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### Isomeric Naphthalimides Bearing Pyran Units: Insight into Mutual

### **Relation between Structure and Photochromic Properties**

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#### **Graphical abstract**



#### Highlights

- Novel naphthopyrans bearing naphthalimide units were synthesized.
- The mutual position of pyran and naphthalimide units effect on the photochromism.
- Long-lived open form of photochrome is due to TT isomer is thermally stable.
- The fluorescence of naphthalimide is switched by photochromic conversion

#### Abstract

Two novel isomeric photochromic naphthopyrans (1 and 2) containing naphthalimide moieties were prepared and studied. In the compound 1, O-atom of pyran cycle is at C-3 position of naphthalene ring, whereas, in compound 2, O-atom of pyran cycle is at C-4 position. In the compound 2 due to *para*-position O-atom of pyran photochrome cycle is involved into the conjugated naphthalimide system. The variety in mutual position of pyran and naphthalimide units leads to remarkable difference in photochromic characteristics. Both compounds demonstrate the switching of the fluorescence by photoinduced conversion between the closed and open forms.

**Keywords:** photoswitching fluorescence, 1,8-haphthalimide, naphthopyran, optical spectroscopy, NMR spectroscopy

#### **1. Introduction**

Nowadays, much attention has been paid to the design, synthesis and working operation of photochemical molecular devices. The development of a device concept to the molecular level is of interest from the fundamental point of view as well as for the growth of supramolecular chemistry, nanoscience and nanotechnology [1]. Molecular and supramolecular devices that show large changes in on-off states are intensively developed as they can be modulated by employing external stimuli such as ions, molecules, light, etc [2]. The switchable states of the molecular-level devices refer to their luminescence, magnetic or electronic properties.

Luminescence is one of the most useful techniques to monitor the operation of molecular devices [3]. A part of this rapidly emerging field is the development of fluorescent sensors, non-destructive data storage, biological fluorescence labeling [4].

Photochromic molecules are able to perform binary states with different fluorescence characteristics [5]. Regulating fluorescence intensity is one of the most attractive uses for molecular photoswitches because of the high sensitivity, resolution, contrast and the fast response provided by fluorescence technology. The realization of the photocontrolled fluorophores requires the design and synthesis of the hybrid photochrome-fluorophore systems where the ecxited state communication between two chromophores has to be effective. A conventional approach to modulating the fluorescence relies on the integration of fluorescent dye and photochromic unit in one molecular skeleton.

Keeping these considerations in mind, we designed and synthesized 3*H*-naphtho[2,1b]pyran (1) and 2H-naphtho[1,2-b]pyran (2) (Scheme 1) bearing naphthalimide units fused to pyran moieties. Naphthalenic acid imides (1,8-naphthalimides) with electron donating substituents attached to the naphthalene moiety are well-known fluorescent dyes high absorption coefficients and high fluorescent quantum yields in the visible region. Such compounds have been used in a large variety of areas, including coloration of polymers and optical brightening [6, 7], laser active media [8], electroluminescent materials [9], optical chemosensors [10] and fluorescent markers in biology [11]. Naphthopyrans are known to exhibit excellent photochromic responses, good colorability, and rapid bleaching [12], and are explored in sensors [13], polymers [14], and organic gels [15].

Recently, naphthalimide units have been incorporated into photochromic spirooxazine, diarylethene systems, especially realizing a significantly long lifetime in the open merocyanine (MC) forms [16]. Two photochromic naphthopyrans containing naphthalimide moieties were studied in solution under flash photolysis conditions, exhibiting predominant thermal reversibility in color-fading and fluorescence switch [17].

The goals of the present investigations are to analyze (i) how the mutual positions of pyran and naphthalimide units in photochromic fluorophore influences on the optical characteristics of closed and open forms (CF and OF respectively); (ii) how the existence of naphthalimide unit with strong electron-withdrawing imide group can somehow change the ratio of *transoid-trans* (TT) and *transoid-cis* (TC), thus facilitating the thermal back to closed form with a preferable color bleaching rate and thermal reversibility; and (iii) how the fluorescence of naphthalimide unit can be switched on-off by photochromic conversion.



