Russian Chemical Bulletin, International Edition, Vol. 56, No. 5, pp. 967—974, May, 2007 967

Synthesis, structures, and optical and electrochemical characteristics of novel crown-containing polythiophene systems

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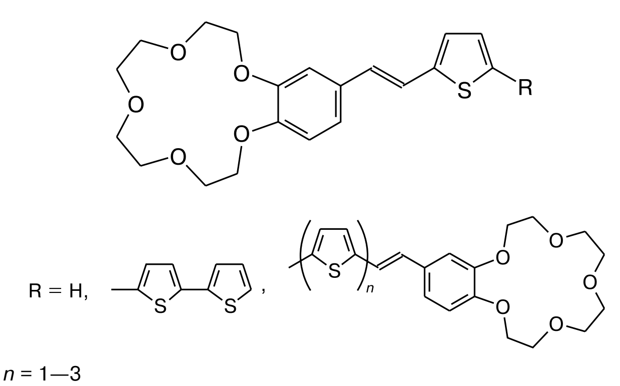
The synthesis, structures, and optical and electrochemical characteristics of novel crown-containing styryl mono- and polythiophenes were described. The double bonds were constructed by the Horner—Wadsworth—Emmons method. The Suzuki and Stille cross-coupling reactions were used to create polythiophene chains. Optical measurements revealed intense absorption and fluorescence of crown-containing polythiophenes; the band positions and shapes in their absorption and emission spectra depend on the structure of the polythiophene. The electrochemical characteristics of the compounds obtained were measured.

Key words: thiophenes, polythiophenes, benzo-15-crown-5 ethers, cross-coupling, electronic absorption spectra, fluorescence spectra, ^{1}H NMR spectra, electrochemistry.

Organic polymeric electrooptical systems are subjects of intensive investigations since they are of practical interest for creation of novel materials for telecommunication systems and optical memory devices.[1—3] Polythiophenes belong to a promising class of organic compounds exhibiting practically useful optical and electrochemical characteristics.[4—8] The physicochemical properties of polythiophenes can be varied by introducing substituents into the thiophene ring; furthermore, polythiophene systems containing different functional groups can recognize organic and inorganic molecules, transfer the electron, and show nonlinear optical properties.[9—11]

Crown compounds serve as an ionophore fragment for introduction into the thiophene system.[12—16] Crown-containing polythiophenes are capable for specific recognition of a guest molecule, the polymeric receptor changing its optical and electrochemical characteristics. However, only a few such compounds have been obtained hitherto. The known examples include macrocyclic derivatives containing the thiophene fragment;[13,14] oligothiophenes linked with the crown ether fragment by a spacer;[9,15] and polythiophenes obtained by free radical polymerization in which the crown ether fragments are annulated with the thiophene rings.[16,17] Complex formation with crown-containing thiophenes has been reported only in a few papers.[13,15] Thus, the influence of complex formation on the optical and electrochemical characteristics of thiophene derivatives has not been studied comprehensively, while possibilities of such an approach to the synthesis of optical or electrochemical receptors have not been revealed yet.

In this study, we developed methods for the synthesis of novel crown-containing styryl derivatives of mono- and polythiophenes.



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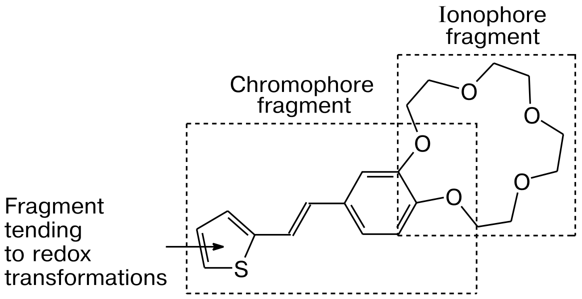
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 932—939, May, 2007.

