(E)-2-(3-cyano-5-hydroxy-4-(2-hydroxy-4-methoxystyryl))-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitrile 2f.** Mp 163–164 °C (dec.).  $^1\text{H}$  NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.65 (3H, s, CH<sub>3</sub>), 3.79 (3H, s, OCH<sub>3</sub>), 6.49 (1H, t,  $J=2.4$  Hz, C<sub>6</sub>H<sub>3</sub>), 6.54 (1H, dd,  $J=8.8$ , 2.4 Hz, C<sub>6</sub>H<sub>3</sub>), 7.11 (1H, s, OH pyrrol), 7.18 (1H, d,  $J=16.2$  Hz, CH=), 7.64 (1H, d,  $J=8.8$  Hz, C<sub>6</sub>H<sub>3</sub>), 8.07 (1H, d,  $J=16.2$  Hz, CH=), 10.36, 10.78 (2H, br s, NH, OH).  $^{13}\text{C}$  NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  26.50, 43.88, 55.80, 93.73, 97.01, 101.84, 107.66, 112.61, 113.65, 114.64, 115.58, 115.86, 131.58, 142.89, 160.29, 161.06, 164.15, 172.40. MS, (EI, 70 eV):  $m/z$  (%) 334 [M]<sup>+</sup> (3), 318 (50), 316 [M-H<sub>2</sub>O]<sup>+</sup> (85). IR (mineral oil, cm<sup>-1</sup>): 3355–3230 (OH, NH), 2221 (CN). 1590 (C=C). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 64.66; H, 4.22; N, 16.76. Found: C, 64.54; H, 4.34; N, 16.60.

**(E)-2-(3-cyano-5-hydroxy-4-(2-hydroxy-5-methoxystyryl))-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitrile 2g.** Mp 156–157 °C (dec.).  $^1\text{H}$  NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.68 (3H, s, CH<sub>3</sub>), 3.75 (3H, s, OCH<sub>3</sub>), 6.88 (1H, d,  $J=8.9$  Hz, C<sub>6</sub>H<sub>3</sub>), 6.96 (1H, dd,  $J=8.9$ , 3.0 Hz, C<sub>6</sub>H<sub>3</sub>), 7.15 (1H, s, OH pyrrol), 7.20 (1H, d,  $J=3.0$  Hz, C<sub>6</sub>H<sub>3</sub>), 7.33 (1H, d,  $J=16.4$  Hz, CH=), 8.09 (1H, d,  $J=16.4$  Hz, CH=), 10.18 (1H, s, OH), 10.50 (1H, s, NH).  $^{13}\text{C}$  NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  25.87, 44.14, 55.69, 93.59, 98.83, 111.96, 112.08, 114.12, 115.35, 116.21, 117.49, 120.52, 121.73, 142.04, 152.29, 152.50, 160.47, 171.44. MS, (EI, 70 eV):  $m/z$  (%) 334 [M]<sup>+</sup> (2), 318 (71), 316 [M-H<sub>2</sub>O]<sup>+</sup> (35). IR (mineral oil, cm<sup>-1</sup>): 3340–3205 (OH, NH), 2226 (CN). 1586 (C=C). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 64.66; H, 4.22; N, 16.76. Found: C, 64.48; H, 4.35; N, 16.58.

**(E)-2-(3-cyano-5-hydroxy-4-(2-hydroxy-6-methoxystyryl))-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitrile 2h.** Mp 152–153 °C (dec.).  $^1\text{H}$  NMR (500.13 MHz, DMSO- $d_6$ ):  $\delta$  1.67 (3H, s, CH<sub>3</sub>), 3.86 (3H, s, OCH<sub>3</sub>), 6.57 (2H, d,  $J=8.3$  Hz, C<sub>6</sub>H<sub>3</sub>), 7.27 (1H, t,  $J=8.3$  Hz, C<sub>6</sub>H<sub>3</sub>), 7.13 (1H, s, OH pyrrol), 7.72 (1H, d,  $J=16.4$  Hz, CH=), 8.27 (1H, d,  $J=16.4$  Hz, CH=), 10.45 (1H, s, OH), 10.78 (1H, s, NH).  $^{13}\text{C}$  NMR (125.67 MHz, DMSO- $d_6$ ):  $\delta$  26.26, 43.69, 56.13, 93.36, 97.94, 102.37, 108.88, 111.07, 112.14, 114.27, 115.48, 118.13, 133.58, 138.72, 159.44, 160.27, 160.55, 172.93. MS, (EI, 70 eV):  $m/z$  (%) 334 [M]<sup>+</sup> (2), 318 (15), 316 [M-H<sub>2</sub>O]<sup>+</sup> (46). IR (mineral oil, cm<sup>-1</sup>): 3355–3160 (OH, NH), 2214 (CN). 1597 (C=C). Anal.

