Synthesis and Spectral Properties of Fluorescent Dithienylmaleimides

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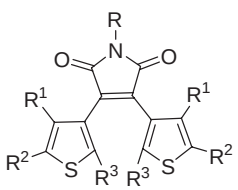
A convenient preparative method of the synthesis of dithienylethenes based on maleimides was proposed. Previously, difficult accessible dithienylethene derivatives, in which 2-thienyl substituents are attached to the double bond of maleimide, have been synthesized. The spectral properties of the dithienylmaleimides were studied and it has been shown that these compounds do not belong to photochromes but they possess fluorescent properties.

Diarylethenes have been extensively studied owing to their potential as optoelectronic materials[1–3] and precursors of medicines.[4–6] The spectral properties of dithienylethenes depend on the nature of the ethene bridge, substituents in the heterocyclic rings and the substitution position on the thiophene ring with the double bond of the ethene moiety.[7–15] So, although most bis(2-thienyl)ethenes display photochromism,[11,12] some of them do not belong to photochromes.[7] Therefore, it is difficult to predict the spectral properties of the diarylethenes before their studies.

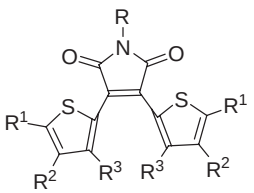
The promising compounds among of diarylethenes are the dithienylmaleimides that have been considered as potential photoswitching materials.[7–9] The ethene bridge of most known dithienylmaleimides is attached to the 3-position of the thiophene ring (structure I). There are only a few examples of these kinds of compounds where the ethene moiety is linked to the 2-position of the thiophene ring (structure II) and the methods for the preparation of them are quite laborious and of low efficiency (Chart 1). In this work, we present the synthesis and spectral properties of new dithienylmaleimides according to the structure II.

Results and Discussion

Recently, we have found that the hydroxythiophene **1** in benzene in the presence of metallic sodium smoothly reacts with an equal mol amount of α-halo ketones exclusively yielding *C*-alkylation products.[16] For the purpose of the preparation of the dithienylmaleimides, we have carried out the reaction of the hydroxythiophene **1** with different 3,4-dichloromaleimides under similar conditions. The reaction takes place in anhydrous benzene in the presence of metallic sodium, with quantitative yields (Scheme 1).



I



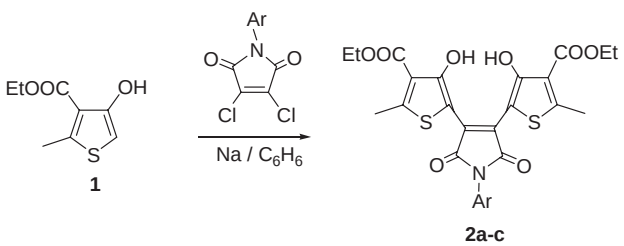
II

Chart 1.

The structures of the compounds obtained were proved by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry, and were confirmed by elemental analysis. These compounds have a reddish yellow color. The characteristic absorption of these compounds is a broad band (3450 cm^{-1}) due to the hydrogen-bonded –OH group. The ^{1}H NMR spectra of these *C*-alkylation products contain characteristic signals for the OH protons (δ_H 10.05).

The *O*-alkylation (methyl iodide, ethyl 2-bromoacetate) of the diols **2a**–**2c** was found to also proceed smoothly at room temperature in DMF in the presence of potassium carbonate yielding the dithienylethenes **3a**–**3f**. *O*-Acylation of the compounds **2a**–**2c** was carried out in an acetic anhydride–pyridine mixture at 90–100 °C (Scheme 2).

We have further studied some spectral properties of the compounds obtained. Our investigations show that these compounds do not belong to the photochromes but they possess fluorescent properties. In Fig. 1, the absorption and fluorescence spectra for the compound **2a** are shown. These spectra are typical for the compounds **2a**–**2c** and **3a**–**3f**. The absorption maxima, the extinction coefficients, and fluorescence intensities for some dithienylethenes are reported in Table 1. The characteristic property for these compounds is the intensity band of the absorption in the visible spectrum (400–530 nm). The displacement of the hydroxy substituent in the thiophene ring by the alkoxy or acetoxy group leads to a



1 **2a-c**

Ar = C_6H_5 (**2a**), 4-Cl-C_6H_4 (**2b**), 4-MeO-C_6H_4 (**2c**)

Scheme 1.

