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Coumarinyl(thienyl)thiazoles: Novel Photochromes with Modulated Fluorescence

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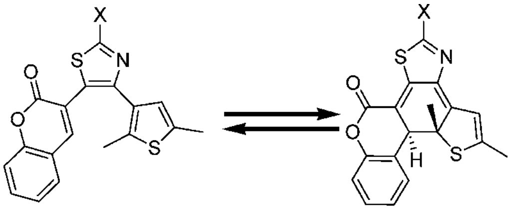
ABSTRACT



A
(intensive fluorescence)

B
(no fluorescence)

Novel photochromic 5-(3′-coumarinyl)-4-(3″-thienyl)thiazoles have been synthesized. These compounds display intensive fluorescence emission in the open form A, which is modulated by light. Fluorescence intensity decreases significantly upon irradiation of A with UV-light (λ < 400 nm) due to formation of the cyclic form B. Irradiation of B with visible light (λ > 470 nm) promotes its opening and the recovering of fluorescence. Novel dihetarylethenes undergo photochromic modulation of fluorescence both in solution and in polymeric matrices.

Efficient photochromes with modulated fluorescence are compounds of potential interest for molecular electronics and optical memory device industries.[1−4] Complex systems integrating both photochromic and fluorescent functions into a single molecule have been reported.[5−8] Fluorescence quenching operates in these systems via the mechanism of energy transfer from emitting moiety to the cyclic form of photochrome. Mixtures of photochromic and fluorescent compounds have also been proposed to provide fluorescence modulation.[9−11] Intermolecular mechanism of energy transfer is responsible for fluorescence modulation in such two-molecule fluorescent photochromes. Coumarin derivatives have also been used in the systems of that kind.[9]

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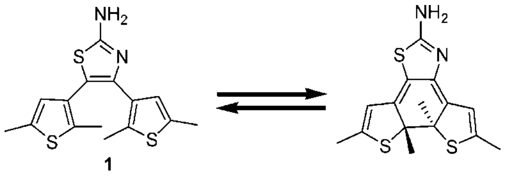
We have earlier designed and prepared novel photochromes with modulated fluorescence—coumarin spiropyranes derivatives.[12] Their fluorescence was modulated by photochromic transformation of spiropyran moiety. The rates of the photoinduced spectral changes were depended both on spiropyran structure and on media.

Herein we report design and synthesis of novel dihetarylethenes that include conjugated double bonds responsible for both photochromism and fluorescence in a single molecule. Numerous studies have been devoted to the photochromic dihetarylethene derivatives.[1] Thienylethenes are among the most promising photochromic compounds owing to efficient photoisomerization reaction, the thermal stability of both isomers, and excellent fatigue resistance. The best structures include an ethene double bond into a cycle, prohibiting cis−trans photoisomerization of the open form, and providing better yields of photoinduced cyclization. Earlier we have synthesized compounds that contain thiazole ring as a cyclic ethene fragment of photochromic dithienylethenes.[13−14] Dithienylthiazoles similar to **1** have been synthesized, and their photochromism has studied (Scheme 1). Some other photochromic dithienylthiazoles[15] and 4,5-bis(thiazol-4-yl)-thiazoles[16] were also reported.

Scheme 1. Photochromic Dithienylthiazole[13]

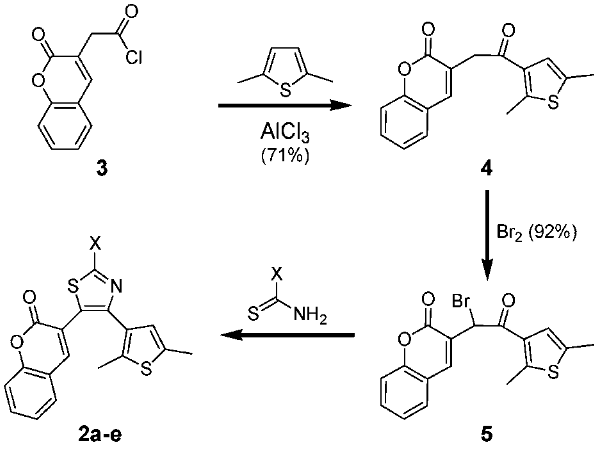


Although many derivatized dithienylethenes exhibit good reversibility of fluorescence intensity, most of the reported examples have relatively small quantum yields of fluorescence. Fluorescence data have not been reported for compounds **1** as well.

In search for novel structures with photomodulated fluorescence, we have synthesized coumarinyl(thienyl)-thiazoles **2** (Scheme 2). Many coumarin derivatives are well-known for their excellent fluorescent properties.[17,18]

A synthetic pathway to **2** started from Friedel−Crafts acylation of 2,5-dimethylthiophene with a 3-coumarinylacetyl chloride **3**, affording ethanone **4** in 71% yield. Treatment of dichloromethane solution of **4** with bromine at room temperature gave corresponding α-bromoketone **5** in high yield (92%). Thiazoles **2a**−**e** were synthesized by refluxing a methanol solution of α-bromoketone and thioamides XC(S)NH$_2$. Thioamides of acetic (**a**), benzoic (**b**), 4-methoxybenzoic acids (**c**), thiourea (**d**), and phenylthiourea (**e**) were used. Yields of thiazoles **2a**−**e** were 61−89%. Coumarinyl(thienyl)thiazoles **2a**−**e** were characterized by ^{1}H and ^{13}C NMR-spectra, mass-spectra, and elemental analysis.