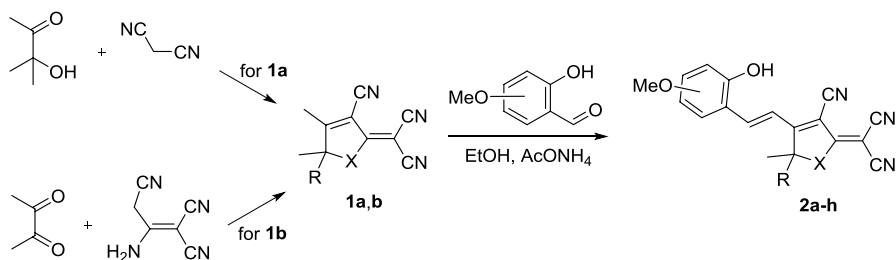
Calcd for  $C_{18}H_{14}N_4O_3$ : C, 64.66; H, 4.22; N, 16.76. Found: C, 64.53; H, 4.29; N, 16.63.

## Results and discussion

In this work, a methoxy group was used as a model substituent; its position was varied across the entire ring of the 2-vinylphenol fragment (Scheme 1). TCF **1a**-based tricyanofuran derivative, as well as HTCP **1b**-based hydroxytricyanopyrrole derivative, were used as a nitrile-rich acceptor. These two BDTC acceptors were chosen because the TCF derivatives had been already used for the synthesis of negative photochromes of the studied group [28, 29], and the HTCP molecules are the closest structural analogues of TCF from all the structures described in the literature [30]. The similarities between TCF and HTCP are the presence of the BDTC acceptor and the geometry of the substituents in heterocycles. The bigger reactivity is another reason to use the less-studied HTCP acceptors for the synthesis of negative photochromes. They can be used to adjust the physicochemical properties of chromophores if necessary [31].

The starting acceptors are synthetically readily available. TCF **1a** was obtained in 52% yield from malononitrile and the hydroxyketone in pyridine in the presence of acetic acid [32], HTCP **1b** was synthesized in 78% yield by the reaction of malononitrile dimer with diacetyl in aqueous ethanol in the presence of sodium hydroxide [30]. The synthesis of the desired chromophores **2a–h** was carried out by the interaction of acceptors **1a, b** with methoxy-substituted salicylic aldehydes in ethanol in the presence of ammonium acetate. The transformation occurred within 1–8 h and resulted in a series of unknown compounds **2a–h** with moderate to good yields of 48–90% (Scheme 1; Table 1).

The structure of compounds **2** is considered with the data of IR,  $^1H$  and  $^{13}C$  NMR spectroscopy, mass spectrometry and elemental analysis. A characteristic feature of the  $^1H$  NMR spectra of compounds **2** is the presence of signals of two vicinal vinyl protons in the 7.27–8.27 ppm region with the coupling constant of 16.2–16.5 Hz, showing the *E*-configuration of a double bond. The presence of a phenolic hydroxyl is proved by the signal at 9.80–11.07 ppm, while the protons of a methoxy group appear at 3.75–3.89 ppm. The characteristic of  $^{13}C$  NMR



