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SYNTHESIS, PHOTOCHROMIC AND FLUORESCENT PROPERTIES OF HYBRID COMPOUNDS OF FULGIMIDES AND BENZOTHIAZOLYLTHIENOTHIOPHENE

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The precursors and hybrid compounds, including photochromic fulgimides and fluorescent benzothiazolylthienothiophene units, have been synthesized. Spectroscopic investigations by absorption and fluorescence methods showed that fulgimide hybrids display photochromism, but do not display fluorescence properties. A possible explanation for this fact is proposed and also the decreased effectiveness of photochromic conversion.

Keywords: benzothiazolylthienothiophenes, hybrid photochromic fulgimides, fulgimides, synthesis, fluorescence properties, photochromism.

Currently photochromic materials are actively under consideration as potential recording media for three-dimensional storage [1]. Important properties which determine their utility for these uses are nondestructive sensing of optical information, which is possible only in those cases when the sensed irradiation is not absorbed by two forms of photochromic compounds mutually transformed under the influence of light. One of the most fruitful routes for the solution of this problem is the creation of photochromic materials capable of sensing optical information by the fluorescence method [2, 3]. For this objective in particular hybrid photochromic compounds were synthesized which contained in their structure both photochromic and fluorophoric units [4-9] in which the absorption bands of the fluorescent part of the molecule were located in addition to the adsorption bands of the two forms of the photochromic part, but the fluorescent spectrum coincides with the absorption spectrum of one of the forms of the photochromic compound.

In the present work an attempt was made to synthesize new hybrid compounds based on photochromic amino-substituted fulgimides and fluorescent derivatives of benzothiazolylthienothiophene.

Dedicated to our colleague L. I. Belen'kii on his splendid Jubilee.

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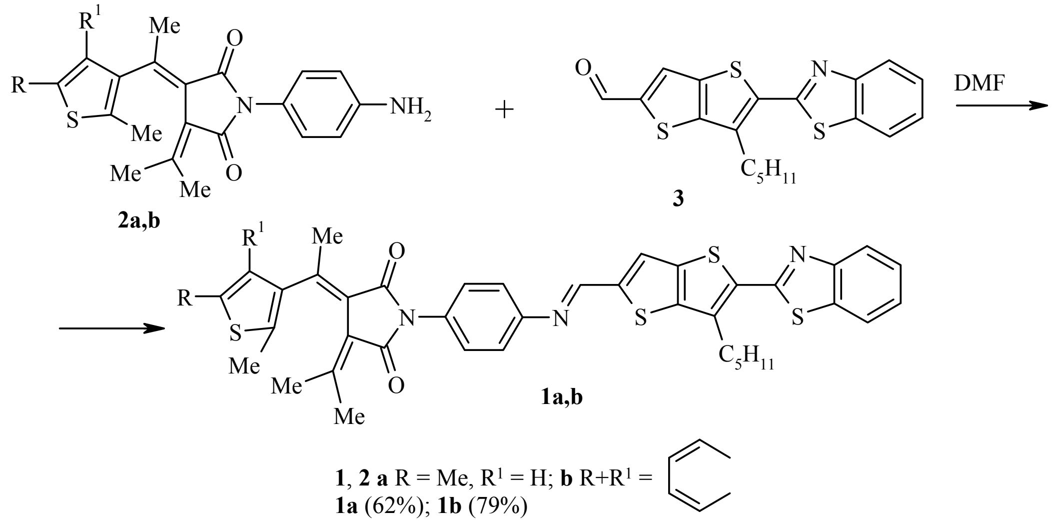
The objects of the study were two hybrid photochromic compounds: (3*Z*)-1-(4-{[5-(1,3-benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thien-2-yl]methylideneamino}phenyl)-3-[1-(2,5-dimethylthien-3-yl)ethylidene]-4-(1-methylidene)-2,5-pyrrolidinedione (**1a**) and (3Z)-1-(4-{[5-(1,3-benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]-thien-2-yl]methylideneamino}phenyl)-3-[1-(2-methylbenzo[*b*]thien-3-yl))ethylidene]-4-(1-methylethylidene)-2,5-pyrrolidinedione (**1b**), synthesized in high yield from the photochromic compounds **2a**,**b** and the fluorescent compound 5-(1,3-benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophene-2-carbaldehyde (**3**) by the following general scheme:



