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Fluorescent photochromic complex of 1,8-naphthalimide derivative and benzopyrane containing benzo-18-crown-6 ether

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ABSTRACT

We present here design, preparation, characterization, and properties of a photochromic supramolecular complex of benzopyran containing benzo-18-crown-6-ether **1** with 4-aminonaphthalimide **2** as a fluorophore. Phototransformation of the supramolecular complex **1**·**2** is accompanied by the appearance of a predominantly open TC form, which is consistent with the monoexponential bleaching curve of an open form at room temperature. Compared with free benzopyran **1**, the bleaching rate is increased by 5–6 times in the presence of **2**. From a synthetic point of view, varying the components in the supramolecular complex is more preferable to obtain a system with the desired characteristics. Thus, this study demonstrates that the supramolecular approach is promising for systems that contain photochromic and fluorescent components that influence each other.

1. Introduction

Fluorescent molecules are widely used in chemistry, biology, medicine as chemical sensors [1] and biological labels [2]. The possibility of photo-switching of a fluorescent signal using light can significantly expand their field of application. Fluorescent photoswitchable molecules have attracted much attention because of their practical importance in bioimaging [3], logic gates [4], information storage [5] and optoelectronic devices [6]. One of the possibilities to realize photo-switching of a fluorescent signal using light is the combination of fluorescent and photochromic fragments in a molecule. Typical organic photochromic compounds include diarylethenes [7], azobenzenes [8], spiropyrans [9], fulgides [10], naphthopyrans [11], spirooxazines [12]. Photochromic fragments can reversibly change their geometry and electronic structure under excitation with light, thus influencing the fluorescent properties of the whole molecule. The introduction of a fluorescent fragment into the photochromic system can be realized through the covalent attachment of a fluorophore to photochrome [13–15] or much less often through supramolecular association. Upon irradiation with UV or visible light, the enhancement or quenching of fluorescence is achieved by changing in electron distribution upon photochromic transformation, energy transfer, or electron transfer between fluorophores and photochromic groups.

1,8-Naphthalimide derivatives are of interest due to their promising photophysical and biological properties [16]. They are particularly attractive as fluorophores. They have high quantum yields and good photostability, and their fluorescence varies from blue to red depending on substituents. 1,8-Naphthalimide-derived fluorescent pigments and fluorescent compounds can be used as sensors for certain metal cations, and as fluorescent markers [17,18].

There are some examples of naphthalimide-containing photochromic systems in literature. When using a 1,8-naphthalimide fluorophore in combination with an indoline-based “donor” and a barbituric acid “acceptor”, the donor-acceptor Stenhouse adduct (DASA) shows a switch of the fluorescence quantum yield from 0.21 to 0.56 [19]. A series of naphthalimides containing dithienylethene fragments in different position of fluorophore molecules was synthesized and their photochromic properties were studied [20–22]. When thienyl fragments are in the 3rd and 4th positions of the naphthalene ring of the naphthalimide derivative, the photochromic conversion to the cyclic form does not

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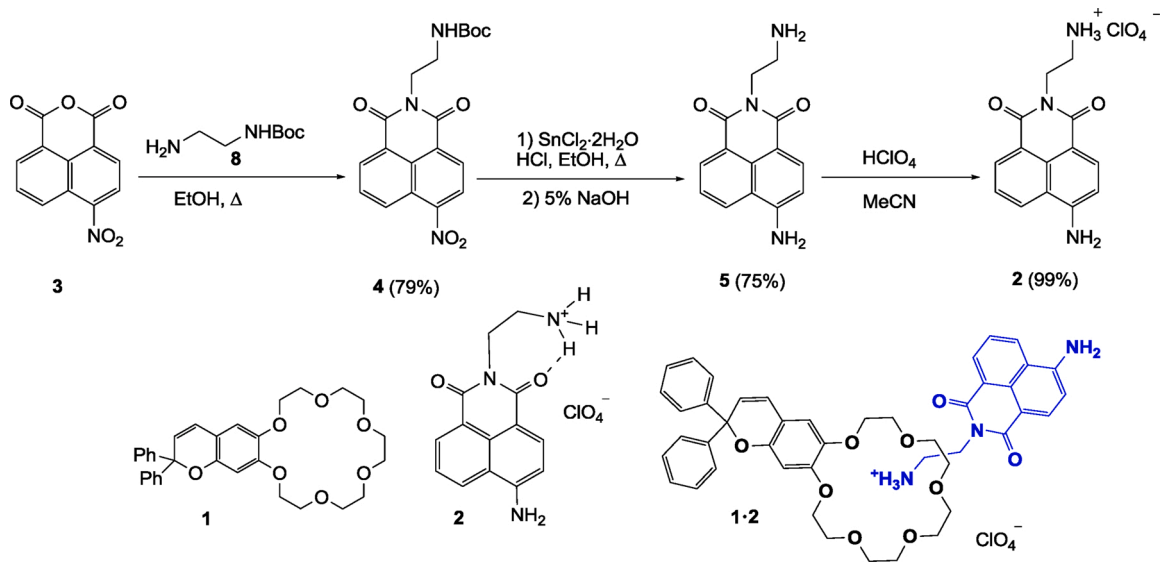


Scheme 1. Synthetic route to the naphthalimide **2**, and structures of compounds **1**, **2** and complex **1·2**.

affect the fluorescence characteristics of naphthlimide [20]. In the next research, the two prepared photochromic bisthienylethene derivatives with a six-membered aryl ring of the fluorescent naphthalimide moiety as the center ethene bridging unit differ from the previous one by OMe group in thienyl heterocycles [21]. They exhibit considerably high cyclization quantum yield and good fatigue resistance. Interestingly, the fluorescence arising from the naphthalimide unit could be well modulated by photochromism and solvatochromism. To the similar photochromic bisthienylethene system based on naphthalimide, the ferrocene unit was added as *N*-substituent. The system demonstrates fluorescence-modulation through photoinduced electron transfer (PET), a decrease in the photochromic cyclization quantum yield, and a selective two-step oxidation process [22].

Photochromic *E,Z*-isomerization in 4-styryl-1,8-naphthalimides does not significantly affect their fluorescent properties [23,24].

In the two photochromic spirooxazines-naphthalimides, the imide group of naphthalimide unit gives strong electron-withdrawing effect favoring the long-lived merocyanine in the dark and good colorability in solution [25]. Remarkably, their open merocyanine forms exhibit significantly long lifetimes, almost three magnitudes longer than that of unsubstituted spironaphthoxazine. Moreover, the fluorescence of naphthalimide unit can be switched on and off by photoinduced conversion between the open and closed forms.

Two photochromic naphthopyrans containing naphthalimide moieties were studied in solution under flash photolysis conditions [26]. Photochromic naphthopyrans exhibit an excellent photochromic response, rapid thermal bleaching rate and good fatigue-resistance. It was shown that the photochromic properties can be modulated with the introduction of different functional groups on the naphthalimide unit and the fluorescence of naphthalimide moiety can be switched on and off by photoinduced conversion between the closed and open forms. Studies of two isomeric photochromic naphthopyrans connected with naphthalimide moieties in different manner showed that the variety in mutual arrangement of pyran and naphthalimide units leads to remarkable difference in photochromic characteristics [27].

