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A novel approach to fluorescent photochromic fulgides

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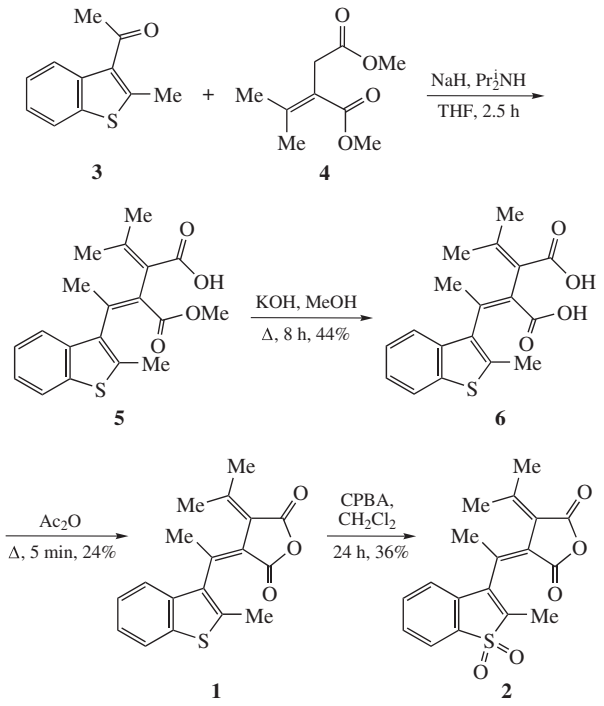
Oxidation of the cyclic sulfide group of 3-(2-methylbenzo[*b*]thienyl)fulgide into the sulfone one affords 3-[1-(2-methyl-1,1-dioxidobenzo[*b*]thiophen-3-yl)ethylidene]-4-(propan-2-ylidene)dihydrofuran-2,5-dione, a new photochromic fulgide that displays photomodulated fluorescence properties.

Heterocyclic fulgides represent one of the most important family of photochromic compounds.[1–5] The mechanism of their photoinduced rearrangements involves interconversion between their hexatriene and cyclohexadiene isomeric forms. Due to high thermal stability and fatigue resistance of the cyclic colored form fulgides are regarded as efficient molecular switches and promising candidates for the use in high capacity three-dimensional multilayer optical memory devices.[6–11] Due to the particular advantages of fluorescence as the non-destructive and most sensitive method of reading light-written information of principal interest are the fulgides possessing fluorescent properties of one or both isomeric forms involved in the rearrangements. We have previously reported on a series of fulgides containing oxazole, naphtho[1,2-*b*]furan, indole and benzo[*g*]indole moieties.[12–15] Herein, we describe an expedient approach to photochromic fulgides with light-modulated emission properties that is based on modification of their π-conjugated system through the conversion of the non-fluorescent 3-(2-methylbenzo[*b*]thienyl)-fulgide **1** to its fluorescent analogue **2**.

3-(2-Methylbenzo[*b*]thienyl)fulgide **1** was previously obtained as a mixture of *Z*- and *E*-configurational isomers[16] or as pure *Z*-isomer.[17] We used the modified procedure leading to *Z*-**1** in higher yield and converted it into sulfone **2** by oxidation with 3-chloroperbenzoic acid (CPBA) (Scheme 1).†

In the total synthesis, the Stobbe condensation of 3-acetyl-2-methylbenzo[*b*]thiophene **3** with dimethyl 2-(propan-2-ylidene)-succinate **4** in the presence of sodium hydride and diisopropylamine in THF afforded adduct **5**‡ which was hydrolyzed to give diacid **6**.§ Its anhydridization with Ac_2O leads to (*Z*)-3-[1-(2-



Scheme 1

† The ^{1}H NMR spectra in $CDCl_3$ were obtained on a Varian Unity 300 spectrometer (300 MHz), the signals were referred with respect to that of residual protons of deutero-solvent (7.24 ppm), δ values were measured with precision 0.01 ppm. The IR spectra were recorded on a Varian Excalibur 3100 FT-IR instrument using the attenuated total internal reflection (ATR) technique (ZnSe crystal). Mass spectra were measured on a Shimadzu GCMS-QP2010SE instrument with direct sample entry into the ion source (EI, 70 eV). The electronic absorption spectra were recorded on a Varian Cary 100 spectrophotometer. The irradiation of solutions with filtered light of a high pressure Hg lamp was performed on a Newport 66941 equipment supplied with a set of interferential light filters. Electronic emission spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. Acetonitrile of the spectroscopic grade (Aldrich) was used to prepare solutions. Elemental analysis was performed on a KOVO CHN-analyzer. Melting points were determined on a Boetius hot stage.