Scheme 1 Synthesis of compounds **2a–h**

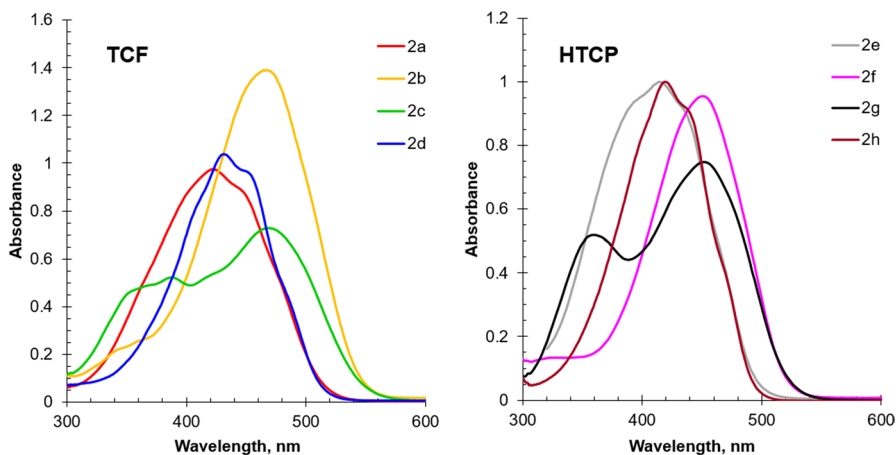
**Table 1** Synthesis of compounds **2a–h**

Entry	Substrate	MeOC <sub>6</sub> H <sub>3</sub>	R	X	Product	Yield % <sup>a</sup>
1	1a	3-MeO	Me	O	2a	87
2	1a	4-MeO	Me	O	2b	70
3	1a	5-MeO	Me	O	2c	66
4	1a	6-MeO	Me	O	2d	90
5	1b	3-MeO	OH	NH	2e	57
6	1b	4-MeO	OH	NH	2f	62
7	1b	5-MeO	OH	NH	2g	71
8	1b	6-MeO	OH	NH	2h	48

<sup>a</sup>Isolated yield

spectra of compounds **2** is an appearance of signals of three cyano groups at 111.18–115.48 ppm and of small intense signals of C-atoms of  $\underline{C}(\text{CN})_2$  fragments at 43.69–53.88 ppm. The mass spectra are characterized by the presence of peaks of molecular ions  $[\text{M}]^+$  with 2–100% intensity.

The light absorption properties of all compounds **2** were studied in THF solutions at  $2.5 \times 10^{-5}$  M. Absorption bands were characterized with maxima in the range of 414–470 nm and the molar extinction coefficient about  $2.98\text{--}4.59 \times 10^4$  (Fig. 3, Table 2). The shortest wavelength absorption (414–431 nm) was observed for the 3- and 6-MeO-derivatives, while 4- and 5-methoxy-substituted chromophores were absorbed at the longest wavelength region (450–470 nm). A type of the heterocycle also affected the absorption properties: the HTCP derivatives **2e–h** have a hypsochromic shift of the absorption maxima by 8–18 nm in comparison with the corresponding TCF compounds **2a–d**.

**Fig. 3** Absorption spectra of compounds **2a–d** (left) and **2e–h** (right) in THF ( $C = 2.5 \times 10^{-5}$  M)

**Table 2** Light absorption and photochromic characteristics of compounds **2a–h**

Comp.	X	MeOC <sub>6</sub> H <sub>3</sub>	$\lambda_{\max}$ (nm)	$\epsilon \times 10^4$ (L × mol <sup>-1</sup> × cm <sup>-1</sup> )	Rate constant, $k^a$	Half-life, $\tau_{1/2}$ (s) <sup>b</sup>	Abs. decrease, % <sup>c</sup>
<b>2a</b>	O	3-MeO	422	3.91	$2.20 \times 10^{-3}$	315	36
<b>2b</b>	O	4-MeO	467	5.54	$2.27 \times 10^{-1}$	3	49
<b>2c</b>	O	5-MeO	470	2.91	$1.14 \times 10^{-7*}$	32	29
<b>2d</b>	O	6-MeO	431	4.59	$3.67 \times 10^{-9*}$	1765	52
<b>2e</b>	NH	3-MeO	414	4.00	$2.45 \times 10^{-3}$	283	31
<b>2f</b>	NH	4-MeO	450	3.82	$1.75 \times 10^{-2}$	40	79
<b>2g</b>	NH	5-MeO	452	2.98	$2.20 \times 10^{-4}$	3150	87
<b>2h</b>	NH	6-MeO	419	4.07	$9.65 \times 10^{-9*}$	1145	90