In the above cases, the naphthalimide fluorophore was conjugated with the photochromic molecule or covalently linked to it *via* a spacer forming dyad compounds. As a review of the literature shows, a combination of photochrome and fluorophore in a supramolecular fashion is rarely realized. It was reported on the design, preparation, characterization and properties of the mechanically interlocked complex of bisspiropyran-containing [2]rotaxane with 4-morpholin-naphthalimide fluorophore [28]. Rotaxane with photochromic fragments in spiro form can respond to various combinations of chemical and photochemical stimuli and displays multiple states with distinguishable fluorescence output. The PET process between the spiro-unit and the naphthalimide fluorescent unit has been observed and found to be capable of switching by acid-base stimuli. In the merocyanine form (MC), both the PET and the electronic energy transfer (EET) processes between the MC fragment and the fluorescent naphthalimide fragment, which can be chemically controlled, were detected.

In this paper, we report on the design, preparation, characterization, and properties of a supramolecular complex between benzopyran containing benzo-18-crown-6-ether **1** and 4-aminonaphthalimide **2** as a fluorophore (Scheme 1). Our research is aimed to reveal the mutual influence of photochromic and fluorophore units on the properties of the obtained supramolecular system.

2. Experimental sections

2.1. Synthesis of compounds

Benzocrown ester-containing pyran **1** was obtained by the reaction of commercially available phenol with β-phenylcinnamic aldehyde in the presence of titanium ethoxide (IV) in toluene as it was described earlier. [29] Naphthalimide derivative **2** was prepared as shown in Scheme 1. The synthesis includes imidation of 4-nitro substituted 1, 8-naphthalic anhydride **3** by ethylenediamine, in which one of the amino groups was protected with di-*tert*-butyl dicarbonate. [30,31] The nitro group reduction in **4** was carried out with tin (II) chloride in the presence of acid to simultaneously deprotect the amino group in the *N*-alkyl fragment. [32] The protonation of 4-amino--*N*-aminoethylnaphthalimide **5** was performed in acetonitrile using perchloric acid to give perchlorate **2**.

Compound **5**. To a stirring mixture of compound **4** (200 mg, 0.52 mmol) and ethanol (10 ml) a solution of $SnCl_2 \cdot 2H_2O$ (780 mg, 2.55 mmol) in concentrated hydrochloric acid (5.0 ml, ρ =1.18 g/mL) was added dropwise at 50 °C. The reaction mixture was refluxed for 2.5 h, cooled to ambient temperature, diluted with water and then 5 mass. % sodium hydroxide aqueous solution was added until slightly alkaline. The product was extracted thrice with dichloromethane, the combined organic extracts were washed with water, dried and evaporated in vacuum to give 100 mg of **5** (yield 75 %). M.p. 170–173 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 21 °C, δ / ppm, J / Hz): 2.77 (t, 2H, CH_2, J = 7.0) 4.03 (t, 2H, CH_2, J = 7.0), 6.84 (d, 1H, ArH, J = 8.4), 7.44 (br. s, 2H, NH_2), 7.64 (dd, 1H, ArH, J_1 = 7.3, J_2 = 8.4), 8.18 (d, 1H, ArH, J = 8.4),

8.42 (dd, 1H, ArH, $J_1 = 7.3$, $J_2 = 1.1$), 8.61 (dd, 1H, ArH, $J_1 = 8.4$, $J_2 = 1.1$). Found (%): C, 65.91; H, 5.19; N, 16.51. Calculated for $C_{14}H_{13}N_3O_2$ (%): C, 65.87; H, 5.13, N, 16.46.

Compound **2**. Compound **5** (50 mg, 0.19 mmol) was dissolved in acetonitrile (15 ml). To a resulting mixture 70 mass. % perchloric acid (14 μl, 0.16 mmol) was added. The precipitate was filtered off, recrystallized from ethanol and dried at 60 °C to give 60 mg of **2** (yield 86 %). M.p. 88 °C (decomp.). ^{1}H NMR (400.13 MHz, DMSO-d_6, 21 °C, δ / ppm, J / Hz): 3.06–3.16 (m, 2H, CH_2), 4.27 (t, 2H, CH_2, $J = 5.7$), 6.86 (d, 1H, ArH, $J = 8.4$), 7.64–7.72 (m, 1H, ArH), 7.75 (br. s, 3H, NH_3^+), 8.21 (d, 1H, ArH, $J = 8.4$), 8.45 (d, 1H, ArH, $J = 7.0$), 8.64 (d, 1H, ArH, $J = 8.0$). Found (%): C, 47.34; H, 4.00; N, 11.86. Calculated for $C_{14}H_{14}ClN_3O_6$ (%): C, 47.27; H, 3.97, N, 11.81.

2.2. Optical spectroscopy

Electronic absorption spectra were recorded on spectrophotometers Varian-Cary 5 G 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 120 W equipped with optical filter 313 nm. To measure the dark lifetime of the colored form of benzopyran **1**, solutions of **1** in acetonitrile or dichloromethane were irradiated in the cuvette box of the spectrophotometer Avantes AvaSpec-2048 with 313 nm light. 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 form at 384 nm.

Fluorescence spectra were recorded on spectrofluorimeters FluoroLog-3-221 and AvaSpec-2048 L. The fluorescence switch was measured using a diode (365 nm). All spectral measurements were carried out in air-saturated solutions at 20 ± 1 °C. The concentrations of studied compounds were of about 10^{-4} or 10^{-5} M.

2.3. Determination of fluorescence quantum yields

Coumarin 481 in acetonitrile ($\varphi^{fl} = 0.08$) was used as a reference for the fluorescence quantum yield measurements. [33]

The fluorescence quantum yields of the individual compounds **2** and **5**, and the complex **1**•**2** were determined in acetonitrile at 25 °C and λ_{ex} = 340 nm according to equation (1) [34]:

$$\varphi^{fl} = \varphi_R^{fl} \frac{S}{S_R} \cdot \frac{(1 - 10^{-A_R}) n^2}{(1 - 10^{-A}) n_R^2} \quad (1)$$

wherein φ^{fl} and φ_R^{fl} are the fluorescence quantum yields of the studied solutions and the standard compound respectively, A and A_R are the absorptions at 340 nm of the studied solutions and the standard respectively, S and S_R are the areas underneath the curves of the fluorescence spectra of the studied solutions and the standard respectively, n and n_R are the refraction indices of the solvents for the substance under study and the standard compound.

