Synthesis of new fluorescent 1-(thien-2-yl)-9*H*-thieno[3,4-*b*]-chroman-9-ones and their fluorescent photomodulation by photochromic dihetarylethenes

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Graphical Abstract

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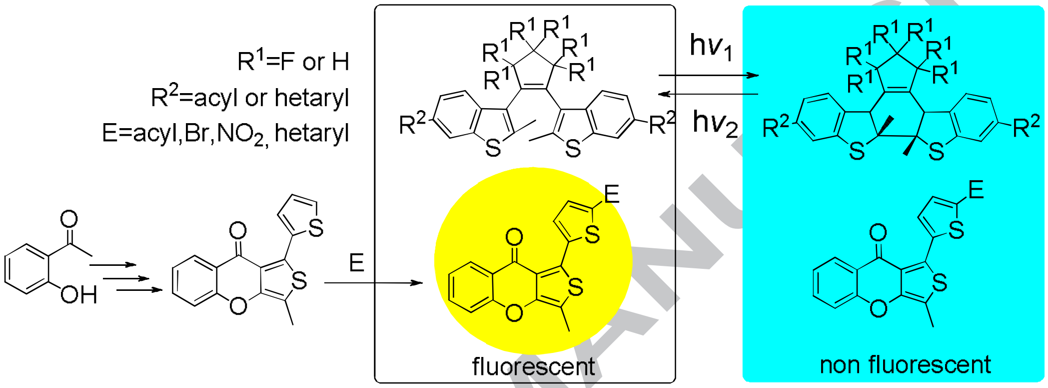

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Synthesis of new fluorescent 1-(thien-2-yl)-9*H*-thieno[3,4-*b*]-chroman-9-ones and their fluorescent photomodulation by photochromic dihetarylethenes

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ABSTRACT

New fluorescent derivatives of 1-(thien-2-yl)-3-methyl-9*H*-thieno[3,4-*b*]-chroman-9-one are synthesized and their spectral properties studied. The prepared fluorescent compounds are combined with several photochromic benzothienyl dihetarylethenes to provide mixed systems exhibiting reversible photo-induced fluorescence modulation in solution. The obtained results are promising for the development of polymeric photochromic recording media with a non-destructive fluorescence readout of optical information for RAM with extra large information capacity

Studies towards the development and improvement of multi-layer recording media for two-photon, three-dimensional (3D) optical memory with ultra high information capacity (recording density 10^{11}-10^{12} bit/cm^3) have been carried out.[1,2,3] One important area of research is the creation of photochromic polymeric recording media with a non-destructive optical fluorescent readout of information that could provide 3D information storage. The development of such recording media is possible by using the phenomenon of inductive energy transfer (Forster or fluorescence resonance energy transfer) between the components, termed FRET effect.[4,5] This effect occurs, for example, in photochromic films or solutions if a mixture of compounds or hybrid materials comprising an organic or inorganic fluorophore and photochromic diarylethene are used.

In this case irradiation of the photochromic compound in open form results in formation of a colored isomer, which absorbs the excitation energy of the fluorophore and hence results in quenching of fluorescence. Modulation of fluorescence intensity is provided by reversible photochromic transformations of dihetarylethenes. The implementation of such an effect is possible under several conditions. Firstly, photochromic and fluorescent molecules should be located at short enough distances to make transfer of excitation energy possible. This is possible by direct crosslinking of photoactive compounds. Secondly, the absorption bands of the photochrome and the emission bands of the fluorophore should overlap. The efficiency of energy transfer is often low in FRET-systems. In this case, switching of the photochromic component contributes to only partial fluorescence quenching. Thirdly, to ensure non-destructive readout of information the wavelength of the fluorescence excitation light should not overlap the absorption bands of both forms of the photochromic compound. One promising alternative is the use of composite mixtures based on fluorescent and photochromic molecules. This approach is used in much recent work and has many advantages.[6,7] For example, Shouzhi Pu et al. designed fluorescence switch based on a photochromic diarylethene and a rhodamine B dye.[6] This photoswitchable system displayed a high fluorescence quenching efficiency (>90%) and remarkable fatigue resistance in both solution and a solid medium. In this case, short distances between photoactive components or their covalent bonding is not required. Moreover the efficiency of fluorescence quenching by photoswitching can be adjusted by variation of the concentration of components.

In continuation of our previous studies, [2,8,9] we herein present the synthesis of new fluorescent 1-(thien-2-yl)-9*H*-thieno[3,4-*b*]-chroman-9-ones and investigations of their spectral properties. The obtained fluorophores were used with previously reported dihetarylethenes[10,11] in the development of photochromic systems with reversible photo-induced modulation of the fluorescence. The spectral characteristics of the fluorophores were adapted for spectral characteristics of photochromes through a series of modifications.