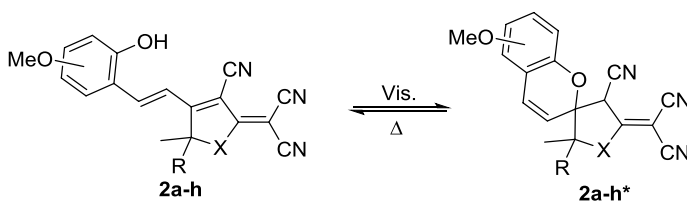
<sup>a</sup>Rate constant of the reverse thermal reaction is in s<sup>-1</sup> (first-order) or in mol × L<sup>-1</sup> × s<sup>-1</sup> (pseudo-zero-order) if marked with an asterisk (\*)

<sup>b</sup>Half-life period of the reverse thermal reaction was found as 0.693/ $k$  (first-order) or as [C<sub>2</sub>]/2 $k$  (pseudo-zero-order)

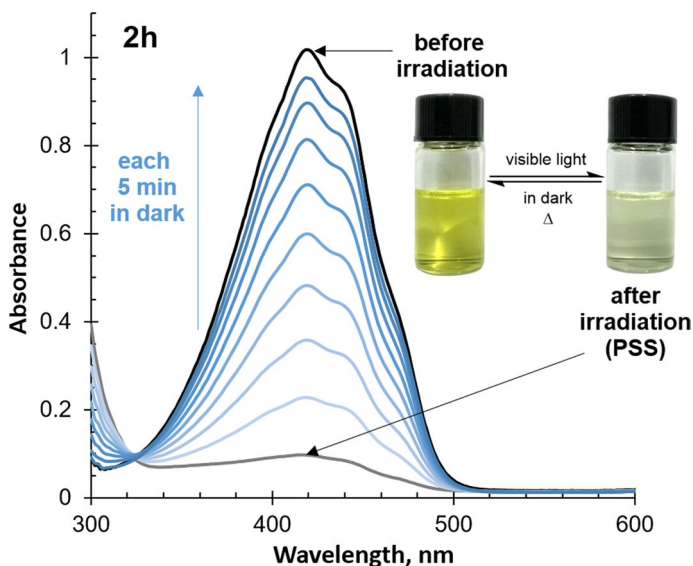
<sup>c</sup>Percentage of the decrease for the long-wavelength absorption band in the photostationary state

The behavior of the THF solutions of compounds **2a–h** under irradiation was studied to evaluate the photochromic properties of the synthesized molecules. We found that all the compounds **2a–h** show negative photochromism under non-filtered visible light irradiation at 20 °C (Scheme 2).

Colored solutions were irradiated with visible light for 3 min to reach a less-colored photo-stationary state (PSS) (Fig. 4). The observed decrease of the long-wave absorbance in the photostationary state varied from 29% for 5-MeOTCF **2c** to 90% for 6-MeOHTCP **2h** (Table 2). An initial absorption was restored in the dark at room temperature apparently due to a reverse thermal transformation of the photo-induced form **2\*** to the starting one **2**. Therefore, all the compounds were found to be thermally unstable (T-type) negative photochromes. We analyzed an influence of the methoxy group position to the photo-transformation degree of compounds **2** and found that the largest decrease of an absorption band among two groups of the TCF **2a–d** and HTCP **2e–h** derivatives is observed for 6-MeO-substituted compounds **2d**—52% and **2h**—90%. Moreover, it can be noted that the HTCP derivatives generally have a better degree of photo-transformation of the initial form in comparison to TCF.