1, **2** **a** R = Me, R¹ = H; **b** R+R¹ =
1a (62%); **1b** (79%)

The synthesis of 2-(3-pentylthieno[3,2-*b*]thien-2-yl)-1,3-benzothiazole (**4**) – the starting compound for the synthesis of aldehyde **3** – was accomplished by the following scheme:

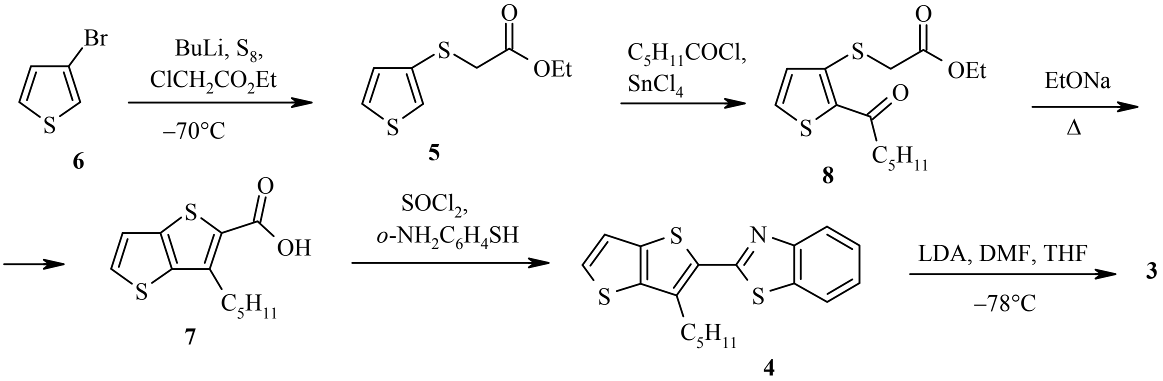


TABLE 1. Absorption and Fluorescent Characteristics* of Benzothiazoles in Toluene

Compound	$\lambda_{\text{max ab.}}$, nm	$D_{\text{max ab}}$	$\lambda_{\text{max ex. fl}}$, nm	$\lambda_{\text{max fl}}$, nm	$\Delta\lambda$, nm	$I_{\text{max fl}}$, nm
3	378	0.25	377	438	60	145
4	353	0.21	353	413	60	1140

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* $\lambda_{\text{max ab}}$, $\lambda_{\text{max ex fl}}$, and $\lambda_{\text{max fl}}$ are the wavelengths of maxima of the waves of absorption, excited fluorescence, and fluorescence, respectively; $D_{\text{max ab}}$ is the optical density at the maximum of the absorption bands; $\Delta\lambda = \lambda_{\text{max fl}} - \lambda_{\text{max ab}}$; $I_{\text{max fl}}$ is the intensity of fluorescence at the maximum of the fluorescence band.

Ester **5** was synthesized from 6-bromothiophene (**6**) using ethyl monochloroacetate. Its acylation with capronyl chloride and subsequent hydrolysis gave 3-pentylthieno[3,2-*b*]thiophene-2-carboxylic acid (**7**) which was obtained by an analogous method [10]. The synthesis of the corresponding acid chloride, and its reaction with *o*-aminothiophenol in N-methylpyrrolidone with the formation of the thiazole derivative of **3** occurred in high yield.