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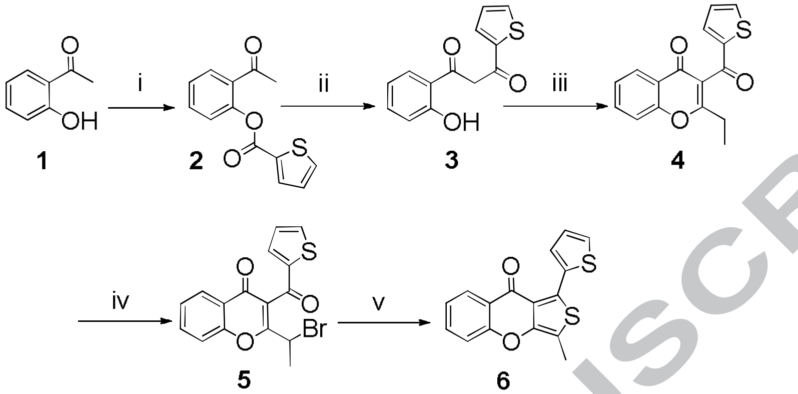
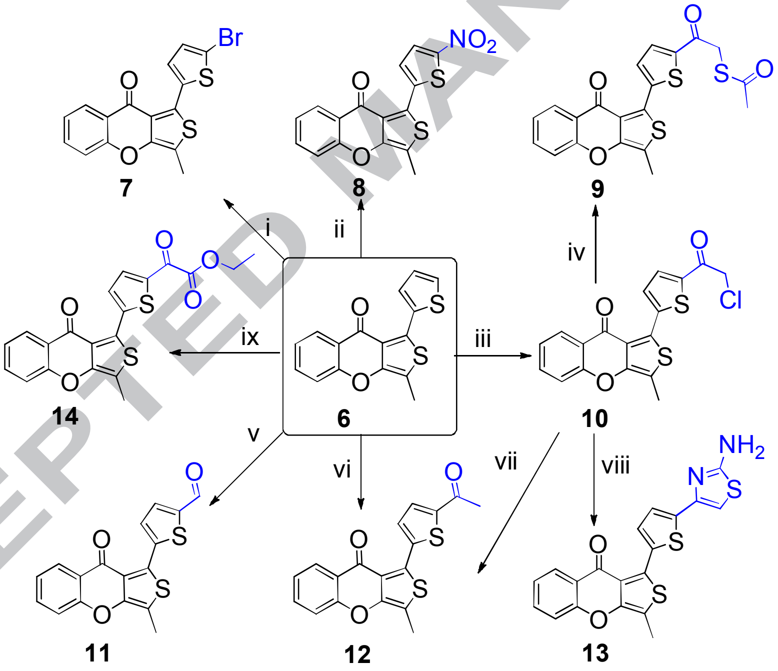
Previously, we have shown that 9*H*-thieno[3,4-*b*]-chroman-9-ones are excellent fluorophores with well-separated absorption and fluorescence bands, and exhibit high fluorescence intensity. Moreover, the fluorescence can be enhanced by the introduction of a thienyl group at position 1 of the 9*H*-thieno[3,4-*b*]-chroman-9-one and an electron-donating group at position 3.[10] In this regard, 1-(thien-2-yl)-3-methyl-9*H*-thieno[3,4-*b*]-chroman-9-one **6** (see Schemes 1 and 2) was selected as the fluorophore. We proposed that introduction of a methyl group at position 3 (as electron-donating group) would improve the fluorescence intensity of the molecule and allow the selective introduction of substituents at the 5-position of the thiophene moiety for tuning of the location of the spectral bands.

The synthesis of the new fluorescent 1-thienyl-9*H*-thieno[3,4-*b*]-chromone-9-one **6** was carried out according to Schemes 1[10] and 2:



Scheme 1. *Reagents and conditions:* i Thiophene-2-carbonyl chloride, pyridine, 0-15 °C, 1 h; ii, *t*-BuOK, DMF, -10 to 10 °C; iii, $(C_2H_5CO)_2O$, C_2H_5COONa, 70-80 °C, 30 min; iv, Br_2, CCl_4, 50-60 °C, 1 h; v, $CH_3C(S)NH_2$, DMF, 70-80 °C, 2 h.