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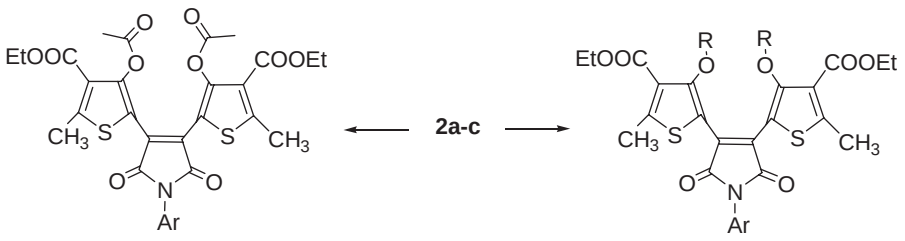

4 (a-c) **3 (f-f)**

2, 4: a) Ar = C_6H_5; b) Ar = 4-Cl-C_6H_4; c) Ar = 4-MeO-C_6H_4;
3: a) Ar = C_6H_5, R = CH_3; b) 4-Cl-C_6H_4, R = CH_3;
c) 4-MeO-C_6H_4, R = CH_3; d) Ar = C_6H_5, R = CH_2COOEt;
e) 4-Cl-C_6H_4, R = CH_2COOEt; f) 4-MeO-C_6H_4, R = CH_2COOEt;

Scheme 2.

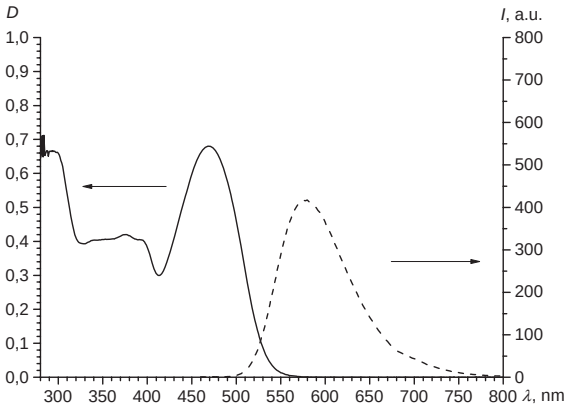

Fig. 1. Absorption $D(\lambda)$ (——) and fluorescence $I(\lambda)$ (– – –) spectra of the dithienylethene **2a** in toluene at 298 K (1×10^{-4} mol L^{-1}).

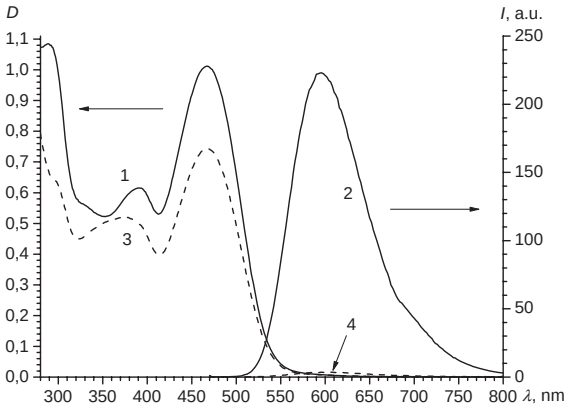

Fig. 2. Absorption $D(\lambda)$ (curves 1 and 3) and fluorescence $I(\lambda)$ (curves 2 and 4) spectra of the dithienylethenes **2a** (——) and **2c** (– – –) in acetonitrile at 298 K (1×10^{-4} mol L^{-1}).

Table 1. Absorption Maxima, Extinction Coefficient, and Fluorescence Intensity for Compounds **2–4**[a)]

Compound	Solvent	$\lambda_{Abs\ max}$ /nm	ε_{max} /L mol^{-1} cm^{-1}	λ_{Ex}/nm	$\lambda_{Fluo\ max}$ /nm	$I_{Fluo\ max}$ /a.u.	$\Delta\lambda$/nm
2a	toluene	469	6800	450	580	6740	111
3a	toluene	457	9150	457	568	530	111
3d	toluene	446	7150	446	564	790	118
4a	toluene	438	9500	438	556	24	118
2a	acetonitrile	466	11600	465	596	226	130
2c	acetonitrile	466	7400	466	600	3.8	134

a) The concentration of all samples was 1.0×10^{-4} mol L^{-1}.