In contrast from most monothienyl derivatives, formylation of compound **4** under typical conditions of the Vilsmeier reaction did not give the aldehyde **3**. The latter was successfully obtained in high yield by the reaction of compound **4** with lithium diisopropylamide (LDA) in THF at -78°C with subsequent treatment with DMF of the first formed organolithium derivative.

The results of absorption and luminescence investigations of the fluorophores **3** and **4** are presented in Table 1 and Fig. 1.

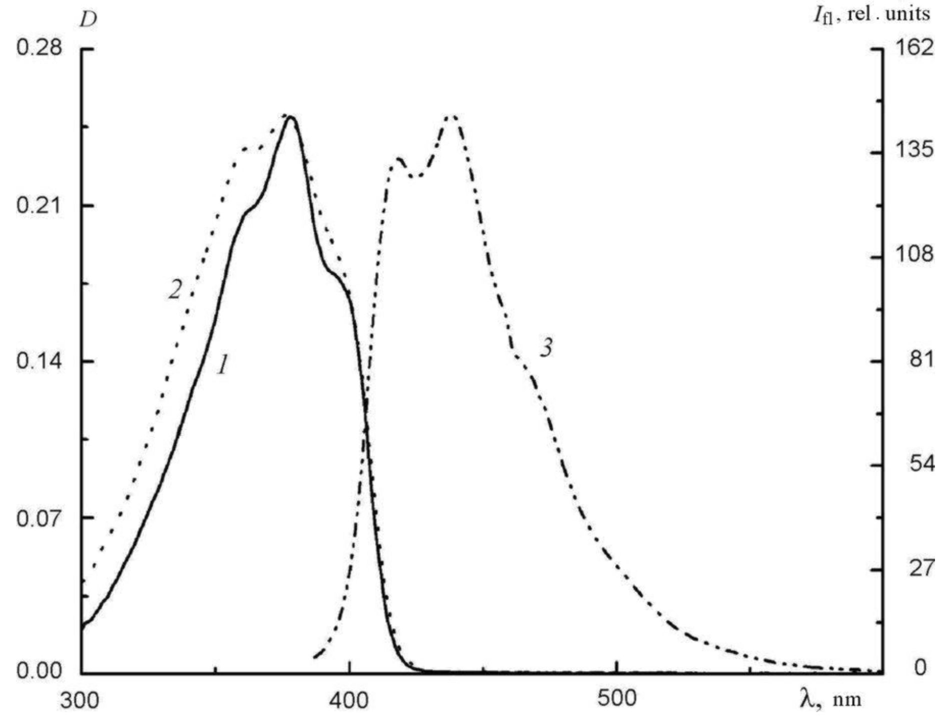

Fig. 1. Absorption spectra (*1*), excited (*2*), and emission (*3*) fluorescence of compound **3** in toluene.

It is seen from the data of Table 1 that introduction of a carbonyl group into benzthiazole **4** led to a bathochromic shift of the absorption, excitation, and fluorescence bands by 24-25 nm. In the same way fluorescence of compound **3** is considerably reduced.

Analysis of the properties of fulgimides **2a** and **2b**, precursors of the hybrid compounds, shows that they possess reversible photoconversion which is normal for fulgimides [1]. It is explained by photoinduced valence photoisomerization, as a result of which the open form **A** is converted into the cyclic form **B.**

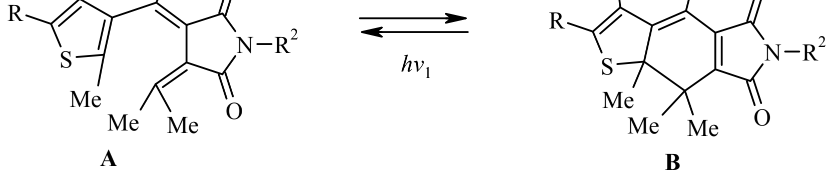

TABLE 2. Absorption Characteristics* of Fulgimides and Hybrid Compounds in Toluene