Scheme 1. Structures of closed and open forms of compounds 1 and 2.

#### 2. Material and methods

Synthesis of 4- and 3-hydroxy-1,8-naphthalimides (Scheme 2) was carried out according to earlier reports [18-22]. The following procedures describe the experimental details of preparation of target compounds 1 and 2.

#### 5,10,10-triphenylbenzo[de]pyrano[2,3-f]isoquinoline-4,6(5H,10H)-dione (1).

*Method 1*. The procedure was adopted from literature [18]. 3-Hydroxy-1,8-naphthalimide (1.00 g, 3.5 mmol) and 0.70 g (3.5 mmol) of 1,1-diphenylprop-2-yn-1-ol while heating to  $50-55^{\circ}C$  were dissolved in 60 ml of toluene, and 0.06 g (0.35 mmol) of p-toluenesulfonic acid was added. The reaction mixture was stirred at 50-60°C for 1 h and then at 70-80°C for 3-4 hours. The solvent was evaporated. After the column chromatography (eluent PhH – EtOH, v/v = 10/1) 0.13 g of naphthopyran **1** was obtained as a yellow powder (yield was 8%).

*Method* 2. The procedure was adopted from literature [19]. 4-Hydroxy-1,8-naphthalimide (1.0 g, 3.5 mmol) and 0.8 g (3.5 mmol) of  $\beta$ -phenylcinnamaldehyde were dissolved in 60 ml of toluene, and a solution of 1.2 g (5.2 mmol) of titanium (IV) tetraethoxide in 18 ml of toluene was added. The mixture was stirred at 100°C in Ar atmosphere for 6 h, cooled to 30-40°C and 30 ml of toluene, 0.5 g of silicagel and 1 ml of water were added to it. The resulting suspension was stirred at 80°C for 30 min. After cooling to ambient temperature, the precipitate was filtered off, washed with dichloromethane several times, and the organic filtrate was evaporated. After the column chromatography (eluent petroleum ether – ethyl acetate, v/v = 40/1) 0.08 g naphthopyran 1 was obtained as an oil (yield was 5%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.52 (d, J = 8.6 Hz, 1H), 8.42 (d, J = 7.3 Hz, 1H), 8.25 (s, 1H), 7.84 (dd, J = 8.6 and 7.3 Hz, 1H), 7.60-7.51 (m, 6H), 7.42 – 7.30 (m, 10H), 6.80 (d, J = 10.0 Hz, 1H).

<sup>13</sup>C NMR (CD<sub>3</sub>CN, 100 MHz): δ 164.0, 163.4, 152.2, 150.8, 144.1, 133.1, 129.1, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 127.8, 126.6, 124.5, 123.4, 121.9, 121.1, 119.3, 82.6 (22 of 33 carbons found).

Found (%): C, 82.68; H, 4.47; N, 2.99. C<sub>33</sub>H<sub>21</sub>NO<sub>3</sub>. Calculated (%): C, 82.65; H, 4.42; N, 2.92. ESI-MASS, calculated, m/z: 479.52; found: 479.47 ([M+H]<sup>+</sup>).

**5,10,10-triphenylbenzo[de]pyrano[2,3-g]isoquinoline-4,6(5H,10H)-dione (2)** was prepared according to the method 1 from 1.00 g (3.5 mmol) of naphthol **8**, 0.70 g (3.5 mmol) of 1,1-diphenylprop-2-yn-1-ol and 0.06 g (0.35 mmol) of p-toluenesulfonic acid. After the column chromatography (eluent petroleum ether – ethyl acetate, v/v = 10/1) 0.15 g (10% yield) of naphthopyran **2** was obtained as a yellow powder.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.68 (d, J = 8.6 Hz, 1H), 8.60 (d, J = 7.3 Hz, 1H), 8.36 (s, 1H), 7.75 (dd, J = 8.6 and 7.3 Hz, 1H), 7.55 – 7.48 (m, 5H), 7.43 – 7.25 (m, 10H), 6.88 (d, J = 10.0 Hz, 1H), 6.32 (d, J = 10.0 Hz, 1H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 164.5, 164.0, 153.6, 144.0, 136.0, 134.8, 133.2, 132.2, 131.0, 131.2, 130.0, 129.6, 129.2, 128.8, 128.4, 127.2, 126.8, 123.2, 123.0, 117.2, 115.6, 85.6 (22 of 33 carbons found).