To determine the fluorescence quantum yield of complex **1**•**2**, we used an acetonitrile solution containing 33.8 μM of **1** and 10.1 μM of **2**. Considering that logarithms of stability constants (log K) for the complexes of **1** and protonated forms of some aliphatic aminoacids (γ-aminobutyric acid (C4), ε-aminocaproic acid (C6) and ω-aminocaprylic acid (C8)) in MeCN are in the range 4.42–4.68, [35] we estimated the concentration of **1**•**2** species in the solution to be as high as 4.8 μM (obtained using log K = 4.5), and concentrations of free naphthalimide **2** and benzopyran **1** are 5.3 μM and 29 μM respectively. The fluorescence quantum yield of complex **1**•**2** ($\varphi_{1\cdot2}^{fl}$) was calculated by the Eq. (2):

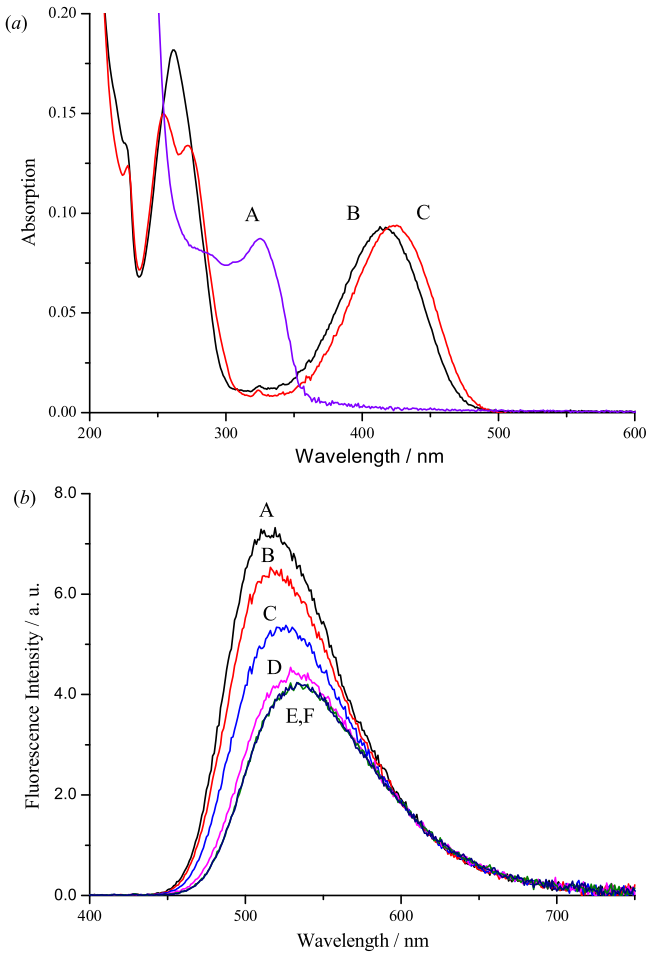


Fig. 1. (*a*) Absorption spectra of the benzopyran **1** (A) ($C_1 = 2.29 \cdot 10^{-5}$ M), naphthalimides **5** (B) and **2** (C) ($C_5 = C_2 = 1.14 \cdot 10^{-5}$ M); (*b*) fluorescence spectra of **5** alone ($C_5 = 1.14 \cdot 10^{-5}$ M) (A) and in the presence of various amounts of perchloric acid: (B) – $0.285 \cdot 10^{-5}$ M, (C) – $0.57 \cdot 10^{-5}$ M, (D) – $0.855 \cdot 10^{-5}$ M, (E) – $1.14 \cdot 10^{-5}$ M, (F) – $1.425 \cdot 10^{-5}$ M. Acetonitrile, 22 °C, λ_{ex} =380 nm.

$$\varphi_{1\cdot2}^{fl} = \varphi_R^{fl} \frac{S}{S_R} \cdot \frac{(1 - 10^{-A_R}) n^2}{(1 - 10^{-A}) n_R^2} \cdot \frac{A}{A_2} - \frac{A_1}{A_2} \cdot \varphi_2^{fl} \quad (2)$$

wherein φ_2^{fl} is the fluorescence quantum yield of the naphthalimide **2**; $A = A_1 + A_2 + A_3$ is the absorption at 340 nm of the mixture of **1** and **2**, where A_1, A_2 and A_3 are the absorptions of complex **1**•**2**, free naphthalimide **2** and free benzopyran **1** respectively; is the area underneath the curve of the fluorescence spectrum of the studied solution containing the mixture of **1** and **2**. A_2 and A_3 values were calculated by the Lambert-Beer law from the known concentrations of the free naphthalimide **2** and benzopyran **1** (5.3 μM and 29 μM respectively, see above) and their molar extinction coefficients at excitation wavelength 340 nm ε_{340} (**2**) and ε_{340} (**1**) (780 and 2970 M^{-1} cm^{-1}). A_1 was found as the difference $A - A_2 - A_3$. Derivation of Eq. (2) is presented in supplementary information.

Fluorescence quantum yield of naphthalimide chromophore in the complex **1**•**2** (φ_{NI}^{fl}) was estimated by the Eq. (3):

$$\varphi_{NI}^{fl} = \varphi_{1\cdot2}^{fl} \frac{A_1}{A_{NI}} \quad (3)$$

wherein A_{NI} is the absorption at 340 nm of naphthalimide chromophore in the complex **1**·**2**. A_{NI} was calculated under the assumption that the values ε_{340} (**2**) and ε_{340} (**1**) do not change upon going from individual