Scheme 2. *Reagents and conditions:* i NBS, CCl_4, reflux, 1 h; ii, $Cu(NO_3)_2{\cdot}3H_2O$, $(CH_3CO)_2O$, 0-5 °C, 12 h; iii, $ClCH_2C(O)Cl$, $AlCl_3$, CH_2Cl_2, 0-25 °C, 1.5 h; iv, $CH_3C(O)SH$, K_2CO_3, DMF, 20 °C; v, CH_3OCHCl_2, $AlCl_3$, CH_2Cl_2, 0-25 °C, 1.5 h; vi, $CH_3C(O)Cl$, $AlCl_3$, CH_2Cl_2, 0-25 °C, 1.5 h; vii $HS(CH_2)_4SH$, K_2CO_3, DMF, 20 °C; viii, $NH_2C(S)NH_2$, EtOH, reflux, 20 h; ix, ClC(O)C(O)Et, $AlCl_3$, CH_2Cl_2, 0-25 °C, 1.5 h;

Compounds **1-3** were prepared according to established procedures.[10] It should be noted that this synthetic route (Scheme 1) is relatively simple. (i) Acylation, (ii) Baker–Venkataraman rearrangement and (iii) cyclization proceed smoothly with yields ranging from good to high. It is noteworthy that bromination of 2-ethylchromone **4** is carried out more selectively than bromination of earlier synthesized 2-methylchromones (which gives 3-acyl-2-bromomethyl- and 2-dibromomethyl-chromen-4-ones) [10] and leads to mono brominated adduct **5** only. Compound **6** was prepared in 74% yield by heating **5** with thioacetamide in DMF solution. We prepared a series of fluorophore derivatives from **6** to improve its optical properties and to expand the possibilities of its application in a variety of photochromic composite systems. In particular, several electron-withdrawing chromophoric groups were introduced at the thiophene 5-position via electrophilic substitution reactions (Scheme 2). In our opinion introduction of an electron-withdrawing group at position 5 of the thiophene ring should improve the fluorescent properties of the products and cause bathochromic shifts of the absorption and fluorescent bands due to the electron push-pull effect. Chloroacetyl (**10**), formyl (**11**), acetyl (**12**) and ethyloxalyl (**14**) substituents were introduced using standard Friedel-Crafts conditions and $AlCl_3$ as the catalyst affording the desired products in 50-65% yields. The best method for the selective synthesis of the nitro derivative **8** involved the use of copper nitrate in acetic anhydride as a nitrating agent. Also, it was decided to synthesize a substance based on compound **10** with a thiazole moiety and sulfur-containing substituents. It should be noted that unlike mercaptoacetic acid, 1,4-butandithiol did not give any products of nucleophilic substitution. Acetyl derivative **12** was isolated instead of disubstituted 1,4-butanedithiol (obviously due to the two step process of nucleophilic substitution and intermolecular reduction).

The absorption and fluorescence spectral data of the synthesized products **6-14** are summarized in Table 1 and show that all compounds have similar properties: fluorescence characterized by a large Stokes shift. Figure 1 shows the absorption and fluorescence spectra of compound **6** in toluene as an example.

Table 1. Spectral characteristics of compounds **6-14**.[a]

Compound	λ^{abs} (nm)	ε ($M^{-1}.cm^{-1}$)	λ^{em} (nm)	SS (nm)	λ^{ex} (nm)	I_{fl}^{max} (a.u.)
6	422	10925	497	75	422	150
7	423	~17750	505	82	432	95
8	444	14938	514	70	460	245
9	432	21875	498	66	432	375
10	430	22375	494	64	431	90
11	430	11500	492	62	432	205
12	429	12750	492	63	428	235
13	455	10625	533	78	460	120
14	442	23625	510	68	448	285

[a] λ^{abs}, λ^{ex}, and λ^{em} are the wavelengths of the maxima of the absorption bands, the fluorescence excitation and fluorescence spectra of compounds **6-14**, respectively; ε - molar extinction coefficient; SS - Stokes shift; I_{fl}^{max} - fluorescence intensity at the maximum of the fluorescence band of compounds **6-14.**

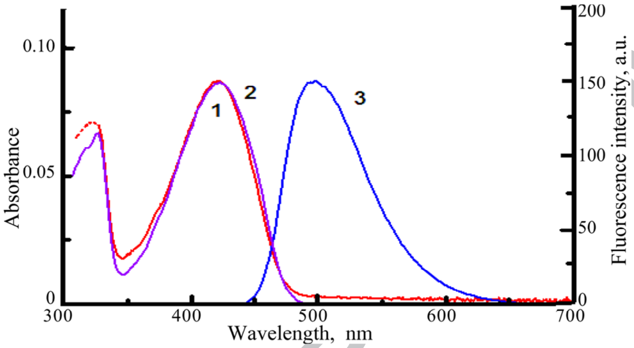
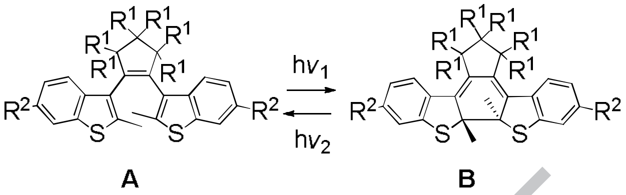