‡ *3-Acetyl-2-methylbenzo[*b*]thiophene* **3** was prepared in 62% yield using the described procedure.[17] Mp 70–71 °C (lit.,[21] 69–70 °C).

Dimethyl 2-(propan-2-ylidene)succinate **4** was synthesized according to known method.[22] Yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19–1.28 (m, 6H, 2Me), 1.86 (s, 3H, Me), 2.14 (s, 3H, Me), 3.36 (s, 2H, CH_2).

*3-Methoxycarbonyl-4-(2-methylbenzo[*b*]thiophen-3-yl)-2-(propan-2-ylidene)pent-3-enoic acid* **5**. A mixture of 3-acetyl-2-methylbenzo[*b*]-thiophene **3** (10 mmol, 1.90 g) and dimethyl 2-(propan-2-ylidene)succinate **4** (10 mmol, 1.86 g) in 20 ml of THF was added to the suspension of NaH (2.9 mmol, 0.70 g) in 10 ml of THF. After addition of a drop of methanol that initiated violent hydrogen evolution, the mixture was stirred for 2.5 h at ambient temperature until the end of hydrogen evolution. The solvent was then removed with the use of rotary evaporator and the residue was dissolved in water (250 ml). The water solution was treated with chloroform and then acidified with 10% aqueous HCl up to pH 1. The organic layer was extracted with diethyl ether and the solvent was evaporated. The resulting oil **5** was used in the further reactions without additional purification.

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methyl[*b*]thiophen-3-yl)ethylidene]-4-(2-propan-2-ylidene)-dihydrofuran-2,5-dione **1**,¶ whose oxidation with CPBA gives rise to (*Z*)-3-[1-(2-methyl-1,1-dioxidobenzo[*b*]thiophen-3-yl)-ethylidene]-4-(2-propan-2-ylidene)dihydrofuran-2,5-dione **2**.†† The IR spectrum of compound **2** exhibits characteristic bands of two exocyclic furandione carbonyl groups at 1762 and 1813 cm^{-1}. The ^1H NMR spectrum contains signals of four methyl groups at 2.07–2.49 ppm, whose position points to *Z*-configuration of fulgide **2**.[18]

The partial disruption of the π-conjugated system of **1** resulted from conversion of the cyclic sulfide center into sulfonyl group gives rise to the significant blue shift of the long wavelength band of **1**, which appeared at 336 nm[17] to 278 nm (the molar absorption coefficient is 1.5×10^5 dm^3 mol^{-1} cm^{-1}). The ring-opened **O** form of **2** does not fluoresce at ambient temperature. Irradiation of its solution in acetonitrile with 313 nm (filtered light of Hg lamp) leads to appearance of a new absorption band at 385 nm, whose intensity increases upon irradiation while the intensity of initial absorption bands decreases (Figure 1). The observed spectral changes are indicative of the occurrence of the electrocyclic rearrangement of the hexatriene open isomer **O** into the 1,3-cyclohexadiene closed form **C** (Scheme 2). Since the colored form **C** can be generated only from the *E*-isomer,[1,2,4] the photostationary state formed under irradiation is characterized by the simultaneous presence of *Z*- and *E*-ring-opened **O** forms and ring-closed **C** isomer.[12,17] For this reason it is difficult to determine the exact value of quantum yield of *Z*-**O** → **C** photorearrangement. Nevertheless, we tried to estimate the efficiency of the complicated photocoloration process of **2** shown in Scheme 2 using fulgide **1**[16] as an actinometer (quantum yield of **O** → **C** process is 0.32) and obtained the value of 0.37.