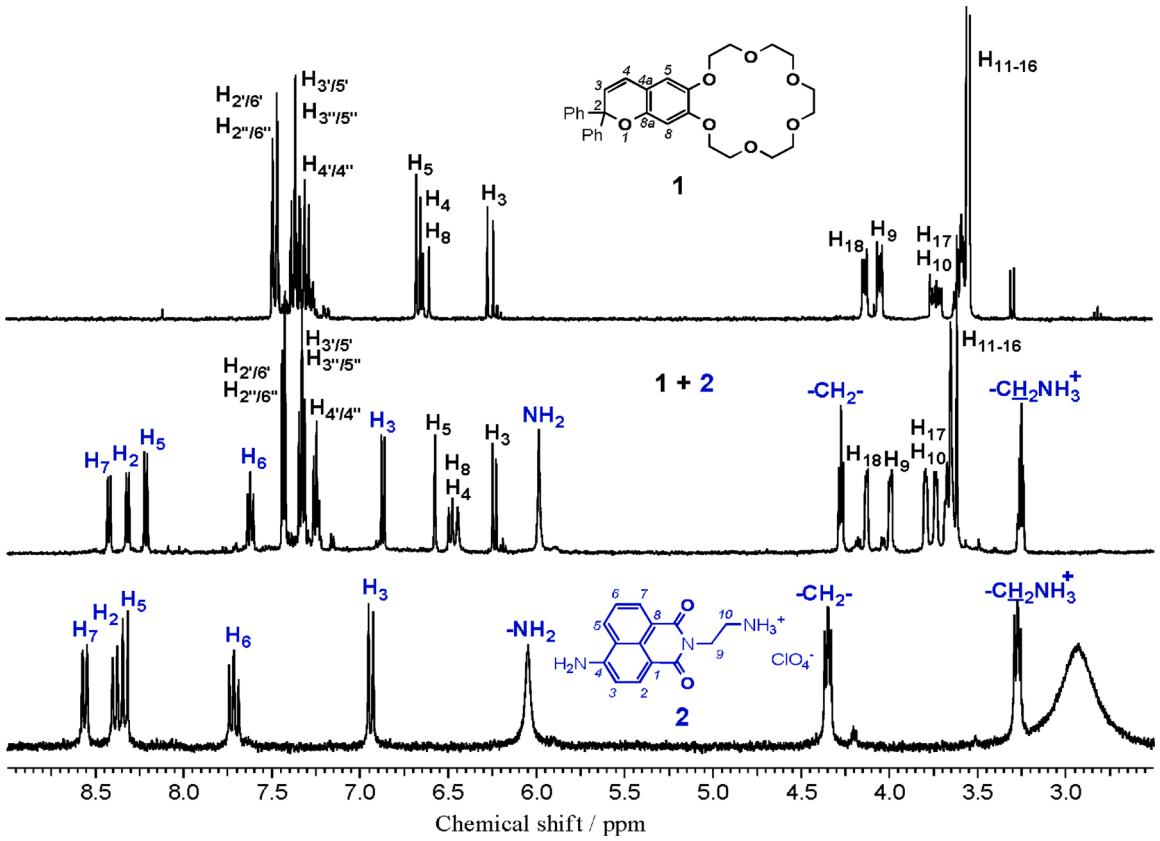


Fig. 2. ^{1}H NMR spectra of solutions of benzopyran **1**, an equimolar mixture of **1** with **2**, and naphthalimide **2** (acetonitrile, 25 °C). The prime and double prime indicate the proton signals of phenyl groups in the compound **1**. Numbering of carbon atoms of the crown ether cavity of **1** is similar to that shown in Fig. 3.

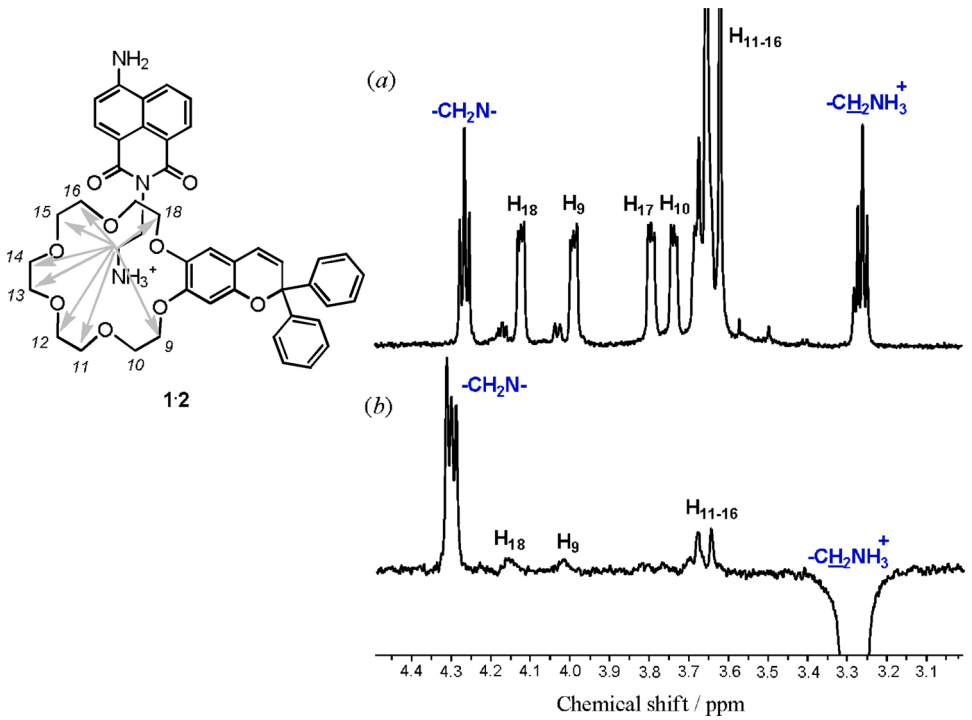


Fig. 3. Aliphatic part of ^{1}H NMR spectrum (*a*) and 1D NOESY spectrum (*b*) of an equimolar mixture of **1** with **2** (acetonitrile, 25 °C). Arrows in the structure of complex **1**·**2** show the protons of the crown ether fragment which are close enough in space to the protons of CH_2 group of the naphthalimide *N*-alkyl substituent to exhibit NOE.

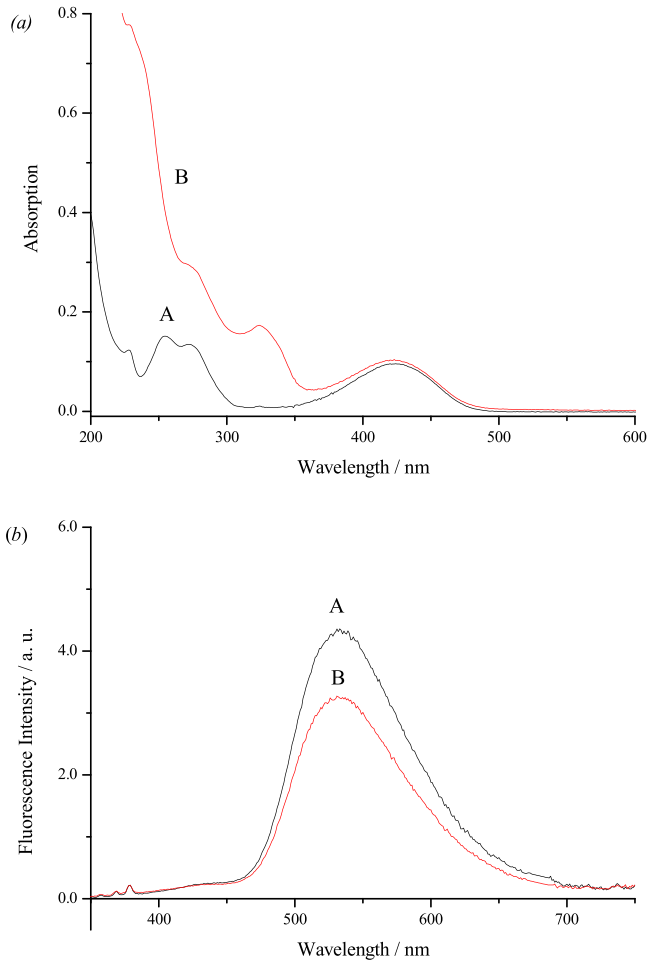


Fig. 4. Absorption (*a*) and fluorescence (*b*) spectra of **2** (A) ($C_2 = 1.01 \cdot 10^{-5}$ M) and mixture of **1** with **2** (B) ($C_1 = 3.38 \cdot 10^{-5}$ M and $C_2 = 1.01 \cdot 10^{-5}$ M), λ_{ex} = 340 nm, acetonitrile, 25 °C.

components **1** and **2** to complex **1·2**, *i.e.* $A_{NI} = A_1 \cdot \varepsilon_{340}(2)/(\varepsilon_{340}(2) + \varepsilon_{340}(1))$

2.4. NMR experiments

NMR spectra were record on Bruker Avance 500 MHz spectrometer equipped with a TXI probe, using standard sequences. Data acquisition and processing were performed with Topspin 2.1 software (Bruker). The experiments were carried out in CD_3CN. Temperature ranges used for NMR measurement and irradiation were 243 K–298 K. The temperature of the sample was controlled with a variable temperature unit (B-VT 1000-Bruker, 123−423 K, *T* range). All UV irradiations were done using a 1000 W Xe-Hg high pressure short-arc lamp (Oriel), filtered by interferential filter (λ = 313 nm).