hypsochromic shift of the absorption maximum. The dithienylethenes **2**, **4a–4c**, and **3a–3f** possess fluorescence in the visible spectrum and have fluorescence maxima at 562–596 nm. The largest value of the fluorescence intensity is observed for the compounds containing hydroxy groups; that value is approximately 8–13-fold more than the values of the fluorescence intensity for the compounds alkylated (compare the value of the fluorescence intensity for compounds **2a** and **3a**, Table 1). The acylation of the hydroxy groups leads to a drastic decrease in the fluorescence intensity. A significant decrease (60-fold) in the fluorescence intensity was also observed by displacement of the benzene ring in the maleimide fragment by a more donor substituent, 4-methoxyphenyl (compare the value of the fluorescence intensity for the compounds **2a** and **2c**, Fig. 2 and Table 1). It should be noted that the displacement of the substituents in the dithienylethenes **2–4** changes in fluorescence intensity but does not influence the spectrum form. These results show that both substituents in the thiophene rings and in the maleimide fragment influence the fluorescence intensity. It is significant that the observed Stokes shift for these compounds was quite large (≈110–120 nm).

Furthermore, we have studied the influence of medium basicity on the spectral properties of these compounds using as a sample the dithienylethene **2a**. The investigations were car-

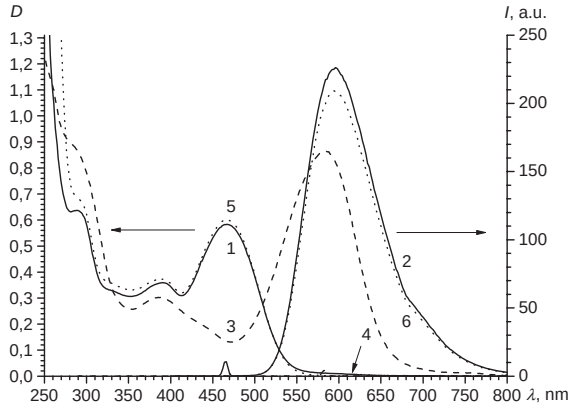

Fig. 3. Absorption $D(\lambda)$ and fluorescence $I(\lambda)$ spectra of the dithienylethene **2a** in acetonitrile at 298 K before (curves 1 and 2) and after adding DBU (curves 3 and 4) and pyridine (curves 5 and 6); the concentrations of the dithienylethene **2a**, DBU and pyridine are 1×10^{-4} mol L^{-1}.

ried out in an acetonitrile solution, and pyridine and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were used as bases. The studies show that using pyridine as a base does not lead to a significant change in the absorption spectrum, while using DBU results in a 1.5-fold increase of the absorption density (D) and shifts the absorbance maximum from $\lambda_{\text{Abs max}} = 466$ nm to $\lambda_{\text{Abs max}} = 583$ nm (Fig. 3). The base influence on the fluorescence, spectrum is as follows: a strong base (DBU) leads to the disappearance of the fluorescence, while pyridine decreases the fluorescence intensity in comparison to the initial value, but keeps the absorption spectrum form invariable. Marked facts could be explained by comparative stability of the resulting complex amine-fluorophore in the case of the stronger base (DBU) and pyridine.[17] Such a shift in the absorbance maximum in the case of DBU occurs due to the strong removal of a proton of the hydroxy group of thiophene and the localization of the negative charge on the oxygen atoms.

Conclusion

We have proposed a new method of dithienylmaleimides synthesis and studied their spectral properties. It has been shown that these compounds do not belong to the photochromes but they possess fluorescence properties. It has been found that fluorescence intensity depends on both substituents in the heterocyclic rings and on medium basicity.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and Bruker AM-300 radio spectrometers in $CDCl_3$. Mass spectra were recorded on a Kratos instrument (EI, 70 eV, direct inlet probe). Melting points were determined on a Boetius microscope stage and are given uncorrected. Reaction completion was checked by TLC data (Silufol UV-254, light petroleum (60–80 °C)–ethyl acetate (3:1) as the eluent). Acros silica gel (C.A.S.-7631-86-9) (0.060–0.200) was used for column chromatography. Ethyl 4-hydroxy-2-methylthiophene-3-carboxylates (**1**)[18] and 3,4-dichloromaleimides[19] were prepared according to a known procedure. The electronic absorption spectra were measured on a Varian "Cary 50 Bio" spectrophotometer. Fluorescence measurements were performed using a Varian "Cary Eclipse" spectrofluorimeter (the maximum value of fluorescence intensity is 1000 arbitrary units for this spectrofluorimeter). Commercially available (Merck) anhydrous acetonitrile and toluene were used for the spectral studies.