Figure 1. Absorption (1) and fluorescence emission (2, λ_{ex}=422 nm) and excitation (3, λ_{em}=497nm) spectra of **6** in toluene.

As expected, derivatives **7-14** were characterized by long-wavelength shifted absorption bands compared to the absorption band of the compound **6**. The value of the bathochromic shift of the absorption band depends on the electron-withdrawing properties of the substituent on the thienyl moiety (Table 1). The strongest bathochromic shifts of the absorption and fluorescence spectra were observed for nitro-substituted **8**, and the compounds with ethyl oxalate **14** and aminothiazole **13** moieties. Most of the compounds are characterized by comparable fluorescence intensities (Table 1). However, the fluorescence intensities of compounds **6**,**7**,**10** and **13** were 2-3 times lower than for the compound **9**.

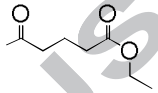
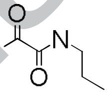
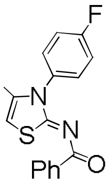
Several thermally irreversible photochromic dihetarylethenes were selected for the preparation of composite systems with reversible photo-induced modulation of the fluorescence. Photochromic transformations of these compounds result from the reversible photoinduced isomerization between open colorless form **A** and the cyclic form **B** (Scheme 3).[12] Photochromic molecules were chosen from previously synthesized compounds[12,13] with characteristics that contribute to the inductive transfer of excitation energy from the fluorescent compounds **6-14** to dihetarylethene in the closed form **B** (Table 2).



Scheme 3. Photoinduced isomerization of compounds **15-17**

Photochromic compounds for the realization of photo-induced fluorescence modulation were selected with the maximum of overlap of the absorption bands of the cyclic isomer **B** and the fluorescence of fluorophores **6-14**. The properties of the photochromic compounds used are shown in Table 2.

Table 2. Spectral characteristics of compounds **15-17**.[a]

Compound	R^1	R^2	λ_A^{abs} (nm)	ε ($M^{-1}.cm^{-1}$)	λ_B^{abs} (nm)	$\Delta D^{phot}/D_A$
15	H		332	12500	490	0.8
16	H		360	12500	523	1.0
17	F		341	40800	565	0.2

[a] λ_A^{abs}, λ_B^{abs}, are the wavelengths of the maxima of the absorption bands of open (**A**) and cyclic (**B**) forms of the dihetarylethenes, respectively; D_A – value of absorbance at the maximum of the absorption band of the form A; ΔD^{phot} - photoinduced change in the optical density at the maximum of the absorption band of the cyclic form **B**.

Table 2 shows that the selected dihetarylethenes **15**, **16** have different spectral characteristics to the cyclic form and have almost the same sensitivity to UV radiation (sensitivity is estimated as the ratio of light-induced optical density at the wavelength of the maximum absorption band of isomer **B** to the optical density at the maximum absorption band of the open form of dihetarylethene **A**). Compound **17** has a significantly higher extinction due to the intensely absorbing chromophoric moiety R^1. In this case, however, the compound is characterized by a significant reduction of the photoinduced optical density at the wavelength of maximum absorption of the cyclic form **B**. As an example, Figure 2 shows the absorption spectra of the open and cyclic isomers of photochromic compound **16** in toluene and the high reversibility of the photochromic transformations of selected compounds. Figure 3 shows the results of a study of the photoinduced modulation of the fluorescence in the composite of photochromic compound **15** and the fluorophore **9** (molar ratio 4:1) in toluene. The decrease of the fluorescence intensity after irradiation with UV light observed is due to the appearance of the absorption band of the cyclic isomer **B** overlapping the emission band of compound **9**. This results in the inductive energy transfer from excited fluorophore to the cyclic form **B** of the dihetarylethene. Subsequent irradiation of the solution with visible light leads to a complete recovery of the absorption spectrum of the original open-isomer and the initial fluorescence intensity of the fluorophore.