2.5. Computational details

Quantum chemical calculations were carried out by the MOPAC 2016 program package using the PM7 semiempirical method. Calculations were performed at optimized geometries, which reached gradient variations less than 0.01 kcal/mol. The solvent effect was included in geometry optimizations following the "COnductorlike Screening MOdel" (COSMO) implemented in MOPAC 2016. A dielectric constant of $\varepsilon = 40$ and a refraction index of solvent (n) such that $n^2 = 2$ were used.

3. Results and discussion

3.1. Optical properties of naphthalimides *5*, *2* and benzopyran *1*

Compound **5** exhibits the long wavelength absorption band at 416 nm in acetonitrile solution (Scheme 1, Fig. 1a). The addition of perchloric acid causes the formation of **2** whose long wavelength absorption band is shifted bathochromically by 6 nm and appeared at 424 nm. Compound **5** emits light at 514 nm with quantum yield $\varphi^{fl} = 0.48$, whereas compound **2** emits at 533 nm with $\varphi^{fl} = 0.31$. The quantum yield of fluorescence of **5** is higher than for **2** (Fig. 1b), which may be due to the presence of an intramolecular hydrogen bond in the protonated naphthalimide **2** (Scheme 1). [36] Benzopyran **1** has a long wavelength absorption band in the UV region of the spectrum at 325 nm in acetonitrile solution and does not fluoresce.

3.2. Coordination of benzopyran *1* with naphthalimide *2*

It is known that protonated amino group is able to coordinate with benzopyran 18-crown-6 ether moiety with stability constant log K_{11} = 4.6 in acetonitrile. [35] It can be assumed that the naphthalimide derivative having an ammonium group in the *N*-substituent will be able to coordinate with the crown ether fragment of the photochromic benzopyran molecule, thereby ensuring the close position of both units in the supramolecular complex. Due to the supramolecular organization of two chromophoric units, the occurrence of PET or EET processes influencing the photochromic and fluorophore charateristics of supramolecular complex can be expected.

We have confirmed the formation of supramolecular complex of benzopyran **1** with naphthalimide **2** by NMR spectroscopy. It was shown that the addition of naphthalimide **2** to the solution of crown-containing benzopyran **1** causes changes in the position of the proton signals of the macrocyclic methylene groups, which confirms the interaction of the ammonium group of **2** with the macrocyclic moiety of **1** (Fig. 2). 1D NOESY spectrum (Fig. 3) evidenced the dipolar correlations between the methylene groups of crown ether fragment and the —CH_2N—H_3^+, which means that —CH_2N—H_3^+ group is placed into the macrocyclic cavity.

The absorption spectrum of a mixture of the closed form of

Table 1
Spectral properties of the supramolecular complex **1·2** and its individual components and the lifetime of the open form of benzopyran **1** and complex **1·2** in acetonitrile and dichloromethane at 22 °C.

Species	Acetonitrile				Dichloromethane		
	λ^{abs}_{max}/nm	λ^{fl}_{max}/nm	φ^{fl}	τ/s	λ^{abs}_{max}/nm	λ^{fl}_{max}/nm	τ/s
1(CF)	325	–	–		326	–	
1(OF)	384; 470	–	–	174	383; 464	–	3200
2	424	533	0.31	–	421	537	
1(CF)+**2**	423	532	0.02 (0.05**; 0.24***)	–	415	513	
1(OF)+**2***	423	532	–	87	408	520	408

* $C_1 = 2.3 \cdot 10^{-5}$ M, $C_2 = 9.2 \cdot 10^{-5}$ M.
** Apparent fluorescence quantum yield of complex **1·2**.
*** Apparent fluorescence quantum yield of naphthalimide chromophore in complex **1·2** estimated by the Eq. (3).

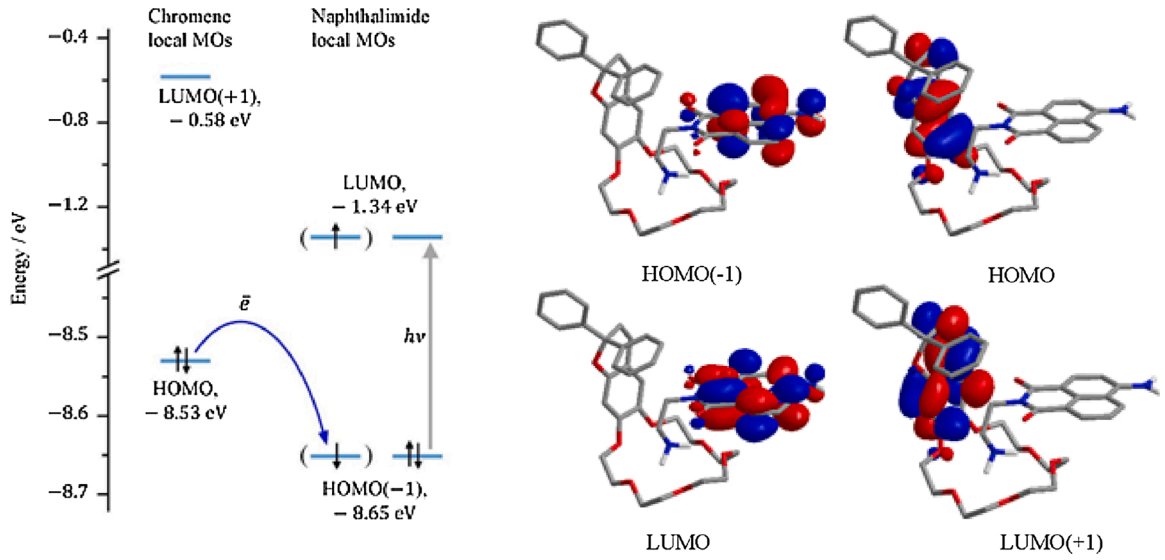
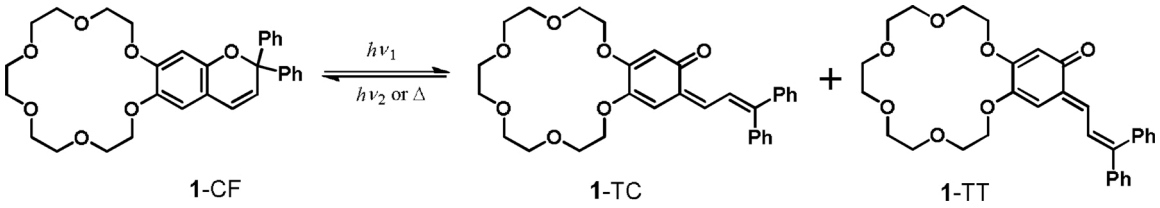


Fig. 5. Energy diagram of the frontier molecular orbitals of the closed form of complex **1**•**2** (MOPAC 2016, PM7 method).