General Procedure for the *C*-Alkylation of Ethyl 4-Hydroxy-2-methylthiophene-3-carboxylate with 3,4-Dichloromaleimides. Metallic sodium (0.01 mol) was added to a solution of compound **1** (0.01 mol) in 5 mL of anhydrous benzene. Then, a solution of the corresponding 3,4-dichloromaleimide (0.005 mol) in 5 mL of anhydrous benzene was added dropwise with stirring at 10–15 °C. The reaction mixture was stirred at 20 °C for 5 h and refluxed until the starting hydroxythiophene disappeared completely. After the reaction was completed (TLC), the solvent was removed and the residue was chromatographed on silica gel in light petroleum (60–80 °C)–ethyl acetate (3:1).

3,4-Bis(4-ethoxycarbonyl-3-hydroxy-5-methyl-2-thienyl)-1-phenyl-1*H*-pyrrol-2,5-dione (2a): Dark-orange crystal. Yield: 78%. mp 193–195 °C (ethanol). IR (KBr) 3060 (OH), 1756 (C=O), 1592, 1588, 1504, 1332 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.42 (t, 6H, $J = 7.2$ Hz), 2.75 (s, 6H), 4.4 (q, 4H, $J = 7.2$ Hz), 7.45 (m, 5H), 10.05 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 170.51, 166.70, 157.92, 153.92, 131.90, 129.03, 127.61, 126.11, 123.09, 114.08, 104.11, 61.42, 17.80, 14.31. MS: m/z 541 [M^+]. Found: C, 57.92; H, 4.27; N, 2.65; S, 11.53%. Calcd for $C_{26}H_{23}NO_8S_2$: C, 57.66; H, 4.28; N, 2.59; S, 11.84%.

3,4-Bis(4-ethoxycarbonyl-3-hydroxy-5-methyl-2-thienyl)-1-(4-chlorophenyl)-1*H*-pyrrol-2,5-dione (2b): Reddish yellow crystal. Yield: 92%. mp 224–226 °C. IR (KBr) 3208 (OH), 1768 (C=O), 1592, 1496, 1336 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.45 (t, 6H, $J = 7.2$ Hz), 2.79 (s, 6H), 4.45 (q, 4H, $J = 7.2$ Hz), 7.45 (m, 4H), 10.05 (s, 2H, OH). ^{13}C NMR ($CDCl_3$) δ 170.20, 166.71, 158.12, 154.02, 133.19, 130.58, 129.21, 127.10, 123.22, 114.71, 104.14, 61.41, 17.68, 14.29. MS: m/z 575, 577 [M^+]. Found: C, 54.65; H, 4.08; Cl, 5.65; N, 2.30; S, 11.3%. Calcd for $C_{26}H_{22}ClNO_8S_2$: C, 54.21; H, 3.85; Cl, 6.15; N, 2.43; S, 11.13%.

3,4-Bis(4-ethoxycarbonyl-3-hydroxy-5-methyl-2-thienyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-2,5-dione (2c): Reddish yellow crystal. Yield: 84%. mp 207–209 °C. IR (KBr) 3280 (OH), 1760 (C=O), 1580, 1516, 1328 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.40 (t, 6H, $J = 7.3$ Hz), 2.78 (s, 6H), 3.85 (s, 3H, OCH_3), 4.41 (q, 4H, $J = 7.3$ Hz), 6.96 (d, 2H, $J = 9.2$ Hz), 7.35 (d, 2H, $J = 9.2$ Hz), 10.05 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 170.71, 166.69, 159.03, 157.89, 153.88, 128.11, 127.62, 123.22, 114.80, 114.41, 104.21, 61.42, 55.61, 17.81, 14.30. MS: m/z 571 [M^+]. Found: C, 56.38; H, 4.31; N, 2.37; S, 11.18%. Calcd for $C_{27}H_{25}NO_9S_2$: C, 56.73; H, 4.41; N, 2.45; S, 11.22%.

General Procedure for the Synthesis of Dithienylmaleimides 3a–3f. To a solution of the hydroxythiophene **1** (0.01 mol) in 7 mL DMF was added (0.021 mol) K_2CO_3. Then, a solution of the corresponding alkyl halide (0.025 mol) in 3 mL of the same solvent was added dropwise with stirring at 10–25 °C. The reaction mixture was stirred at ≈20 °C until the starting compound disappeared completely. After the reaction was completed (TLC), the mixture was poured into ice and the product was extracted with ethyl acetate, washed with saturated sodium hydrogen carbonate and water, and dried. The solvent was removed and the residue was chromatographed on silica gel in light petroleum (60–80 °C)–ethyl acetate (3:1).