Compound	$\lambda_{\mathbf{A}\,\max}$, nm	$D_{\mathbf{A}\,\max}$	$\lambda_{\mathbf{B}\,\max}$, nm	$\Delta D_{\mathbf{B}}^{\text{phot}}{}_{\text{ab.}}$	$\Delta D_{\mathbf{B}}^{\text{phot}}{}_{\text{ab}} / D_{\mathbf{A}\,\max}$
2a	332 sh	0.35	525	0.18	0.51
2b	316 sh	0.29	490	0.18	0.62
1a	404	3.23	528	0.10	0.03
1b	404	2.78	~490	0.06	0.02

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* $\lambda_{\mathrm{A}\,\max}$ and $\lambda_{\mathrm{B}\,\max}$ are the wavelengths of the absorption maxima of the open form **A** and the photoinduced closed **B** form; $D_{\mathrm{A}\,\max}$ is the optical density at the maximum of the absorption bands of the open form **A**; $\Delta D_{\mathrm{B}}^{\text{phot}}{}_{\text{ab}}$ is the photoinduced change in the optical density at the maximum of absorption bands of the cyclic form **B** in the visible region of the spectrum in the photo-equilibrium state; sh is the shoulder in the absorption spectrum.

Results of the investigation of the absorption properties of the photochromic compounds **2a** and **2b** in toluene are shown in Table 2 and Fig. 2.

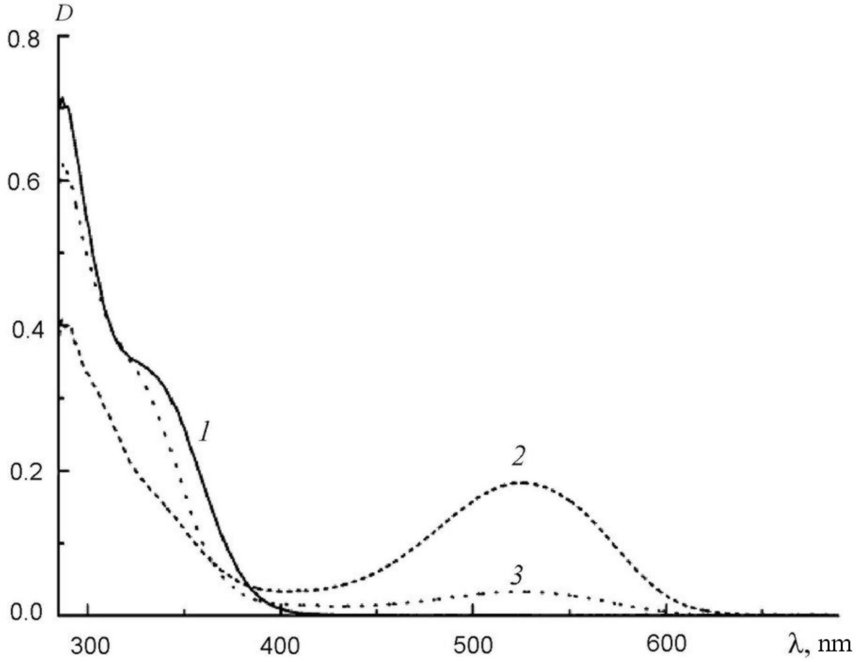

Fig. 2. Absorption spectra of fulgimide **2a** in toluene before (*1*) and after irradiation successively with UV (*2*) and visible light (*3*).

The results of the spectral-kinetic investigations of the amide-substituted fulgimides **2a** and **2b** agree with the data presented previously [1].

Fluorescence was not observed for either the open form nor for the closed form of the amino derivatives of the fulgimides studied.

The results of the spectral-kinetic investigations of the photochromy of the conversions of the synthesized hybrid fulgimides **1a** and **1b** in toluene solution are shown in Table 2 and Fig. 3.