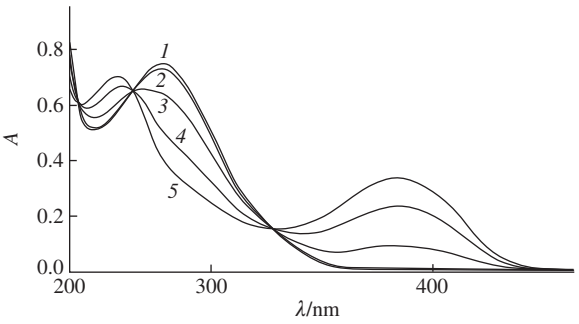
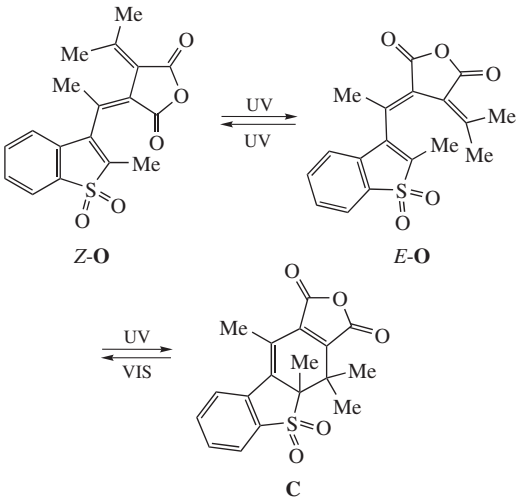


Figure 1 Electronic absorption spectra of **2** in acetonitrile (5.0×10^{-5} M) (*1*) before and after (*2*) 1, (*3*) 5, (*4*) 15 and (*5*) 35 min of irradiation by 313 nm light.



Scheme 2

The ring-closed isomers **1C** and **2C** demonstrate high thermal stability, the intensities of their longest wavelength absorption bands remain non-decreased within 48 h at 293 K. Irradiation of the colored solution of **2C** with the light of λ_{irr} = 436 nm results in its complete bleaching due to the reopening into the initial form **2O**. A similar transformation was found previously for **1C**.[16] The ring-opened isomers **O** of **1** and **2** as well as cyclic **C** form of **1** do not reveal fluorescent properties. In contrast with this, **2C** exhibits emission at 480 nm whose intensity increases (Figure 2) with the growth in the intensity of the photoinduced long wavelength absorption band of **2C** at 385 nm (see Figure 1). The fluorescence excitation spectrum well matches the above long wavelength band. Quantum yield of the fluorescence of the ring-closed isomer **C** of fulgide **2** was measured and found to be 0.006.

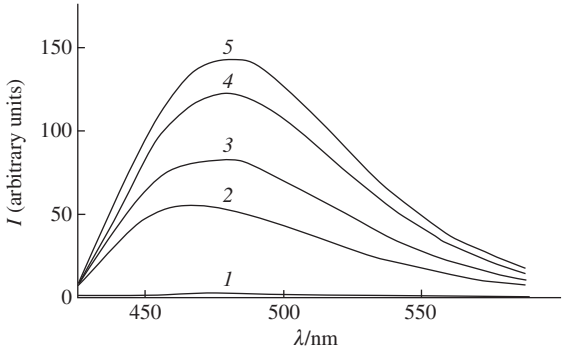


Figure 2 Electronic emission spectra of **2** in acetonitrile (5.0×10^{-5} M) (*1*) before and after (*2*) 5, (*3*) 15, (*4*) 25 and (*5*) 35 min of irradiation by 313 nm light.

§ *2-[1-(2-Methylbenzo[*b*]thiophen-3-yl)ethylidene]-3-(propan-2-ylidene)-succinic acid* **6**. Acid **5** was added to 30 ml of 10% KOH methanol solution and refluxed for 8 h. Methanol was removed, the residue was dissolved in water (250 ml) and acidified with 10% aqueous HCl up to pH 1. The crude product **6** was filtered and dried. Yield 1.44 g (44%), cream crystals, mp 238–239 °C. IR (ν/cm^{-1}): 1635, 1680 (C=O), 3412 (OH). ^1H NMR (300 MHz, $CDCl_3$) δ: 1.88 (s, 3H, Me), 1.92 (s, 3H, Me), 2.19 (s, 3H, Me), 2.39 (s, 3H, Me), 7.20–7.46 (m, 3H, H_{Ar}), 7.81–7.85 (m, 1H, H_{Ar}), 12.06 (br. s, 2H, 2OH). Found (%): C, 65.27; H, 5.69. Calc. for $C_{18}H_{18}O_4S$ (%): C, 65.43; H, 5.49.