Found (%): C, 82.71; H, 4.51; N, 2.97. C<sub>33</sub>H<sub>21</sub>NO<sub>3</sub>. Calculated (%): C, 82.65; H, 4.42; N, 2.92. ESI-MASS, calculated, m/z: 479.52; found: 479.48 ([M+H]<sup>+</sup>).

Electronic absorption spectra were recorded on spectrophotometers Varian-Cary 5G and Avantes AvaSpec-2048. Spectra of the colored forms were obtained when samples in the spectrometer cell were simultaneously exposed to continuous irradiation, generated by Hg high pressure lamp 120W equipped with optical filters (365 and 525 nm). To measure the bleaching lifetime of the colored form **2** (OF**2**), sample was irradiated in the cuvette box of the spectrophotometer. The irradiation was performed till the photostationary conditions (equilibrium between closed and opened forms) were achieved. Then the irradiation was interrupted and the kinetic curves corresponding to the recovery of the system to the initial closed form were recorded. The decay kinetics was monitored at the absorption maximum of the colored forms. To study the kinetics of the naphthopyran **1** photochromic transformation flash photolysis was used. The probing impulse light from a Fil-105 camera flash passed through the sample in a 1 cm quartz cell. Fluorescence spectra were recorded on spectrofluorimeters FluoroLog-3-221 and AvaSpec-2048L. The fluorescence switch was measured using a diode (365 nm). All spectral measurements were carried out in air-saturated solutions at  $20 \pm 1$  °C. The concentrations of studied compounds were of about  $10^{-6}$  m.

LC-ESI-MS analyses were performed on a Finnigan LCQ Advantage mass spectrometer equipped with octopole ion-trap mass-analyzer, MS Surveyor pump, Surveyor auto sampler, Schmidlin-Lab nitrogen generator (Germany), and Finnigan X-Calibur 1.3 software for data collecting and processing. Acetonitrile was used as the mobile phase. The isocratic elution was maintained at a flow rate of 0.1 mL/min without column. The effluent from LC was passed directly into the electrospray ion source without a split. Positive electrospray ionization was achieved using an ionization voltage at 2.5 kV with temperature at 100°C.

NMR experiments were recorded on Bruker Avance 500 MHz spectrometer with a TXI 5mm probe. The experiments were carried out in toluene– $d_8$ . The concentration of solutions used was  $10^{-2}$  M. Temperature ranges used for NMR measurement and irradiation were 193K - 233 K for **1** and 213K-233K for **2**. All UV irradiations were done using a 1000W Xe-Hg high pressure filtered short-arc lamp (Oriel), filtered by band–pass glass filter and interferential filter (365 nm).

The temperature of the sample was controlled with a variable temperature unit (B-VT 1000-Bruker, 123-423K, *T* range).

#### **3. Results and Discussion**

#### 3.1. Synthesis of the naphthalimides 1 and 2.

, The target compounds 1 and 2 were synthesized as illustrated in Scheme 2. The synthesis of 3-hydroxy-1,8-naphthalimide included four steps, the order of synthetic operations was imidation (d) - reduction (a) - diazonium salt formation (b) - hydrolysis (c) (Scheme 2). 4-Hydroxy-1,8-naphthalimide was synthesized from the 4-nitro-1,8-naphthalic anhydride via routine procedure which involved reduction of nitro group (a), formation of diazonium salt (b), hydrolysis (c), and imidation (d) as it was described earlier [20-24]. 2H-Chromene derivative 1 preparation procedure is based on a 'one-pot reaction' starting from a 3-hydroxy-1,8naphthalimide. In our research, two different methods were used for obtaining of **1**. Method 1 (step *e* in Scheme 2) involves the acid-catalyzed reaction of naphthol with propargylic alcohol [18]. The reaction proceeds via Claisen rearrangement of alkynyl aryl ethers resulting from naphthol 'O-alkylation', followed by [1,5]H sigmatropic shift and electrocyclic ring closure. Another approach (method 2) suggests condensation of naphthol with  $\beta$ -phenylcinnamaldehyde in the presence of titanium (IV) ethoxide (step f in Scheme 2) [19]. So as the yields in methods 1 and 2 are comparable, for the synthesis of **2** only method 1 was applied. The chemical structures and composition of compounds were well confirmed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, elemental analysis data and ESI-MS (see the Experimental Section and Supporting Information (SI) for details).