It follows from the data of Table 2 that the hybrid fulgimides are typical photochromes. The initial open forms of these hybrid compounds are characterized by absorption bands, the maxima of which occur in the region of 404 nm, significantly shifted to the longwave length region of the spectrum in comparison with their fulgimide precursors (see Fig. 2). Such shifts of the absorption bands of the open forms are evidently explained by the absorption of the benzothiazolylthienothiophene units (see Fig. 1). When hybrid fulgimides are irradiated long enough with filtered UV light with alternate separation of the different mercury lines new broad absorption bands appear in the visible region of the spectrum with maxima in the 490-528 nm range (Fig. 3), which practically coincide with the absorption bands of the cyclic forms of the fulgimide precursors.

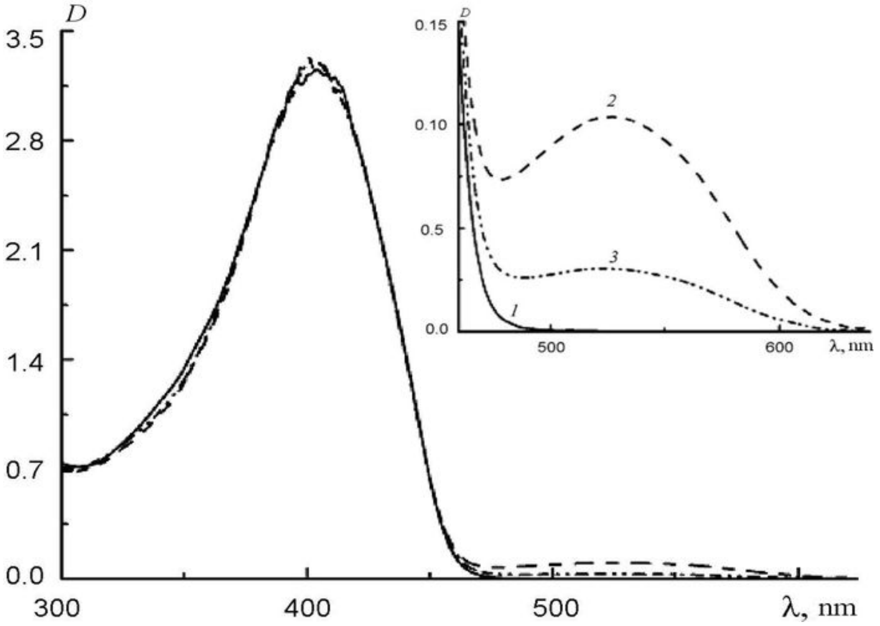

Fig. 3. Absorption spectra of the hybrid fulgimide **1a** in toluene before (*1*) and after irradiation in UV (*2*) and visible light (*3*).

Comparison of the results of spectral investigations carried out with data obtained for the fulgimide precursors permits the conclusion that the observed reversible photoconversion of the hybrid fulgimides is also explained by photoinduced valence isomerization, but the process of photocoloring is sharply reduced after introduction into the structure of the precursors of the fluorescent units. In this respect it was observed that in the hybrid fulgimides **1a** and **1b**, as in the fulgimide precursors, neither the open nor cyclic forms possess fluorescent properties. The decrease in the effectiveness of the photocoloring process can be explained, in our view, by transformation of the activating radiation of the nonphotochromic fragment or the deactivation of the photoexciting energy into heat as a result of additional vibration processes, explained by the presence of non-photochromic fragments which may undergo *cis-trans* isomerization. The last factor is possibly the reason for the absence of fluorescence in the hybrid fulgimide.

So as a result of carrying out this study, two new hybrid fulgimides were synthesized with photochromic properties, but not fluorescence, despite the presence of fluorescent fragment in their structures. The observed decrease in the effectiveness of the photochromic conversion and the absence of fluorescent properties, it is proposed, is connected to the optical properties and structural factors of the benzothiazolyl-thienothiophene fragments.