When performing molecular design, we were guided by the desire to obtain the molecules for which complex formation could substantially affect their optical and electrochemical properties. The macrocyclic fragment has two O atoms bound to the benzene ring of benzocrown ether (Scheme 1). The formation of metal complexes *via* these heteroatoms will affect the electron density distribution in the molecule and, consequently, the spectroscopic and electrochemical characteristics of the conjugated thiophene fragment. An increase in the number of thiophene fragments, which are responsible for the electrochemical characteristics, will allow systems with a steady electrochemical response.

Scheme 1

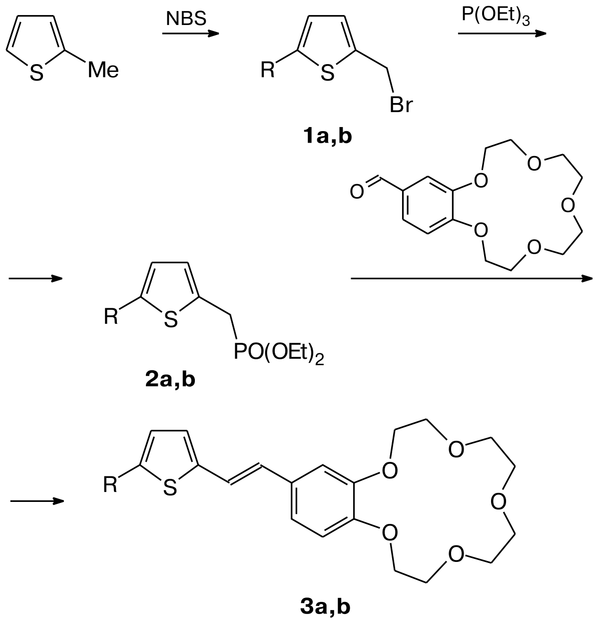


Results and Discussion

Synthesis. 2-Methylthiophene was used as a starting reagent (Scheme 2). Its bromination with NBS in CCl_4 according to a known procedure[18] gave 5-bromo-2-bromomethylthiophene (**1a**) in 63% yield and 2-bromomethylthiophene (**1b**) in 50% yield; the molar 2-methylthiophene : NBS ratios were 1 : 1 and 1 : 2, respectively. Bromides **1a,b** were converted into diethyl phosphonates **2a,b**. Their condensation with 4-formylbenzo-15-crown-5 in the presence of 50% NaOH and aliquat 336 afforded 15-[2-(5-bromo-2-thienyl)vinyl]benzo-15-crown-5 (**3a**) and 15-[2-(2-thienyl)vinyl]benzo-15-crown-5 (**3b**) in 78 and 76% yields, respectively. The coupling constants of the olefin protons (J_{trans} = 15.8 Hz) suggest the *E*-configuration of compounds **3a,b**.

Compound **3a** was used for the synthesis of crown-containing oligothiophenes **4a—d** (Scheme 3). Symmetrical compound **4a** was obtained from crown-containing bromo(styryl)thiophene according to the modified Suzuki method[19] in 70% yield. The cross-coupling with bis(pinacolato)diboron was catalyzed by $PdCl_2$(dppf) (dppf is 1,1´-bis(diphenylphosphino)ferrocene). Polythiophenes **4b—d** containing three and four thiophene fragments were obtained[20] by cross-coupling reactions of bromide **3a** with 2,5-bis(tributylstannyl)thiophene (**5a**) and 5,5´-bis(tributylstannyl)-2,2´-bithiophene (**5b**) in the presence of $Pd(PPh_3)_4$ in 77, 82, and 50% yields, respectively. The reaction conditions for the synthesis of compounds **4b—d** are specified in Table 1.

Scheme 2



R = Br (**a**), H (**b**)

The structures of all the compounds obtained were proven by ^1H and ^{13}C NMR spectroscopy, ESI mass spectrometry, and UV spectroscopy and confirmed by elemental analysis.