Scheme 2. Synthetic routes to the naphthopyrans 1 and 2. Reagents and conditions: (a)  $SnCl_2 \cdot 2H_2O$ , HCl, AcOH or EtOH, 80°C; (b) 1)  $H_2SO_4$ ,  $NaNO_2$ ,  $H_2O$ , 0-5°C; 2) HBF<sub>4</sub>; (c)  $H_2O$ ,  $H_2SO_4$ , 100°C; (d) PhNH<sub>2</sub>, AcOH, 120°C; (e) 1,1-diphenylprop-2-yn-1-ol, TsOH, MeCN, 25-50°C; (f) 3,3-diphenyl-acrylaldehyde, Ti(OEt)<sub>4</sub>, PhCH<sub>3</sub>, 100°C.

#### 3.2. Optical and photochromic properties of naphthopyrans 1 and 2

All photochromic properties of **1** and **2** induced by photoirradiation at 365 nm were measured in acetonitrile, methylene chloride and toluene solutions under flash photolysis at 293 K. The obtained characteristics are summarized in Table 1 and Figures S1-S14 in SI.

The absorption bands of closed form in the region of 352-355 nm and 412-415 nm for **1** and in region 341-352 nm and 387-392 nm for **2** result from the incorporated naphthalimide moiety into molecular skeleton of naphthopyran (320 nm) (Figure 1, S1-S6 in SI, Table 1) [16b].

#### Table 1

Solvent	Closed form		Open form				
	$\lambda_{\max}^{abs}$ , nm	$\lambda_{\max}^{\text{fluor}}$ , nm	$\phi^{\text{fluor}}$	$\lambda_{\max}^{abs}$ , nm	$\lambda_{\max}^{\text{fluor}}$ , nm	$\tau^{b}$ , s	$\phi^{\text{fluor}}$
Naphthopyran <b>1</b>							
MeCN	352, 412	461	0.09	495	-	0.098	-
CH <sub>2</sub> Cl <sub>2</sub>	355, 415	458	0.14	505	-	0.176	-
Toluene	355, 415	446	0.04	501	-	0.153	-
Naphthopyran 2							
MeCN	341, 388	476	0.12	336, 386, 505	534	532.3	0.005
CH <sub>2</sub> Cl <sub>2</sub>	352, 392	471	0.20	336, 391, 515	-	10.3	-
Toluene	345, 387	461	0.09	343, 387, 520	525	2.7	0.003

Spectral characteristics of compounds 1 and  $2^{a}$ 

<sup>a</sup>As a standard to determine the fluorescence quantum yield of closed and open forms, coumarine 6 and rhodamine 6G in ethanol were used respectively;<sup>b</sup>  $\tau$ <sup>1</sup>/<sub>2</sub> is the half bleaching time.

Upon irradiation of naphthopyran **1** in MeCN with UV light (365 nm), a new visible absorption band centered at 495 nm emerged, while the original peaks in region 352, 412 nm gradually decreased, indicative of the formation of the open MC form (Table 1, and Figures S1-S6 in SI). The spectrum obtained after irradiation of compound **2** includes peaks (336, 386 nm) and longwavelength peak at 505 nm belonging to the merocyanine (MC) form OF**2** (Figure 1a). Some diversity in position of absorption bands of CF or OF of the isomeric naphthopyrans is due to difference in the structures of the chromophores **1** and **2**.

The colored forms of **1** and **2** can be thermally converted back to their closed form when the photoirradiation is ceased. The bleaching kinetics, determined from the absorption-time data sets, can be fitted well to the monoexponential decay in MeCN and  $CH_2Cl_2$  (Figures 1b, Table 1, and Figures S7-S14 in SI). The open form of naphthopyran **2** is stable enough; its  $\tau$  in MeCN is 532.2 s. Open form of compound **1** lives shorter time. The difference in values of life times of open forms OF**1** and OF**2** can be explained by the fact that OF**2** is stabilized by the conjugation between the oxygen atom at C-4 position and carbonyl groups of carboxyimide moiety.