**Scheme 2** Photo-induced transformation of compounds **2a–h**

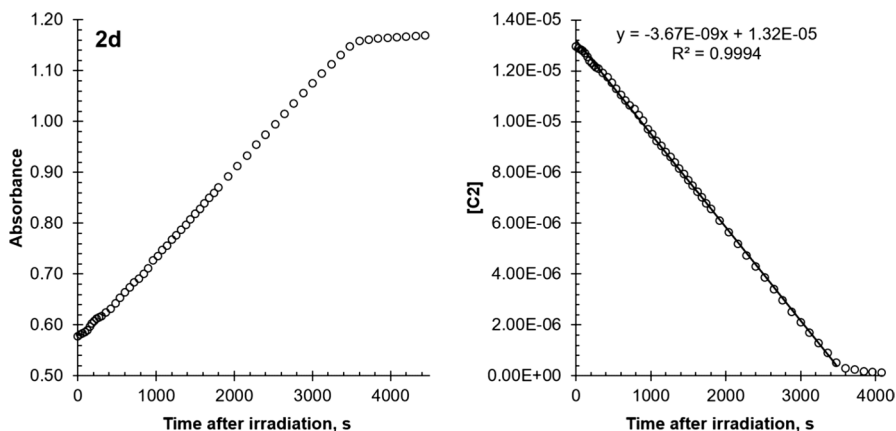




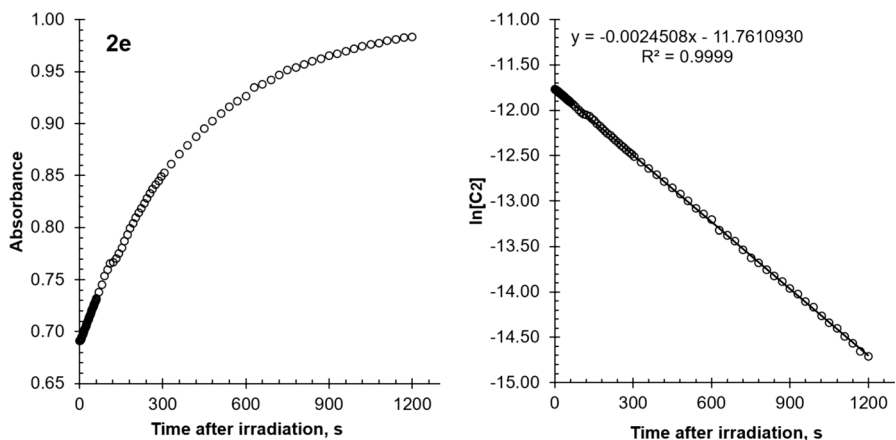
**Fig. 4** Absorption spectra of the compound **2h** in THF ( $C = 2.5 \times 10^{-5}$  M) before and after irradiation

The kinetic curves of the reverse thermal reaction were recorded. It was found that the half-life period ( $\tau_{1/2}$ ) of the photo-induced form **2\*** transformation (Scheme 2) depends on the position of a methoxy group and the type of the heterocycle. We found that  $\tau_{1/2}$  is varied in the range from 3 s for 4-MeOTCF **2b** to 52.5 min for 5-MeOHTCP **2g** (Table 2). The smallest thermal stability was observed for a couple of 4-MeO substituted chromophores **2b** and **2f** ( $\tau_{1/2}$  are 3 s and 40 s, respectively). A photo-induced form of 6-MeO-substituted compounds **2d** and **2h** showed a significantly larger half-life period of about 19–29 min. Accordingly, 3-MeO-substituted chromophores **2a** and **2e** are intermediate in  $\tau_{1/2}$  values which are around 5 min. For these three couples of chromophores, the type of heterocycle affects  $\tau_{1/2}$  insignificantly in comparison with the influence of the methoxy group position. The only exceptions are 5-MeO-substituted compounds **2c** and **2g** for which  $\tau_{1/2}$  values differ dramatically—about 0.5 min and 52.5 min, respectively, and the latter is the highest  $\tau_{1/2}$  that was observed for chromophores **2** (Table 2).