EXPERIMENTAL

Spectrophotometric measurements (photostationary spectra) and also kinetics of the processes of photocoloring, photoachromatism and photodegradation of photoinduced cyclic forms of the compounds studied in toluene solution were carried out with a Varian Cary 50 Bio (Australia) spectrophotometer. Spectrofluorometric measurements of the initial and cyclic forms were carried out on a Varian Cary Eclipse Fluorescence spectrophotometer (Australia).

Quartz cuvettes with a width of 2 mm were used to measure absorption characteristics (kinetic measurements) and cuvettes with a width of 10 mm were used for spectrophotometric studies. To record absorption, excited and emission spectra of compounds **1a**,**b**, **2a**,**b** a solution concentration of $4 \cdot 10^{-5}$ mol/l was chosen, and for compounds **3** and **4** a solution concentration $5 \cdot 10^{-6}$ mol/l was chosen. Radiation was carried out with the light from a mercury-xenon lamp LC4 100−240 V−300 VA (Japan) on a HAMAMATSU lightning cure^{TM} irradiation set-up using UFS-1, ZhS-11, ZhS-16, and ZhS-17 filters.

^{1}H NMR spectra were recorded with a Bruker AC-300 (300 MHz) spectrometer of $CDCl_3$ solutions (compounds **1a**,**b**, **7**) and DMSO-d_6 solutions (compounds **3**-**5**, **8**) with residual protons of the deuterated solvents as internal standards. Mass spectra were recorded on a Kratos instrument with direct insertion of the sample into the ionizing chamber with an ionization energy of 70 eV and an control voltage of 1.76 kV. Melting points were measured on a Boetius block and were not corrected.

Commercial available reagents from Acros and toluene solvent from Aldrich were used in this study.

Ethyl (3-Thienylmercapto)acetate (5) was obtained by metallation [11] of 3-bromothiophene (**6**) [12, 13] with butyllithium at -70°C with subsequent treatment of the organolithium derivative formed with sulfur and ethyl monochloroacetate. Yield 79%; bp 146-150°C (12 Torr), (bp 140-142°C (9 Torr) [14]), n_D^{20} 1.5610. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, t, $J = 7.1$, CH_3); 3.75 (2H, s, CH_2); 4.10 (2H, q, $J = 4.55$, CH_2); 7.15 (1H, s, H-2); 7.65 (2H, m, H-4,5). Mass spectrum, *m/z* (I_{rel}, %): 202 [M^+] (67), 129 (100). $C_8H_{10}O_2S_2$.

Ethyl [(2-Hexanoylthien-3-yl)mercapto]acetate (8). A solution of tin(IV) chloride (7.2 ml) in benzene (10 ml) was added dropwise at -5°C to a solution containing compound **5** (12.14 g, 60 mmol) and capronoyl chloride (8.76 g, 65 mmol) in benzene (80 ml). The mixture was stirred for 2 h at room temperature. The reaction mixture was cooled to -5°C and 70 ml of 10% HCl was added. It was cooled again. The aqueous layer was separated and extracted with benzene. The combined benzene extract was washed with water and dried over magnesium sulfate. The benzene was evaporated. Yield 82%; mp 55-56°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 (3H, t, $J = 6.9$, CH_3); 1.25 (3H, t, $J = 7.0$, CH_3); 1.45 (4H, m, $2CH_2$); 1.75 (2H, m, CH_2); 2.80 (2H, t, $J = 6.9$, CH_2); 3.75 (2H, s, CH_2); 4.20 (2H, q, $J = 4.7$, $C\underline{H_2}CH_2$); 7.15 (1H, d, $J = 5.25$, H-4); 7.50 (1H, d, $J = 5.2$, H-5). Mass spectrum, *m/z* (I_{rel}, %): 300 [M^+] (11), 156 (90), 71 (100). Found, %: C 55.85; H 6.80; S 21.43. $C_{14}H_{20}O_3S_2$. Calculated, %: C 55.97; H 6.71; S 21.35.