¶ *(Z)-3-[1-(2-Methylbenzo[*b*]thiophen-3-yl)ethylidene]-4-(2-propan-2-ylidene)dihydrofuran-2,5-dione* **1**. The solution of diacid **6** (4.4 mmol, 1.44 g) in 1 ml of acetic anhydride was refluxed for 5 min. The precipitate of fulgide **1** was filtered, rinsed with methanol (5 ml) and recrystallized from 1-butanol. Yield 0.33 g (24%), colorless crystals, mp 169–170 °C. IR (ν/cm^{-1}): 1758, 1811, 1831 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ: 2.15 (s, 3H, Me), 2.22 (s, 3H, Me), 2.44 (s, 3H, Me), 2.49 (s, 3H, Me), 7.26–7.36 (m, 1H, H_{Ar}), 7.57–7.78 (m, 3H, H_{Ar}). ^{13}C NMR (600 MHz, DMSO-d_6) δ: 163.0, 160.7, 155.0, 145.9, 138.5, 138.3, 137.8, 131.2, 125.2, 124.4, 123.9, 122.3, 121.1, 120.9, 27.4, 25.1, 22.5, 14.4. MS (EI), *m*/*z* (%): 312 $[M]^+$ (100), 297 (85), 253 (53), 148 (52). Found (%): C, 69.11; H, 5.33. Calc. for $C_{18}H_{16}O_3S$ (%): C, 69.21; H, 5.16.

†† *(Z)-3-[1-(2-Methyl-1,1-dioxidobenzo[*b*]thiophen-3-yl)ethylidene]-4-(2-propan-2-ylidene)dihydrofuran-2,5-dione* **2**. A mixture of fulgide **1** (0.32 mmol, 0.10 g) and 3-chloroperoxybenzoic acid (15 mmol, 0.25 g) in 8 ml of dichloromethane was stirred for 24 h at ambient temperature. The mixture was treated by a saturated solution of $NaHCO_3$ (50 ml). The solvent was evaporated *in vacuo* to give the crude product, which was filtered, dried, and purified by recrystallization from DMFA–2-propanol (3:1). Yield 0.12 g (35.7 %), colorless crystals, mp 268–269 °C. IR (ν/cm^{-1}): 1762, 1813 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ: 2.07 (s, 3H, Me), 2.12 (s, 3H, Me), 2.15 (s, 3H, Me), 2.49 (s, 3H, Me), 6.99–7.01 (m, 1H, H_{Ar}), 7.47–7.50 (m, 2H, H_{Ar}), 7.76–7.79 (m, 1H, H_{Ar}). ^{13}C NMR (600 MHz, DMSO-d_6) δ: 162.6, 161.4, 158.0, 139.0, 137.6, 135.3, 134.4, 134.1, 131.1, 129.7, 126.2, 122.9, 121.4, 119.5, 27.4, 23.1, 22.3, 6.8. MS (EI), *m*/*z* (%): 344 $[M]^+$ (17), 139 (100). Found (%): C, 62.59; H, 4.82. Calc. for $C_{18}H_{16}O_5S$ (%): C, 62.78; H, 4.68.

The principal difference in fluorescence properties of sulfide **1** and sulfone **2** is connected with the presense of sulfonyl SO_2 group in the latter.[19,20] To the best of our knowledge, it is the first example of imparting emission properties to non-fluorescent photochromic fulgides through the direct oxidation of benzo[*b*]-thienyl moiety into 1,1-dioxidobenzo[*b*]thienyl one. The ring-closed form of novel photochromic fulgide, 3-[1-(2-methyl-1,1-dioxidobenzo[*b*]thiophen-3-yl)ethylidene]-4-(propan-2-ylidene)dihydrofuran-2,5-dione, displays fluorescence emission which can be modulated by light. This result may be considered as a useful step in the development of a new preparative strategy for the design of fluorescent photochromic fulgides.