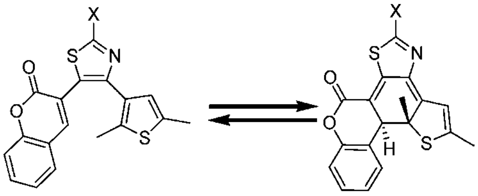
Scheme 2. Synthetic Route to Coumarinyl(thienyl)thiazoles



2a, X = Me (64%)
2b, X = Ph (76%)
2c, X = 4-OMeC$_6$H$_4$ (61%)
2d, X = NH$_2$ (80%)
2e, X = NHPh (89%)

One can suggest a new method for fluorescence photomodulation of dihetarylethene system in **2**: 3−4 double bond of the coumarin moiety is responsible both for photochromic and fluorescent properties of the molecule (Scheme 3).

Scheme 3. Photoisomerisation of Coumarinyl(thienyl)thiazoles



Besides, coumarin derivatives can undergo thermally irreversible photochemical $2\pi + 2\pi$ dimerization upon photoirradiation, thus providing another method to modulate fluorescence.[19,20]

Spectral and photochemical properties of coumarinyl(thienyl)thiazoles **2** have been studied using acetonitrile as a solvent (Table 1). These compounds have two intersected

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Table 1. Spectral Data for Open **A** and Cyclic **B** Forms of 3-(4-Thienylthiazole-5-yl)coumarins **2**

entry	λ^{A}_{max}, nm	ϵ	λ^{fl}_{max}, ($I^{A}_{fl.}$)	λ^{B}_{max}, nm
2a	350	7300	504 (125)	500
2b	374	14100	501 (295)	517
2c	382	16300	510 (280)	515
2d	398	7400	543 (7)	496
2e	410	13400	551 (50)	500

bands at 300−410 nm in electron absorption spectra and emission bands at 500−550 nm in fluorescence spectra. A bathochromic shift of absorption and emission maxima in spectra of compounds **2a**−**e** is observed due to increase of electron donation of substituent X. However, amino-functions at position 2 of thiazole ring (**2d**, **2e**) provide significant decrease of fluorescence intensity if compared with compounds, bearing aryl- and alkyl groups at that position (**2a**−**c**).

Photochemical transformations of coumarinyl(thienyl)-thiazoles **2** have been induced by irradiation of their solutions in acetonitrile with filtered light of Hg−Xe lamp. Thus, each of the compounds **2** has been irradiated by light at its longest wavelength absorption maximum.

Absorption and emission spectra of compounds **2** are changed upon UV irradiation. Figure 1 shows UV/visible absorption spectra of **2b**, irradiated by 365 nm light for different times. A new absorption band, corresponding to cyclic form of **2b**, appears at 400−500 nm region. Its intensity increases gradually upon irradiation while absorption intensity at 350−400 nm decreases (Figure 1, lines 2−6).

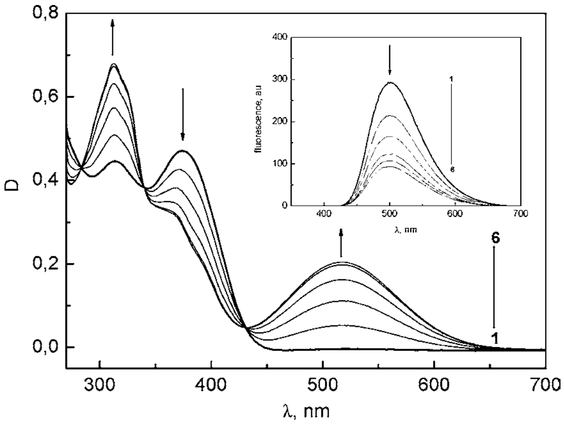

Figure 1. Absorption spectra of **2b** (4 × 10^{-5} M, CH_3CN, 25 °C) before (line 1) and after irradiation with UV light (365 nm) for 1, 2, 4, 8, 12 s (lines 2−6). (Inset) Fluorescence spectra of the same solution.

Similar changes are observed in the emission spectra, shown as an inset in Figure 1. Fluorescence intensity of **2** decreases significantly with no change of the emission maxima position. It is obvious that only open form **A** of **2** is responsible for fluorescence of the photochromic system.

We have found the decrease of fluorescence intensity to not follow the first-order kinetics model. One can suggest that at least two processes are responsible for the decrease of fluorescence: (1) concentration of fluorescent open form **A** decreases due to photocyclization reaction, and (2) fluorescence photoquenching operates in this system via intermolecular mechanism of energy transfer in photostationary state from fluorescent open form **A** to cyclic form **B**, since emission band of **A** and absorption band of **B** are located in the same spectral region.