Scheme 2. Photochromic equilibrium of benzopyran **1**.

benzopyran **1** and naphthalimide **2** in acetonitrile (Fig. 4a) is close to the sum of the spectra of individual components (Fig. 1a), which indicates that no noticeable spectral changes occur during the formation of the supramolecular complex **1** with **2**. More significant changes were found in the fluorescence spectra upon excitation at 340 nm when adding **1** to **2**. The interaction of **1** with **2** results in decrease of fluorescence (Fig. 4b), the apparent quantum yield of the solution containing the mixture of **2** (10.1 μM) and **1** (33.8 μM) is 0.02 which is much lower than that of **2** (0.31, see Table 1). In part, this could be explained by the relatively high absorption at 340 nm of the non-fluorescent chromene species. However, some reduction in emission efficiency of the naphthalimide chromophore (from 0.31 to 0.24) on going from compound **2** to the complex **1**•**2** was found (see Experimental part for the details of the quantum yield calculations). To explain this effect, semiempirical calculations of the frontier molecular orbitals (HOMO and LUMO) for **1**•**2** were performed by the PM7 method. As Fig. 5 shows, the HOMO is localized over the benzopyran fragment and the highest molecular orbital of naphthalimide fluorophore appears to be HOMO(–1). In such a situation, PET between benzopyran HOMO and singly occupied HOMO (–1) of naphthalimide in the excited state would be thermodynamically feasible which leads to some decrease in the fluorescence quantum yield of naphthalimide chromophore in the **1**•**2** complex.

3.3. Photochromic behavior of *1* and complex *1*•*2*

The photochromic transformations of **1** and complex **1**•**2** were studied in acetonitrile and dichloromethane solutions. Dichloromethane was chosen as a solvent because the stability constants for the complexes of ammonium derivatives with 18-crown-6-containing ligands are higher in CH_2Cl_2 than in MeCN. [35,37] On the other hand, compounds **1** and **2** as well as their complex **1**•**2** are well soluble in MeCN solution, which is appropriate for NMR analysis of the structures of photochromic species in their closed and open forms. The solubility of complex **1**•**2** in CH_2Cl_2 was found to be not sufficient for the NMR experiments. Therefore, only optical studies were carried out in both solvents.

As shown in Scheme 2, UV light irradiation of benzopyran **1** causes heterolytic cleavage of the pyran carbon-oxygen bond with the formation of an open ring merocyanine structure represented by two isomers: transoid-cis (TC) and transoid-trans (TT). The changes in the absorption spectra in MeCN and CH_2Cl_2 are shown in Figs. 6a and S1a. The relaxation kinetics of the open form of benzopyran in acetonitrile or dichloromethane at ambient temperature is described by a monoexponential dependence with a lifetime of $\tau = 174$ s (MeCN) and 3200 s (CH_2Cl_2), which apparently corresponds to the TC isomer (Fig. 6b, Fig. S1b). [35] TT-isomer is significantly more stable as evidenced by the presence of residual absorption exceeding absorption of benzopyran **1** closed form even after prolonged relaxation (Fig. 6b).

^{1}H NMR spectrum of benzopyran **1** recorded in acetonitrile solution at –30 °C after irradiation with UV light ($\lambda = 313$ nm) highlighted the conversion of free benzopyran **1** into the two photomerocyanines TC and TT (Fig. 7). More particularly, the formation of TC isomer is predominant and well characterized by the downfield doublet at 8.6 ppm for H-3 with the coupling constant $^3J = 12.2$ Hz, whereas the presence of TT is identified by the singlet at 5.7 ppm. Study of the relaxation kinetics of benzopyran **1** open form at low temperatures (–30 °C and −10 °C) using NMR spectroscopy has allowed to determine the lifetime of TC isomer which was 77 h at –30 °C and 6 h at −10 °C (Table 2). In this case, the minor TT form of benzopyran **1** is more stable and lives for several days at room temperature. Taking into account these findings and the known behavior of chromenes, [10,26,35] we conclude that (*i*) the TC form is generated first, (*ii*) the TT form accumulation requires prolonged or/and high intensity irradiation, and (*iii*) the TC form exhibits bleaching rate considerably higher than that of the TT form.

Upon irradiation of supramolecular complex **1**·**2** with 313 nm light,

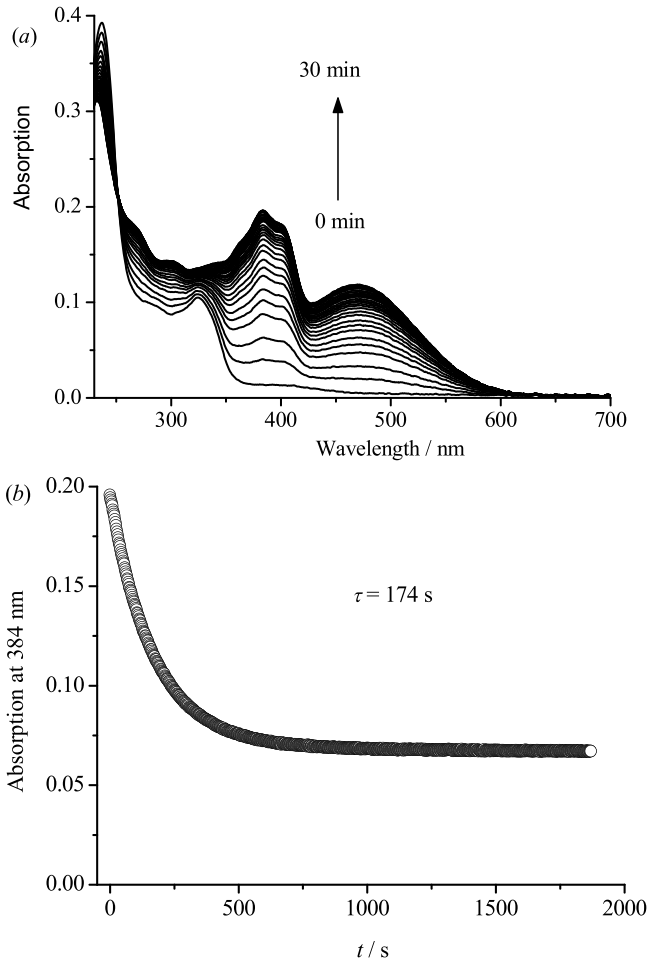


Fig. 6. Changes in the absorption spectrum of the benzopyran **1** during UV irradiation at 313 nm (a) and the relaxation kinetics of its open form (b) in acetonitrile at 22 °C ($C = 2.3 \cdot 10^{-5}$ M, λ =384 nm).

the formation of the colored open form of benzopyran **1** has been also observed (Fig. 8a, Fig. S2). It was found that complexation significantly affects the lifetime of the open form of benzopyran **1**. A study of the bleaching kinetics using optical spectroscopy showed that the relaxation of the open form is monoexponential, and its lifetime is 87 s in MeCN and 408 s in CH_2Cl_2 at 22 °C (Table 1, Fig. 8b), which is lower than the corresponding values for the compound **1** (176 and 3200 s, see above).