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References

1 Y. Yokoyama, *Chem. Rev*., 2000, **100**, 1717.
2 Y. Yokoyama, T. Gushiken and T. Ubukata, in *Molecular Switches*, eds. B. L. Feringa and W. R. Browne, Wiley-VCH, Weinheim, 2011, p. 81.
3 H. Bouas-Laurent and H. Dürr, *Pure Appl. Chem*., 2001, **73**, 639.
4 Y. Yokoyama and M. Köse, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and F. Lenci, CRC Press LLC, Boca Raton, FL, 2004, vol. 1, ch. 86.
5 V. I. Minkin, *Russ. Chem. Rev.*, 2013, **82**, 1.
6 Y. Yokoyama and M. Köse, *J. Photochem. Photobiol. A: Chem*., 2004, **166**, 9.
7 Y. C. Liang, A. S. Dvornikov and P. M. Rentzepis, *Macromolecules*, 2002, **35**, 9377.
8 Y. C. Liang, A. S. Dvornikov and P. M. Rentzepis, *Res. Chem. Intermed*., 1998, **24**, 905.
9 A. V. Metelitsa, O. T. Lyashik, S. M. Aldoshin, O. A. Kozina, N. V. Volbushko, E. A. Medyantseva, M. I. Knyazhanskii, V. I. Minkin and A. O. Atovmyan, *Chem. Heterocycl. Compd. (Engl. Transl.)*, 1990, **26**, 28 (*Khim. Geterotsikl. Soedin.*, 1990, 33).
10 Y. Yokoyama, T. Tanaka, T. Yamane and Y. Kurita, *Chem. Lett.*, 1991, **20**, 1125.
11 Y. C. Liang, A. S. Dvornikov and P. M. Rentzepis, *Opt. Commun.*, 2003, **223**, 61.
12 V. P. Rybalkin, E. N. Shepelenko, V. V. Tkachev, G. V. Shilov, S. K. Balenko, A. V. Tsukanov, L. L. Popova, A. D. Dubonosov, S. M. Aldoshin, V. A. Bren and V. I. Minkin, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 101 (*Izv. Akad. Nauk, Ser. Khim.*, 2006, 97).
13 S. K. Balenko, V. P. Rybalkin, E. N. Shepelenko, L. L. Popova, N. I. Makarova, A. V. Metelitsa, V. A. Bren and V. I. Minkin, *Russ. J. Org. Chem.*, 2006, **42**, 1861 (*Zh. Org. Khim.*, 2006, **42**, 1869).
14 S. K. Balenko, V. P. Rybalkin, N. I. Makarova, S. O. Bezuglyi, E. N. Shepelenko, L. L. Popova, V. V. Tkachev, S. M. Aldoshin, A. V. Metelitsa, V. A. Bren and V. I. Minkin, *Russ. Chem. Bull., Int. Ed*., 2008, **57**, 1435 (*Izv. Akad. Nauk, Ser. Khim.*, 2008, 1409).
15 S. K. Balenko, N. I. Makarova, V. P. Rybalkin, E. N. Shepelenko, L. L. Popova, V. V. Tkachev, S. M. Aldoshin, A. V. Metelitsa, V. A. Bren and V. I. Minkin, *Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 954 (*Izv. Akad. Nauk, Ser. Khim*., 2010, 932).
16 M. Kose and E. Orhan, *J. Photochem. Photobiol. A: Chem*., 2006, **177**, 170.
17 S. I. Luyksaar, V. A. Migulin, B. V. Nabatov and M. M. Krayushkin, *Russ. Chem. Bull., Int. Ed*., 2010, **59**, 446 (*Izv. Akad. Nauk, Ser. Khim.*, 2010, 436).
18 A. P. Glaze, S. A. Harris, H. G. Heller, W. Johncock, S. N. Oliver, P. Strydom and J. Whittall, *J. Chem. Soc., Perkin Trans. 1*, 1985, 957.
19 Y.-C. Jeong, S. I. Yang, K.-H. Ahn and E. Kim, *Chem. Commun*., 2005, **19**, 2503.
20 Y.-C. Jeong, S. I. Yang, E. Kim and K.-H. Ahn, *Tetrahedron*, 2006, **62**, 5855.
21 D. A. Shirley, B. H. Gross and M. J. Danzig, *J. Org. Chem*., 1958, **23**, 1024.
22 W.-W. W. Lee, L.-M. Gan and T.-P. Loh, *Synlett*, 2005, 2473.

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