As one can see in Table 1 the variation of life time values in different solvents was observed for **2**. It could be connected with polar betain structure of OF**2** which is more effective stabilized in polar solvent.



**Fig. 1.** a) Absorption spectra of CF2 (solid line), after irradiation for 6 min at 365 nm (dashed line)  $(1 \cdot 10^{-4} \text{ M})$  and after thermal fading (dash-dotted line) in acetonitrile at 293K; b) Thermal fading kinetics of OF2  $(1 \cdot 10^{-4} \text{ M})$  in acetonitrile at 293K. The monitored wavelength was 510 nm.

The photocoloration with light irradiation can induce the formation of two open forms *Transoid-Cis* (TC) and *Transoid-Trans* (TT): while TC isomer rapidly returns to the uncolored closed form, the TT isomer is thermally more stable. After thermal back reaction, the MC forms of **1** in all studied solvents and **2** in MeCN and  $CH_2Cl_2$  are almost transformed to the colorless closed forms (figs. S8, S10, S12, S14 in SI).

When the UV irradiation was ceased, the colored form of 2 in toluene commenced bleaching, and after about 2.7 s, the optical density reduced near to half of its original state value (fig. 2a). Although the thermal back reaction time was maintained for an additional 120 s, the optical density value still maintained stability. That is, the residual visible coloration cannot be spontaneously faded to the full colorless. However, upon 525 nm light irradiation, the residual color can be efficiently faded to colorless state (fig. 2b). The similar phenomenon was mentioned in [17] for naphthalimide derivatives with closed to 2 structure.



**Fig. 2.** a) Thermal fading kinetics of the OF2 ( $C = 4.2 \cdot 10^{-5}$  M) in toluene at 293K; b) timedependent photocoloration cycles of 2 ( $C = 4.2 \cdot 10^{-5}$  M) in toluene upon alternate UV (365 nm) and visible (525 nm) light irradiation. The monitored wavelength was 515nm.

As mentioned above, two steps proceed in the color-faded course, that is, from TT to TC form, and then thermal back to CF forms (usually slow). This means that, for **2**, the thermal relaxation from TT to TC form was extremely slow; it might be the predominant dynamic step in the thermal back process.

Figure 2b performs the fatigue resistance of the studied compound **2**. The present results reveal the slight effect of coloration intensity decrease of as well as a residual visible absorbance remained. We believe that the observed phenomenon might not result from the photodegradation. This is explained by assuming that the TT isomeric photoproduct is thermally stable but photoreversible, and needs to be under visible light to revert to the original colorless form. Aimed to support the idea, we prepare the photocoloration-thermal bleaching cycles at 10 s time of initial irradiation (fig.3). According to data in fig. 2b, the content of long-lived TT form

a)

b)

should be small after so short time of irradiation; this is why the time of photoirradiation was 10 s. Indeed, in this case the decoloration process is thermal; the optical density at a photostationary state after successive coloration and decoloration cycles was not altered (fig. 3).



**Fig. 3.** Time-dependent photocoloration of **2** ( $C = 4.2 \cdot 10^{-5}$  M) in toluene at 293K upon UV (365 nm) light irradiation during 10 s and thermal fading cycles. The monitored wavelength was 515nm.

#### 3.3. NMR studies of the photochromic transformation of naphthopyrans 1 and 2

To get deeper insight into the nature of processes occurring after the irradiation is ceased, we studied photoproduct mixture by NMR spectroscopy. Irradiations of **1** were done at 193, 203, 213, 223 and 233K and thermal relaxation of solution was followed at each temperature by measuring the peak-intensities of signals associated to new photoproducts and residual initial forms (Figure S24). At 213K (fig 4a), three groups of signals corresponding to the residual initial closed form and two new photoproducts were detected. The doublet signal at the most deshielded chemical shift (9.41 ppm) with the transoid coupling constant  ${}^{3}J=11.4$ Hz and its rapid thermal evolution allow to straightforwardly identify the H-2' proton of the TC [25]. The second group of new signals is deduced to correspond to the second open isomer, TT, characterized by the doublet signal at 8.24 ppm, with  ${}^{3}J=11.4$  Hz attributed to the H-1' proton, and a high thermal stability at low temperature and its decrease at highest temperature (Scheme 3).