3,4-Bis(4-ethoxycarbonyl-3-methoxy-5-methyl-2-thienyl)-1-phenyl-1*H*-pyrrol-2,5-dione (3a): Yellow crystal. Yield: 82%. mp 142–144 °C. IR (KBr) 2984, 1700 (C=O), 1532, 1504, 1444, 1396 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.38 (t, 6H, $J = 7.2$ Hz), 2.69 (s,

6H), 3.49 (s, 6H, OCH_3), 4.35 (q, 4H, $J = 7.2$ Hz), 7.48 (m, 5H). MS: m/z 569 [M^+]. Found: C, 59.48; H, 4.92; N, 2.49; S, 11.08%. Calcd for $C_{28}H_{27}NO_8S_2$: C, 59.04; H, 4.78; N, 2.46; S, 11.26%.

3,4-Bis(4-ethoxycarbonyl-3-methoxy-5-methyl-2-thienyl)-1-(4-chlorophenyl)-1*H*-pyrrol-2,5-dione (3b): Reddish yellow crystal. Yield: 84%. mp 121–123 °C. IR (KBr) 2936, 1704 (C=O), 1540, 1500, 1388 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.39 (t, 6H, $J = 7.2$ Hz), 2.70 (s, 6H), 3.51 (s, 6H), 4.37 (q, 4H, $J = 7.2$ Hz), 7.49 (m, 4H). MS: m/z 603, 605 [M^+]. Found: C, 55.46; H, 4.54; Cl, 5.66; N, 2.30; S, 10.24%. Calcd for $C_{28}H_{26}ClNO_8S_2$: C, 55.67; H, 4.34; Cl, 5.87; N, 2.32; S, 10.62%.

3,4-Bis(4-ethoxycarbonyl-3-methoxy-5-methyl-2-thienyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-2,5-dione (3c): Brown crystal. Yield: 72%. mp 133–135 °C. IR (KBr) 2972, 1704 (C=O), 1584, 1516, 1448, 1396 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.36 (t, 6H, $J = 7.2$ Hz), 2.68 (s, 6H), 3.50 (s, 6H), 3.82 (s, 3H), 4.36 (q, 4H, $J = 7.2$ Hz), 6.99 (d, 2H, $J = 9.2$ Hz), 7.38 (d, 2H, $J = 9.2$ Hz). MS: m/z 599 [M^+]. Found: C, 56.82; H, 4.96; N, 2.31; S, 10.71%. Calcd for $C_{29}H_{29}NO_9S_2$: C, 58.08; H, 4.87; N, 2.34; S, 10.69%.

3,4-Bis(4-ethoxycarbonyl-3-ethoxycarbonylmethoxy-5-methyl-2-thienyl)-1-phenyl-1*H*-pyrrol-2,5-dione (3d): Brownish yellow crystal. Yield: 76%. mp 171–174 °C. IR (KBr) 2984, 1704 (C=O), 1544, 1476, 1400 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.18 (t, 6H, $J = 7.5$ Hz), 1.34 (t, 6H, $J = 7.2$ Hz), 2.71 (s, 6H), 4.12 (q, 4H, $J = 7.5$ Hz), 4.36 (q, 4H, $J = 7.2$ Hz), 7.5 (m, 5H). MS: m/z 713 [M^+]. Found: C, 56.42; H, 4.98; N, 2.04; S, 8.46%. Calcd for $C_{34}H_{35}NO_{12}S_2$: C, 57.21; H, 4.94; N, 1.96; S, 8.98%.

3,4-Bis(4-ethoxycarbonyl-3-ethoxycarbonylmethoxy-5-methyl-2-thienyl)-1-(4-chlorophenyl)-1*H*-pyrrol-2,5-dione (3e): Yellow crystal. Yield: 86%. mp 181–183 °C. IR (KBr) 2980, 1700 (C=O), 1540, 1472, 1440, 1400 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.20 (t, 6H, $J = 7.5$ Hz), 1.38 (t, 6H, $J = 7.2$ Hz), 2.68 (s, 6H), 4.16 (q, 4H, $J = 7.5$ Hz), 4.34 (q, 4H, $J = 7.2$ Hz), 4.48 (s, 4H), 7.5 (m, 4H). MS: m/z 747, 749 [M^+]. Found: C, 53.87; H, 4.69; Cl, 4.79; N, 1.84; S, 9.59%. Calcd for $C_{34}H_{34}ClNO_{12}S_2$: C, 54.58; H, 4.58; Cl, 4.74; N, 1.87; S, 8.57%.