3-Pentylthieno[3,2-*b*]thiophene-2-carboxylic Acid (7). A solution of ester **8** (14.814 g, 49 mmol) in absolute ethanol (45 ml) was added to a solution of sodium ethoxide (3.97 g, 172 mmol) in absolute ethanol (100 ml). The reaction mixture was boiled for 5 h, the ethanol was evaporated, the residue was dissolved in water (200 ml) and acidified with HCl. The yellowish precipitate was filtered off, washed with water and dried in a vacuum dessicator. Yield 80%; mp 105-107°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.89 (3H, t, $J = 5.9$, CH_3); 1.35 (4H, m, $2CH_2$); 1.80 (2H, m, CH_2); 3.75 (2H, t, $J = 7.6$, CH_2); 7.15 (1H, d, $J = 5.0$, H-6); 7.53 (1H, d, $J = 5.0$, H-5). Mass spectrum, *m/z* (I_{rel}, %): 254 [M^+] (16), 198 (100). Found, %: C 56.58; H 5.46; S 25.32. $C_{12}H_{14}O_2S_2$. Calculated, %: C 56.66; H 5.55; S 25.21.

2-(3-Pentylthieno[2,3-*b*]thien-2-yl)-1,3-benzothiazole (4). A solution of compound **7** (4.4 g, 17 mmol) in N-methylpyrrolidone (85 ml) was cooled to 0°C and $SOCl_2$ (1.46 ml, 21 mmol) was added with stirring. The mixture was removed from the cold bath, the temperature of the mixture was allowed to rise to 20°C, kept at that temperature for 20 min, and *o*-aminothiophenol (2.00 ml, 18.2 mmol) was added. After this the mixture was boiled for 4 h 30 min, then cooled to 5°C, 1 N NaOH solution (120 ml) was added, and stirred for 30 min at 20°C. The precipitate was filtered off, washed with 2% NaOH solution and water and then dried. The residue was chromatographed on silica gel with a 3:1 petroleum ether–ethyl acetate mixture. Yield 77%; mp 85-86°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.88 (3H, t, *J* = 6.9, CH_3); 1.40 (4H, m, $2CH_2$); 1.80 (2H, m, CH_2); 3.20 (2H, t, *J* =7.8, CH_2); 7.52 (3H, m, H-6, 2H arom); 7.89 (1H, d, *J* = 5.25, H-5); 8.03 (1H, d, *J* = 7.9, H arom); 8.18 (1H, d, *J* = 7.5, H arom). Mass spectrum, *m/z* (I_{rel}, %): 343 $[M]^+$ (3), 314 $[M+H\text{-}Et]^+$ (8), 300 $[M+H\text{-}Et\text{-}Me]^+$ (100). Found, %: C 62.69; H 5.16; N 4.29; S 27.86. $C_{18}H_{17}NS_3$. Calculated, %: C 62.93; H 4.99; N 4.08; S 28.00.

5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thiophene-2-carbaldehyde (3). Compound **4** (3 g, 8.73 mmol) was dissolved in dry THF (100 ml) in an atmosphere of argon, cooled to -78°C and lithium diisopropylamide (4.8 ml – 2 mol/l in THF) was added. The mixture was removed from the cold bath and the mixture temperature allowed to rise to 0°C, kept at this temperature for 5 min, then cooled again to -78°C and a solution of DMF (1 ml) in THF (8 ml) was added. The mixture was removed from the cooling bath and the temperature allowed to reach room temperature. After 12 h the reaction mixture was added to 1% HCl (300 ml), extracted with methylene chloride, washed with water, the extract was dried over magnesium sulfate, and evaporated. The residue was chromatographed on silica gel in a 4:1 hexane–ethyl acetate mixture. Yield 73%; mp 121-123°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.88 (3H, t, *J* = 6.55, CH_3); 1.42 (4H, m, $2CH_2$); 1.80 (2H, m, CH_2); 3.20 (2H, t, *J* = 7.7, CH_2); 7.53 (2H, m, 2H arom); 8.08 (1H, *J* = 8.1, H arom); 8.18 (1H, d, *J* = 8.1, H arom); 8.42 (1H, s, H-3); 10.02 (1H, s, COH). Mass spectrum, *m/z* (I_{rel}, %): 371 $[M]^+$ (40), 342 $[M+H\text{-}Et]^+$ (17), 328 $[M+H\text{-}Et\text{-}Me]^+$ (100). Found, %: C 61.65; H 4.39; N 3.95; S 25.68. $C_{19}H_{17}NOS_3$. Calculated, %: C 61.42; H 4.61; N 3.77; S 25.89.