Scheme 3. Photochromic reaction between 1 and TC1 and TT1 isomers with characteristic chemical shifts  $\delta$  in ppm.

Thermal evolution shows that TC is rapidly decreasing while TT almost remains at the same concentration throughout the time interval when TC is being converted to the closed form (Table 2). From these rate constants, the thermodynamic parameters were calculated using Arrhenius and Eyring equations (Table 3, Figs. S25-S26).



**Fig. 4.** <sup>1</sup>H NMR spectra after UV irradiation of a) naphthopyran **1** at 213K and b) naphthopyran **2** at 223K, with characteristic signals of open forms TC and TT

Irradiation of naphthopyran 2 was carried out and led to the formation of two new photoproducts TC characterized by a doublet signal at 9.38 ppm, with  ${}^{3}J=11.4$  Hz attributed to

the H-2' proton, and TT characterized by a singlet signal at 8.72 ppm attributed to H-7 (Fig. 4b, Scheme 4). The main difference when compared with previously investigated compound 1, concerns the highest conversion into TT isomer, and, in addition its thermal evolution being significant, while stable in the case of TT1. This can be explained by the fact that the TT form of 2 has a lower steric repulsion between hydrogen atoms at positions 7 and 1' in comparison with the steric repultion between H-atoms 1 and 1' in the TT form of compound 1 [26].



Scheme 4. Photochromic reaction between CF2 and TC2 and TT2 isomers with characteristic chemical shifts  $\delta$  in ppm.

Time-evolution of concentration was followed at 213, 223, 228 and 233K by measuring the intensities of characteristic signals for the three species (Figure S32). Using the model (eq. 1), and fitting the concentration profiles, the rate constants  $k_1$ ,  $k_2$  and  $k_3$  were calculated (Table 2) and the thermodynamic parameters extracted (Table 3, Figure S33-S34).

$$2 \stackrel{k_1}{\longleftarrow} TC \stackrel{k_2}{\longleftarrow} TT \quad (1)$$

#### Table 2

Rate constants of thermal relaxation of 1 and 2; Gibbs free energy of activation for TC2  $\leftarrow \rightarrow$ TT2 process.

Т	193 K	203 K	213 K	223 K
$k_1 (\mathrm{TC1} \rightarrow \mathrm{CF1}) / \mathrm{s}^{-1}$	2.5×10 <sup>-5</sup>	$1.85 \times 10^{-4}$	9.0×10 <sup>-4</sup>	3.1×10 <sup>-3</sup>
Т	213 K	223 K	228 K	233 K
$k_1 (\mathrm{TC2} \rightarrow \mathrm{CF2})/\mathrm{s}^{-1}$	$1.24 \times 10^{-5}$	$4.17 \times 10^{-5}$	$8.82 \times 10^{-5}$	$1.78 \times 10^{-4}$
$k_2 (\mathrm{TC2} \rightarrow \mathrm{TT2}) / \mathrm{s}^{-1}$	$4.36 \times 10^{-5}$	$6.85 \times 10^{-5}$	$8.16 \times 10^{-5}$	$1.47 \times 10^{-4}$
$k_3 (\mathrm{TT2} \rightarrow \mathrm{TC2})/\mathrm{s}^{-1}$	8.47×10 <sup>-6</sup>	$1.83 \times 10^{-5}$	$2.30 \times 10^{-5}$	4.68×10 <sup>-5</sup>
$\Delta G^{\#}(kJmol^{-1})$	-2.87	-2.54	-2.34	-2.20

For both investigated compounds 1 and 2, the thermodynamic parameters are lower than the values generally reported for naphthopyrans. [27]. Comparison of 1 with 3-3-diphenyl-3Hnaphtho[2,1-b]pyran [28] and comparison of 2 with 2,2-diphenyl-2*H*-naphtho[1,2-b]pyran [29] show the same trend, that is the predominant formation of TC isomer for 1 and the predominant formation of TT-isomer for 2. However, the thermal stabilities of open forms are greatly affected by the strong electron withdrawing imide groups, leading to their destabilization. Indeed, all rates constants are accelerated.