Spectroscopic characteristics of the compounds obtained. The ^1H NMR spectra of compounds **4a,b** (Fig. 1) show signals for one crown-containing styryl fragment and one thiophene heterocycle, which suggests their highly symmetrical structures. The signals for the H(3″) and H(4″) protons of the additional third thiophene ring in compound **4b** have the same chemical shifts and resonate as an intense singlet at δ 7.05 (s, 2 H). Interestingly, the signals for the protons of the macrocycles in compounds **4a,b** and **3b** have equal chemical shifts and multiplicities; *i.e.*, variation in the number of the thiophene fragments in the molecule does not affect the NMR spectra of its macrocyclic portion (see Fig. 1).

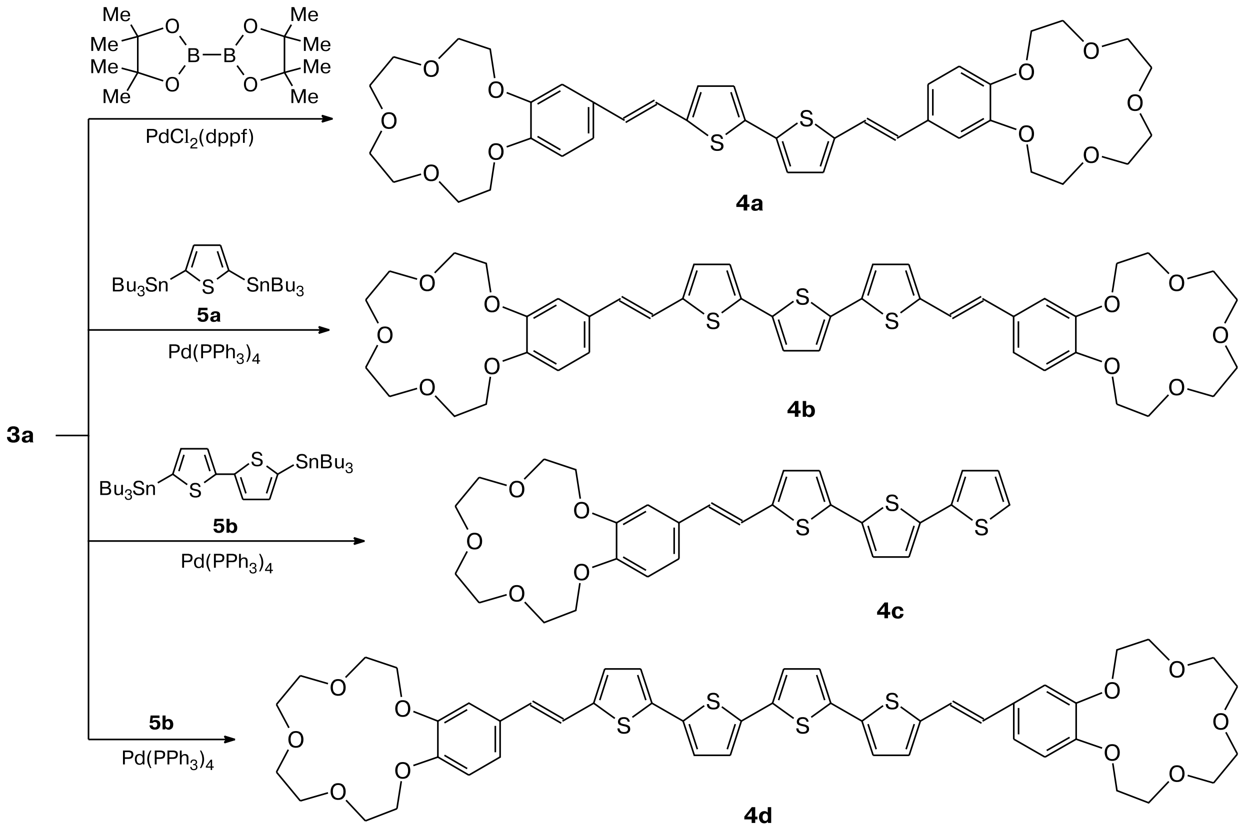
Table 1. Reaction conditions and the yields of compounds **4b—d**

Compound	Ratio of the starting reagents*	Solvent	*T* /°C	*t*** /h	Yield (%)
4b	**3a** : **5a** = 2 : 1	DMF	85	11.0	77
4c	**3a** : **5b** = 1 : 1	DMF	70	5.0	82
4d	**3a** : **5b** = 2.5 : 1	Toluene	111	4.5	50

* In moles.