3,4-Bis(4-ethoxycarbonyl-3-ethoxycarbonylmethoxy-5-methyl-2-thienyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-2,5-dione (3f): Dark-orange crystal. Yield: 73%. mp 136–140 °C. IR (KBr) 2924, 1704 (C=O), 1600, 1544, 1444, 1408, 1340 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.21 (t, 6H, $J = 7.2$ Hz), 1.34 (t, 6H, $J = 7.2$ Hz), 2.67 (s, 6H), 3.84 (s, 2H), 4.10 (q, 4H, $J = 7.2$ Hz), 4.32 (q, 4H, $J = 7.2$ Hz), 4.4 (s, 3H), 7.0 (d, 2H, $J = 9.1$ Hz), 7.34 (d, 2H, $J = 9.1$ Hz). MS: m/z 743 [M^+]. Found: C, 55.95; H, 5.03; N, 1.98; S, 7.11%. Calcd for $C_{35}H_{37}NO_{13}S_2$: C, 56.52; H, 5.01; N, 1.88; S, 8.62%.

General Procedure for the Synthesis of Compounds 4a–4c. Pyridine (0.002 mol) was added dropwise with stirring at 10–25 °C to a solution of the compounds **2a–2c** (0.001 mol) in 10 mL acetic anhydrate, and then the reaction mixture was heated to 100 °C until the starting compound disappeared completely. After the reaction was completed (TLC), the mixture was poured into ice and the product was extracted with ethyl acetate, washed with 3% hydrochloric acid and water, and dried ($MgSO_4$). The solvent was removed and the residue was recrystallized from ethanol.

3,4-Bis(3-acetoxy-4-ethoxycarbonyl-5-methyl-2-thienyl)-1-phenyl-1*H*-pyrrol-2,5-dione (4a): Bright yellow crystal. Yield: 72%. mp 226–228 °C. IR (KBr) 2988, 1780 (C=O), 1712, 1600, 1552, 1492, 1396 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.35 (t, 6H, $J = 7.2$ Hz), 1.85 (s, 6H), 2.79 (s, 6H), 4.31 (q, 4H, $J = 7.2$ Hz), 7.49 (m, 5H). MS: m/z 625 [M^+]. Found: C, 57.37; H, 4.53; N, 2.24; S, 9.82%. Calcd for $C_{30}H_{27}NO_{10}S_2$: C, 57.59; H, 4.35; N, 2.24; S, 10.25%.

3,4-Bis(3-acetoxy-4-ethoxycarbonyl-5-methyl-2-thienyl)-1-(4-chlorophenyl)-1*H*-pyrrol-2,5-dione (4b): Yellowish green crystal. Yield: 80%. mp 173–175 °C. IR (KBr) 2988, 1772 (C=O), 1708, 1596, 1552, 1492, 1396 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.35 (t, 6H, $J = 7.2$ Hz), 1.81 (s, 6H), 2.78 (s, 6H), 4.31 (q, 4H, $J = 7.2$ Hz), 7.45 (m, 4H). MS: m/z 659 [M^+]. Found: C, 54.61; H, 4.11; Cl, 5.19; N, 2.13; S, 9.38%. Calcd for $C_{30}H_{26}ClNO_{10}S_2$: C, 54.59; H, 3.97; Cl, 5.37; N, 2.12; S, 9.71%.

3,4-Bis(3-acetoxy-4-ethoxycarbonyl-5-methyl-2-thienyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-2,5-dione (4c): Yellow crystal. Yield: 69%. mp 171–175 °C. IR (KBr) 2980, 1780 (C=O), 1708, 1600, 1540, 1516, 1404 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.36 (t, 6H, $J = 7.2$ Hz), 1.72 (s, 6H), 2.79 (s, 6H), 3.87 (s, 3H), 4.32 (q, 4H, $J = 7.2$ Hz), 7.02 (d, 2H, $J = 9.2$ Hz), 7.32 (d, 2H, $J = 9.2$ Hz). MS: m/z 655 [M^+]. Found: C, 56.37; H, 4.41; N, 2.26; S, 9.43%. Calcd for $C_{31}H_{29}NO_{11}S_2$: C, 56.79; H, 4.46; N, 2.14; S, 9.78%.

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