#### Table 3

Process	Ea (kJ mol <sup>-1</sup> )	<b>∆H</b> <sup>≠</sup> (kJ mol <sup>-1</sup> )	$\Delta S^{\neq} (J \text{ mol}^{-1} \text{K}^{-1})$
TC1 $\rightarrow$ CF1	56.6	59.9	-43.6
TC2 $\rightarrow$ CF2	54.9	53.1	-87.7
$TC2 \rightarrow TT2$	23.3	21.4	-225.7
$TT2 \rightarrow TC2$	33.3	31.5	-192.1

Thermodynamic parameters of thermal relaxation of 1 and 2

#### **3.4. Fluorescence switchable properties**

The studied compounds **1**, **2** combine photochromic pyran and fluorophoric naphthalimide fragments. The absorption of photons generates an excited singlet state from which ring-opening of the pyran ring ensues. Fluorescence emission is also derived from a singlet excited state and it may be that the most efficient (or rapid) energy dissipation process occurs via fluorescence rather than the required electrocyclic bond reorganization leading to the photomerocyanine and hence photochromism. The closed forms of **1** and **2** show the characteristic fluorescence from the naphthalimide moiety in the region of 445-475 nm, whereas, the emission bands of open forms lay between 525 and 535 nm. It was found that the quantum yields of fluorescence of CF**1** and CF**2** are of fair values (see Table 1), thus, photoactivation causes an effective photochromic transformation as well as fluorescence. In case of stable OF**2** we were able to estimate the quantum yield of fluorescence in MeCN and toluene (see Table 1). Its value is low. The reason of this phenomenon could be the more high polar open form in which energy dissipation can occur through the competitive TICT process.

Under the UV light irradiation the intensity of fluorescence diminishes quickly (fig. 5). During the irradiation with visible light (515nm), the fluorescence of the solution can be

recovered. As depicted in Figure 5 and Figures S15-S18 (in SI), upon irradiation with a UV light of 365 nm, the fluorescence intensity of **2** reduced quickly in a few seconds. Upon irradiation for 6 min, the fluorescence reached a photostationary state ( $\lambda_{ex} = 365$  nm,  $\lambda_{em} = 490$  nm), and the intensity reduced by 36%. The process of fluorescence intensity switch can be repeated by using of transformation between the closed and open forms.



**Fig. 5.** Changes in the fluorescence of compound **2** ( $C = 4.2 \cdot 10^{-5}$  M) in acetonitrile upon 365 nm irradiation at room temperature, excitation at 365 nm.

#### 4. Conclusions.

Two new isomeric photochromic naphthopyrans 1 and 2 bearing naphthalimide units have been synthesized and studied. Taking into account the obtained data we are able to do relevant conclusions on the points listed at the beginning of study. (i) The mutual position of pyran and naphthalimide units in photochromic fluorophore influences unsubstantial on the optical characteristics of closed and open forms, but demonstrates large effect on the photochromic photo- and thermal transformation between CF and OF. The involvement of O-atom of pyran photochrome cycle into the conjugated naphthalimide system provides the substantial stabilization of open form of 2. (ii) The NMR analysis of the ratio of TT and TC showed the existing of relatively stable TC form in case of OF1 and large amount of TT form in OF2. So as TC isomer rapidly returns to the uncolored closed form, we observed the fast thermal back reaction OF1 to CF1. The TT isomer of OF2 is thermally more stable, this is why it is possible to obtain the long-lived open form of photochrome 2. (iii) The fluorescence of naphthalimide unit can be switched on-off by photochromic conversion between the closed and open forms.

The analysis of the ways of combination of photochromic and fluorophoric units in one molecule prepared in this study can help in development of promising photoswitchable

candidates for practical applications. The design and synthesis of efficient photoswitchable molecules or systems are essential to execute such applications as components for "single-molecule optical memory" and "super-resolution fluorescence microscopy".

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