The study of the phototransformation of the supramolecular complex **1•2** by NMR spectroscopy at –30 °C in acetonitrile showed the appearance of an open form of benzopyran **1** upon UV irradiation (Fig. 9). Analysis of the spectra of the open form revealed the presence of a predominant TC form, which is consistent with the monoexponential bleaching curve of the open form at room temperature. By analogy with the starting benzopyran **1** for complex **1•2**, kinetic studies were carried out and the kinetic characteristics of bleaching were obtained. Compared with free benzopyran **1**, in the presence of **2**, the bleaching rate is increased by 5–6 times (Table 2).

In order to elucidate the difference in bleaching rates for the open forms of complex **1•2** and compound **1**, we calculated the charges on the carbonyl oxygen atom O(1) and carbon atom C(2) of the CPh_2-group in the TC forms of **1** and **1•2** responsible for thermal relaxation (see Fig. 2 for the atom numbering in the chromene fragment). Calculations were performed using PM7 method. The results show that in the **1**-TC, these charges are both negative: –0.026 for C(2) and –0.597 for O(1). As a result of π-conjugated push-pull character of the chromene open form, complexation with the positively charged $CH_2NH_3^+$ fragment of **2** decreases to some extent the charge on O(2) atom, which appears to be –0.588 in **1•2**-TC, and also brings a slight positive charge (+0.010) to C (2). Hence, the ring closure by the nucleophilic attack of carbonyl oxygen on C(2) atom would be more complicated in the case of individual chromene **1** compared with its complex **1•2**. This is consistent with the faster kinetics of decoloration for **1•2** in our experiments.

3.4. Fluorescence photoswitching behavior

It is known that 1,8-naphthalimides are highly fluorescent with high chemical stability. Interestingly, the fluorescence intensity of naphthalimide molecule **2** in complex **1•2** can be modulated by photoinduced conversion between the open and closed forms of benzopyran **1**.

Table 2
The lifetime of the TC isomer of benzopyran **1** alone and in the complex **1•2**, k_{TC} - relaxation rate constant of TC form in acetonitrile.

Species	Temperature / °C	k_{TC} / s^{-1}	τ / h
1	–30	$2.51 \cdot 10^{-6}$	77
	–10	$3.17 \cdot 10^{-5}$	6
1•2	–30	$1.12 \cdot 10^{-5}$	17
	–10	$1.87 \cdot 10^{-4}$	1

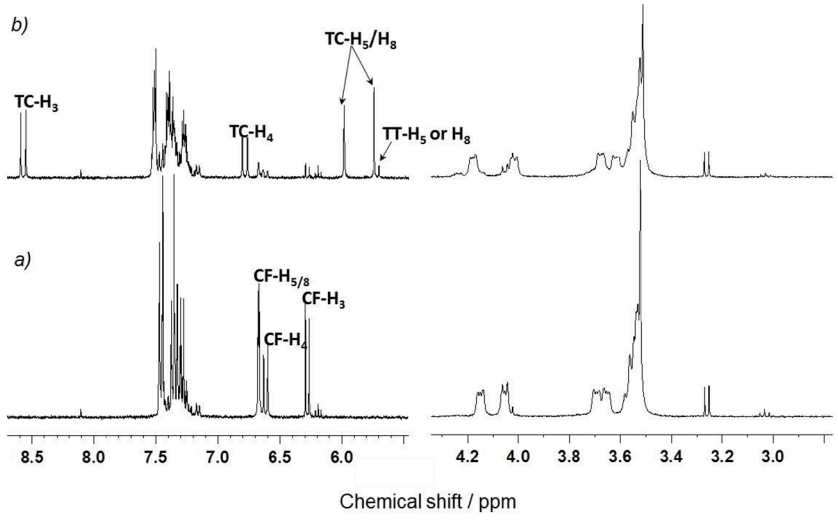


Fig. 7. ^{1}H NMR spectra of the benzopyran **1** a) before irradiation; b) after UV irradiation at 313 nm for 60 min (acetonitrile, –30 °C).

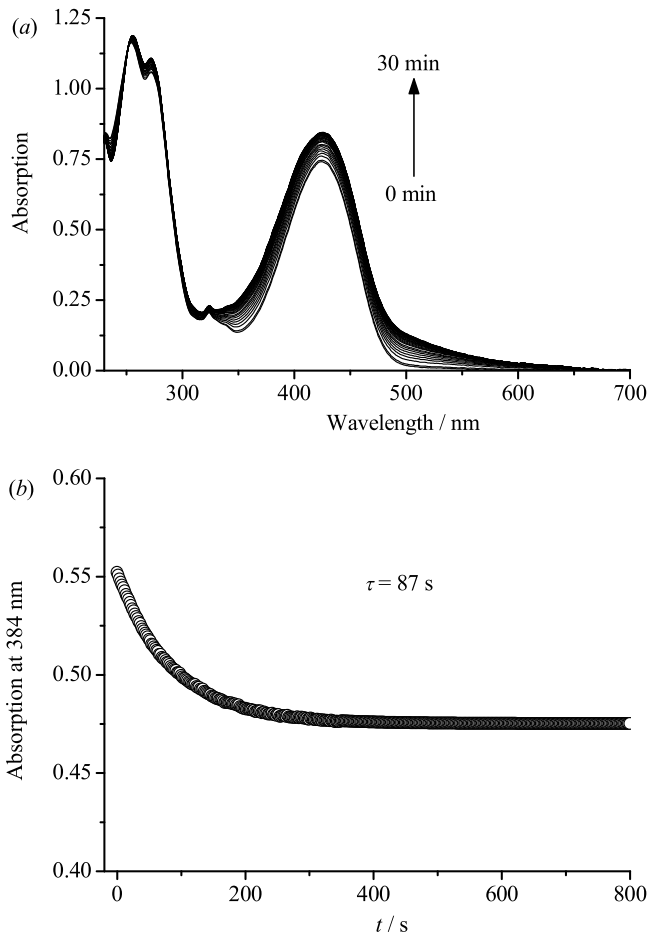


Fig. 8. Changes in the absorption spectrum of the supramolecular complex **1**•**2** during UV irradiation at 313 nm (*a*); and the relaxation kinetics of its open form (*b*) in acetonitrile at 22 °C ($C_1 = 2.3 \cdot 10^{-5}$ M, $C_2 = 9.2 \cdot 10^{-5}$ M, λ=384 nm).