** The reaction time.

Scheme 3



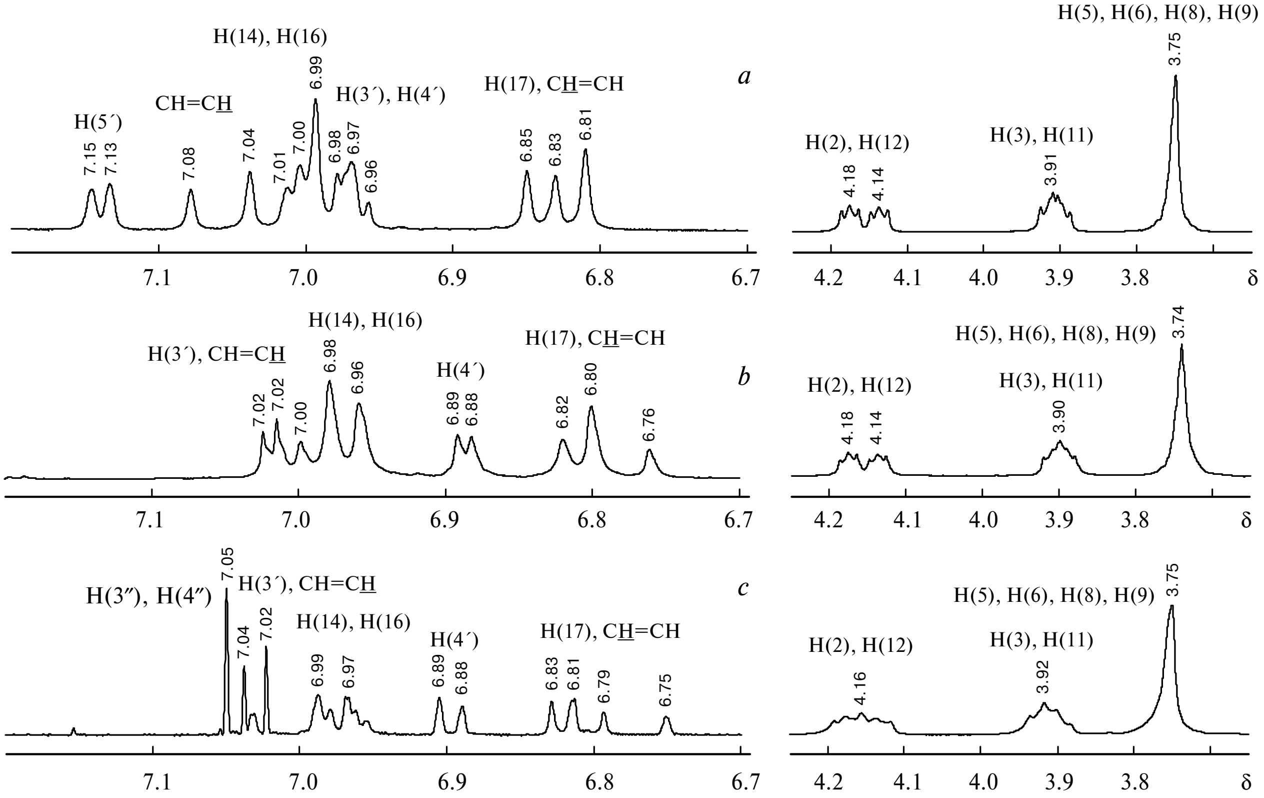


Fig. 1. ^{1}H NMR spectra of compounds **3b** (*a*), **4a** (*b*), and **4b** (*c*) in CD_2Cl_2 (25 °C).