An interesting feature was the observed difference in the kinetics of the reverse thermal transformation. Assuming that there are only two forms in the solution (**2** and **2\***), the concentration of the photo-induced form **2\*** [ $C_2$ ] was evaluated as the difference between the initial concentration ( $C_0 = 2.5 \times 10^{-5}$  M) and the concentration of the form **2** [ $C_1$ ] during the reverse thermal reaction, in which [ $C_1$ ] was found using the optical density values and known molar absorptivity ( $\epsilon$ ) from the Beer–Lambert–Bouguer law. Thus, for the thermal coloration of compounds **2c**, **d**, **h**, the concentrations of the **2\*** forms were fitted in a pseudo-zero-order kinetic equation (Fig. 5, e.g., compound **2d**), whereas for chromophores **2a**, **b**, **e–g**, the concentrations of the photo-induced forms **2\*** were fitted for first-order kinetics (Fig. 6; e.g. compound **2e**).



**Fig. 5** Kinetics of the reverse thermal transformation for the compound **2d** (left), the plot of fitting the concentration of photo-induced form ( $C_2$ ) in a pseudo-zero-order kinetic equation (right)

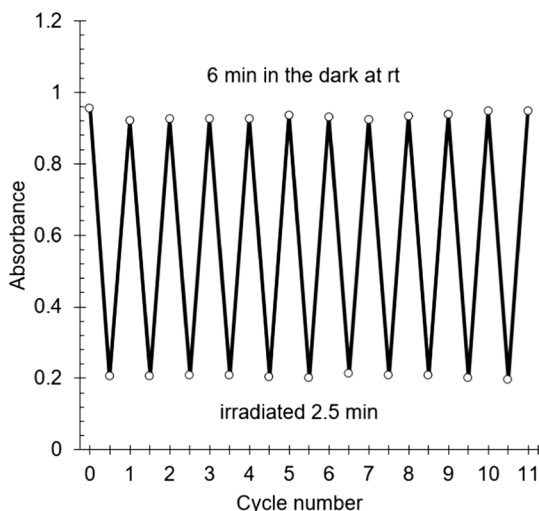


**Fig. 6** Kinetics of the reverse thermal transformation for the compound **2e** (left), the plot of fitting the concentration of photo-induced form ( $C_2$ ) in a first-order kinetic equation (right)

A different rate of the reverse thermal reaction is probably related to the structural features of photo-induced forms **2\***, which are affected by the position of a methoxy group at the aryl ring and the type of a five-membered heterocycle. It also should be noted that, for the known analogue of structures **2\***, a CH-acidity and a dissociation were described [28]. This probably affects the kinetics of the reverse reaction in the case of the compounds studied in this work.

An important characteristic of the photochromic compounds, which largely defines their practical use, is the cyclicity of the transformations. The HTCP acceptor has not previously been reported in any photochromic system, and

**Fig. 7** The photo-thermal cycles of **2f**. For each cycle, the solution of **2f** was irradiated with visible light for 2.5 min, then kept in the dark for 6 min



therefore we studied the cyclicality of the photo-thermal transformations for chromophore **2f** (Fig. 7).

It was found that THF solution of compound **2f** after irradiation with visible light until PSS is reached, followed by keeping the solution in the dark for 6 min, restores the initial absorbance (Fig. 7). This process was repeated 10 times, and after that, the solution was kept in dark for about 10 min, and the final solution showed almost no decrease in the optical density in comparison with the initial solution. This result indicates a good fatigue resistance of compound **2f** as well as a resistance to photodegradation.

## Conclusion

Thus, a series of the TCF and HTCP chromophores have been synthesized, containing a methoxy-substituted 2-vinylphenol fragment. All the obtained compounds were found to be thermally reversible (T-type) negative photochromes in solution, for which a photo-induced form could be generated by the action of visible light. It was found that a degree of photochromic transformation, a thermal stability of the photo-induced form, and the kinetics of the reverse thermal reaction can be varied both by changing the position of the methoxy group at the aryl moiety, and by the type of a nitrile-rich acceptor.

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