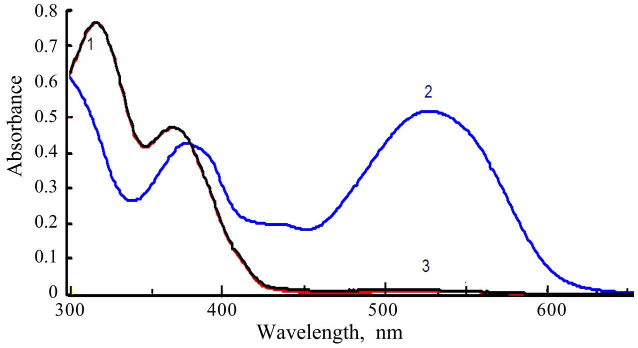


Figure 2. Absorption spectra of **16** in toluene ($c = 2\times10^{-4}$ M) before (1) and after irradiation with UV light (λ=300-360 nm) (2) and subsequent irradiation with visible light (λ>500 nm) (3).

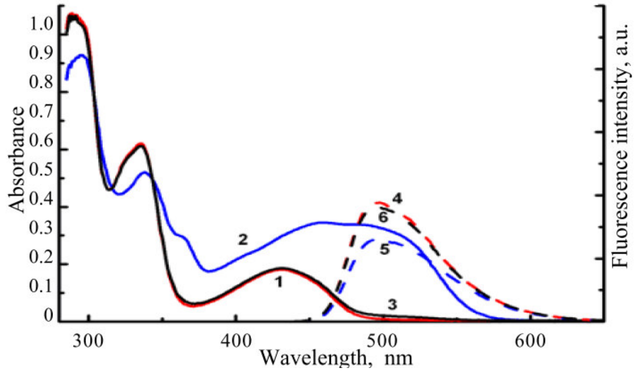


Figure 3. The absorption (1-3) and fluorescence (4-6, λ_{ex} =430 nm) spectra of a mixture of photochrome **15** ($c = 4\times10^{-5}$ M) and the fluorophore **9** ($c = 1\times10^{-5}$ M) in a molar ratio of 4:1 in toluene before (1,4) and after irradiation with UV light (λ=300-360 nm) (2,5) and subsequent irradiation with visible light(λ>500 nm) (3,6).

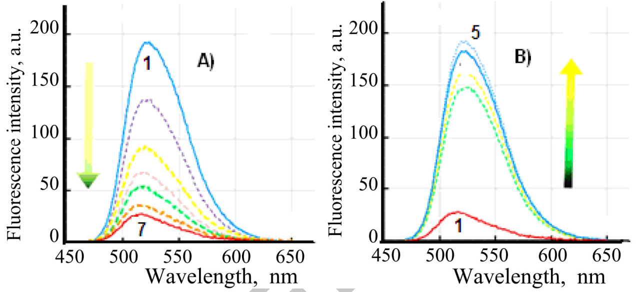


Figure 4. Photoinduced change in the fluorescence intensity of the fluorophore **8** in a mixture with diarylethene **17** (molar ratio 1:36) in chlorobenzene after irradiation with UV light (λ=300-360 nm) (A) and subsequent irradiation with visible light (λ>500 nm) (B).

Similar photoinduced modulation of the fluorescence was observed for the solution containing dihetarylethene **16** (4×10^{-5} M) and fluorophore **14** (1×10^{-5} M). For photochromic dihetarylethene **17**, fluorophores **8** and **13** were most appropriate for its spectral properties (see data in Tables 1 and 2). Exposure of a chlorobenzene solution of **17** and **13** (molar ratio of 9:1) to UV light results in a reduction of the fluorescence intensity by 10 times. However, irradiation with visible light did not lead to complete recovery of the fluorescence intensity due to photodegradation of the fluorophore **13**. Obviously, the insufficient stability can be attributed to the introduction of an aminothiazole fragment.

A practically acceptable result was obtained when using a mixture of photochromic compounds **17** and the nitro derivative **8** with excellent stability in chlorobenzene solution. Efficient fluorescence quenching was achieved by using a ratio of fluorescent and photochromic compounds of 1:36 (Figure 4).

In conclusion, we have developed efficient methods for the synthesis and modification of new fluorescent 1-(thien-2-yl)-3-methyl-9*H*-thieno[3,4-*b*]-chroman-9-one derivatives. The synthesized fluorescent compounds were used with photochromic benzothienyl dihetarylethenes to provide systems with reversible photo-induced modulation of fluorescence in solution. The obtained results are promising for the development of photochromic polymeric recording media with non-destructive fluorescence readout of optical information for RAM with extra large information capacity.

Acknowledgments

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Supplementary Material

Supplementary data (experimental procedures and characterization data of synthesized compounds) associated with this article can be found, in the online version.

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