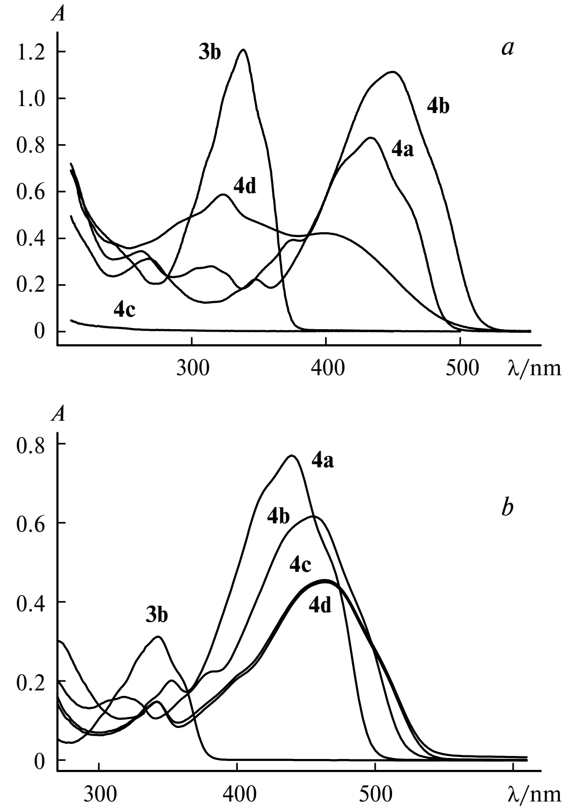


Fig. 2. Electronic absorption spectra of compounds **3b** and **4a—d** in MeCN ($c = 4 \cdot 10^{-5}$ (for **3b**) and $2 \cdot 10^{-5}$ mol L^{-1} (for **4a,b**); saturated solutions of compounds **4c,d**) (*a*) and in CH_2Cl_2 ($c = 1 \cdot 10^{-5}$ mol L^{-1} for **3b** and **4a—d**) (*b*).

The electronic absorption spectra of compounds **3b** and **4a—d** in acetonitrile and dichloromethane are shown in Fig. 2. Unfortunately, we detected no absorption by compound **4c** in acetonitrile because of its poor solubility in this solvent.

Attention should be drawn to a large bathochromic shift experienced by the longer-wavelength peak when moving from compound **3b** to di-, tri-, and tetrathiophene derivatives **4a—d**. The styryl derivatives under discussion belong to compounds of the donor—acceptor type.[21] The longer-wavelength peak of such compounds is due to photoinduced charge transfer from the donor part of the molecule to its acceptor part (Scheme 4). In compound **3b**, the crown-ether O atoms bound to the benzene ring act as donor sites and the S heteroatom acts as an acceptor. Because compound **4a** is formally a dimer of compound **3b** and has the same set of donor and acceptor sites, their electronic absorption spectra could be expected to coincide, with a double intensity for compound **4a**. However, the longer-wavelength peak of the latter is shifted bathochromically by 100 nm compared to that of compound **3b**. Such a large bathochromic shift can be explained by the charge phototransfer in **4a** from the benzene ring of one styryl fragment to the crown-ether O atom in the other styryl fragment. A similar bathochromic shift for symmetrical bisstilbenes with respect to monostilbenes has been reported earlier.[22,23]

The longer-wavelength absorption peaks in the spectra of compounds **4b,d**, which contain three and four thiophene rings between the crown-containing styryl fragments, are shifted by 15 and 30 nm, respectively, compared to the absorption peak of compound **4a**. These shifts are due to one and two more conjugated thiophene rings. It should be noted that $\Delta\lambda = 15$ nm is characteristic of styryl polythiophenes differing by one conjugated thiophene unit.[24]