Schiff Bases 1a,b (General Method). Compounds **2a**,**b** (0.41 mmol) were dissolved in DMF (5 ml) and aldehyde **3** (0.15 g, 0.41 mmol) was added and the mixture was kept at room temperature for 12 h with heating. The formed yellow crystals were filtered off, washed on the filter with ethanol, and dried in a vacuum dessicator.

(3Z)-1-(4-{[5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thien-2-yl]methylideneamino}phenyl-3-[1-(2,5-dimethylthien-3-yl)ethylidene]-4-(1-methylethylidene)-2,5-pyrrolidinedione (1a). Yield 62%, yellow crystals; mp 210-212°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.88-0.97 (3H, m, CH_3); 1.36-1.58 (4H, m, $2CH_2$); 1.80-1.95 (2H, m, CH_2); 2.07 (3H, s, CH_3); 2.16 (3H, s, CH_3); 2.38 (3H, s, CH_3); 2.43 (3H, s, CH_3); 2.52 (3H, s, CH_3); 3.18-3.27 (2H, m, CH_2); 6.55 (1H, s, H-4); 7.21-7.32 (2H, m, H arom); 7.34-7.45 (3H, m, H arom); 7.48-7.51 (1H, m, H arom); 7.64 (1H, s, H-3'); 7.88-7.93 (1H, m, H arom); 8.05-8.12 (1H, m, H arom); 8.58 (1H, s, −N=CH−). Mass spectrum, *m/z* (I_{rel}, %): 720 $[M]^+$ (100). Found, %: C 66.64; H 5.13; N 5.81; S 17.72. $C_{40}H_{37}N_3O_2S_4$. Calculated, %: C 66.73; H 5.18; N 5.84; S 17.81.

(3*Z*)-1-(4-{[5-(1,3-Benzothiazol-2-yl)-6-pentylthieno[3,2-*b*]thien-2-yl]methylideneamino}phenyl-3-[1-(2-methylbenzo[*b*]thien-3-yl)ethylidene]-4-(1-methylethylidene)-2,5-pyrrolidinedione (1b). Yield 79%, yellow crystals; mp 252-259°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.87-1.00 (3H, m, CH_3); 1.33-1.64 (4H, m, $2CH_2$); 1.79-1.94 (2H, m, CH_2); 2.16 (3H, s, CH_3); 2.20 (3H, s, CH_3); 2.48 (3H, s, CH_3); 2.55 (3H, s, CH_3); 3.13-3.27 (2H, m, CH_2); 7.18-7.54 (8H, m, H arom); 7.61 (1H, s, H-3); 7.68-7.77 (1H, m, H arom); 7.87-7.94 (1H, m H arom); 8.02-8.11 (1H, m, H arom); 8.54 (1H, s, −NH=CH−). Mass spectrum, *m/z* (I_{rel}, %): 756 $[M]^+$ (100). Found, %: C 68.33; H 4.86; N 5.51; S 16.81. $C_{43}H_{37}N_3O_2S_4$. Calculated, % : C 68.31; H 4.93; N 5.56; S 16.96.

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