That is, the closed form of complex shows the characteristic fluorescence from naphthalimide unit at 520 nm, which decreases quickly under the UV irradiation in CH_2Cl_2 (Fig. 10) and in MeCN (Fig. S3). During the decoloration in the dark, the fluorescence of the solution is also recovered. The effect of luminescence quenching of naphthalimide derivative is more pronounced in non-polar CH_2Cl_2. It could be due to the more stable and long-lived open form of benzopyran in this solvent if compared with MeCN. Considering the high degree of overlap between the absorption spectrum of the compound **1** open form and fluorescence band of **2** (see Fig. S4 for the graphical representation), the emission quenching at 520 nm can be rationalized in terms of resonance energy transfer from the excited naphthalimide fluorophore to the acceptor merocyanine form of chromene unit.

4. Conclusions

Supramolecular complex of the photochromic benzopyran **1** and naphthalimide derivative **2** has been prepared and investigated. Complex **1**·**2** can reversibly change color under UV light and the removal of

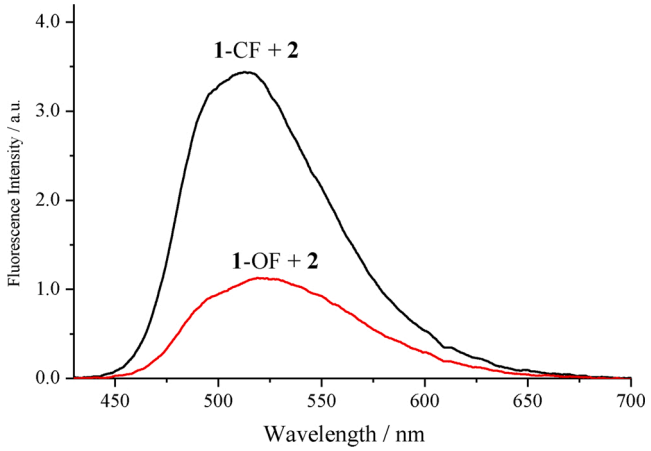


Fig. 10. The fluorescence spectra of a solution of complex **1**·**2** before (denoted as «**1**-CF + **2**») and after (denoted as «**1**-OF + **2**») irradiation (313 nm, 25 min) in dichloromethane (C_1 = 2.3·10⁻5 M, C_2 = 2.3·10⁻5 M, λ_{ex} =355 nm).

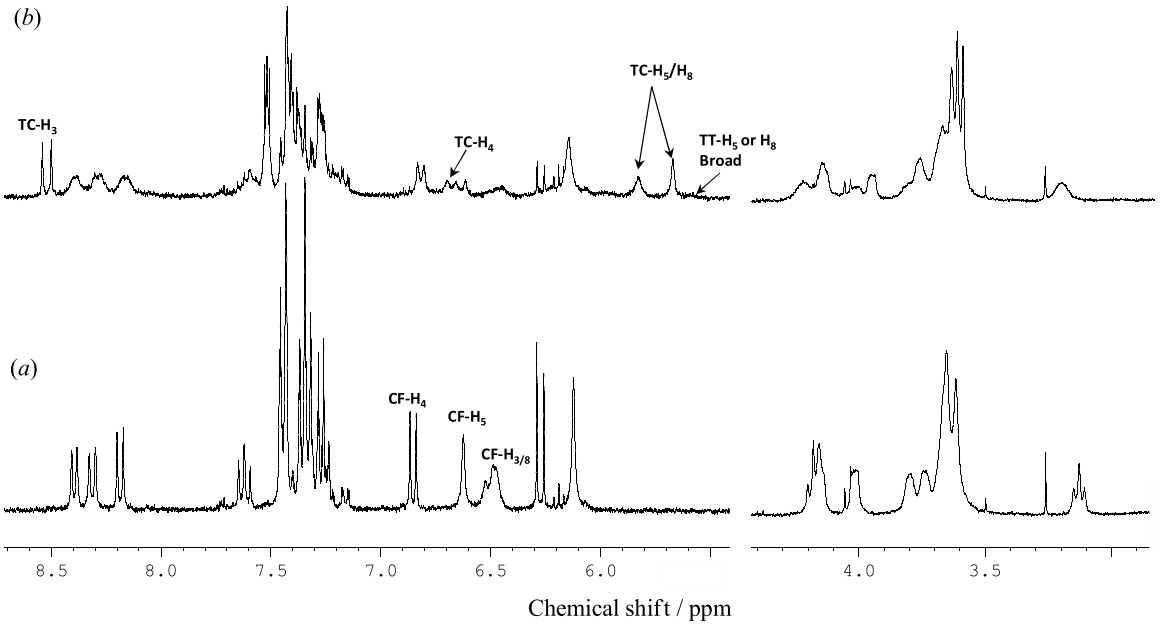


Fig. 9. [1]H NMR spectra of supramolecular complex **1**•**2** *a*) before UV irradiation; *b*) after UV irradiation at 313 nm during 1 h (acetonitrile, –30 °C).

irradiation. The combination of two functional molecules in supramolecular complex affects on both photochromic and fluorescence characteristics of the components. Thus, the open form of benzopyran **1** in complex **1·2** exhibits a significantly higher rate of thermal bleaching than in free benzopyran. The obtained results are similar to what was observed earlier for naphthopyrans covalently linked to naphthalimide chromophore. [26] The fluorescence of complex **1·2** can be switched on and off by photoinduced conversion between the closed and open forms. Moreover, the changes in fluorescence intensity between closed and open forms are more pronounced in non-polar solvent CH_2Cl_2. The proposed reason of the fluorescence photoswitching is PET process between benzopyran and naphthalimide components of the supramolecular complex and, in part, additional absorption of non-fluorescent chromene species at the excitation wavelength.

Thus, the present research demonstrates that supramolecular approach can be useful for obtaining systems where the mutual influence between photochromic and fluorescent components can be reached. Comparison of complex **1·2** with molecule combining two covalently linked pyran and naphthalimide components shows the similar effect on photochromic conversion of naphthalimide linked to photochromic pyran by supramolecular or covalent ways [26]. In supramolecular complex the possible occurrence of PET and EET processes between the photochromic and fluorophore components can be proposed. These processes can drastically influence on the fluorescent characteristics of complex. From the synthetic point of view the variation of components in supramolecular complex is more accessible to obtain the system with desirable characteristics.

Author agreement statement

We the undersigned declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We understand that the Corresponding Author is the sole contact for the Editorial process. He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020.112975.

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