Upon visible light irradiation (>470 nm) of cyclic forms of **2**, reverse spectral transformations, shown in Figure 2, are displayed: both absorption and emission are gradually reverted to the initial spectra, specific to open forms of **2**.

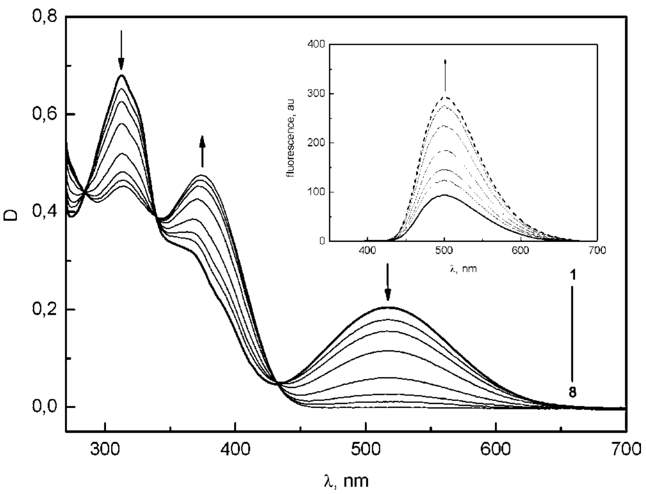

Figure 2. Absorption spectra of **2b** (4 × 10^{-5} M, CH_3CN, 25 °C) after UV-irradiation (365 nm) (line 1) and after irradiation with visible light (>470 nm) for 1, 2, 4, 8, 12, 16, 24 s (lines 2−8). (Inset) Fluorescence spectra of the same solution.

In contrast to dark irreversibility of cyclic forms of dihetarylethenes where heteroaryl fragments are bound to cyclopentene or perfluorocyclopentene ring,[1] cyclic forms of dihetarylthiazoles undergo ring-opening reactions in the dark.[13−16] The rate of this transformation is much dependent on the substituents at positions 2 and 5 of the thiazole ring. Compounds **1** show the lowest dark stability and undergo 50% transformation for several hours.[13] Cyclic forms of coumarinyl(thienyl)thiazoles **2** are much more stable: half-life of cyclic form of **2b** in the dark is about 3 days and the best thermal stability shows **2e**—its cyclic form concentration decreases only for 27% after being stored for 8 days in the dark. Apparently, electron donating substituents (for example, phenylamino-group) at position 2 of thiazole ring provide the highest stabilization effect for cyclic forms **B**.

We have recently shown,[21,22] that stability of photoinduced forms is definitely increased in the polymeric matrices. For

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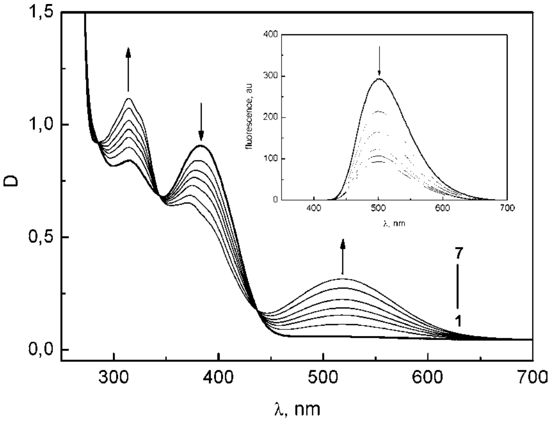

Figure 3. Absorption spectra of **2b** (PMMA-film, 25 °C) before (line 1) and after irradiation with UV light (365 nm) for 20, 40, 60, 90, 150, 250 s (lines 2−7). (Inset) Fluorescence spectra of the same sample.

example, introduction of indoline spiropyrans of coumarin series into polymethylmetacrylate (PMMA) film significantly increases thermostability of photoinduced form if compared with that in solution. We have found coumarinyl(thienyl)-thiazole **2b** in the PMMA film to undergo photochromic reaction, accompanied with photomodulated fluorescence. The photoinduced changes of its spectra are shown in Figure 3.

It follows from the comparison of the obtained spectral data that the position of the absorption band maximum of the photoinduced cyclic form has not been changed when compared with that of coumarinyl(thienyl)thiazole **2b** in CH_3-CN solution. Besides, the photoinduced cyclic form in PMMA becomes rather more stable (half-life is 14 days).

In conclusion, the effects of the introduction of coumarin moiety in dihetarylthiazoles include: coumarinyl(thienyl)-thiazoles possess prominent fluorescence in the open form and much better thermal stability of their cyclic forms. Insertion of methyl group in the position 4 of coumarin moiety might provide further increase of thermal stability of these novel photomodulated fluorophores. The structural modification of coumarinyl(thienyl)thiazoles and study of their behavior in polymeric matrices are in progress now.

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Supporting Information Available: Experimental details, ^1H and ^{13}C NMR-spectra, mass spectra, elemental analysis, UV/vis absorption and fluorescence spectra, irradiated by UV and visible light for different times. This material is available free of charge via the Internet at http://pubs.acs.org.

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