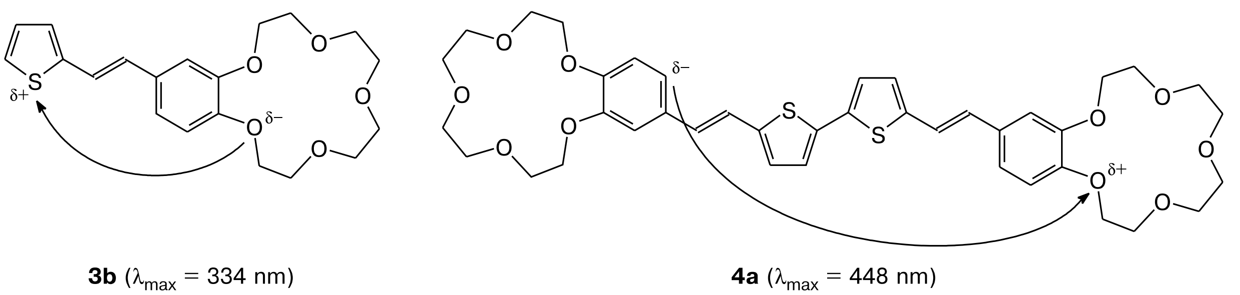
The spectrum of compound **4d** in acetonitrile shows two peaks. A second absorption peak for polythiophenes has been noted earlier[25] and attributed to an increased rigidity of a longer conjugated system that gives rise to vibrational bands in the absorption spectra and additional bands due to various electron transitions in the long conjugated system. In less rigid systems, different conformers coexist to produce the overall electronic absorption spectrum as a wide unresolved band.

The fluorescence spectra of crown-containing polythiophenes in acetonitrile and dichloromethane are shown in Fig. 3. The quantum yields of fluorescence φ_{fl} in CH_2Cl_2 are given below.

Compound	**3b**	**4a**	**4b**	**4c**	**4d**
φ_{fl}	0.087	0.19	0.11	0.084	0.085

Their values indicate good fluorescent characteristics of these compounds. It is worth noting that the fluorescence

Scheme 4



3b (λ_{max} = 334 nm) **4a** (λ_{max} = 448 nm)

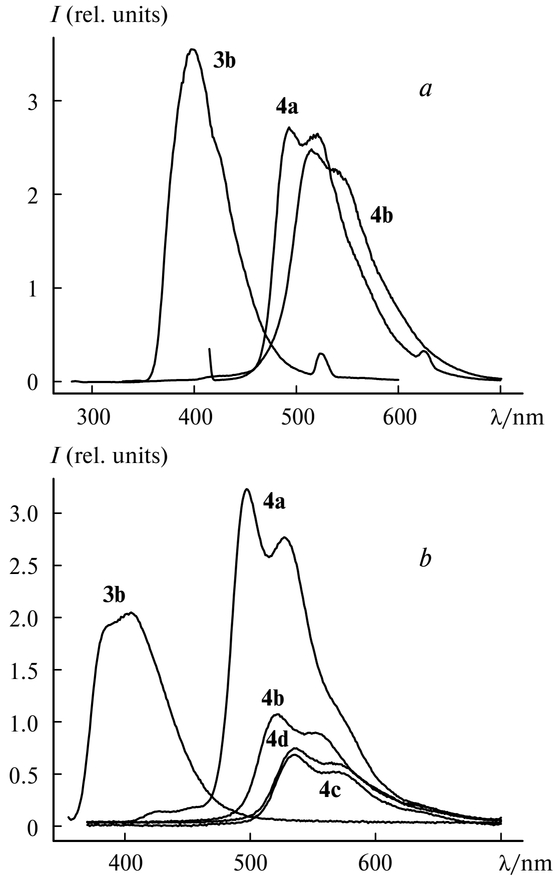


Fig. 3. *a*. Fluorescence emission spectra of compounds **3b** and **4a,b** in MeCN ($c = 2 \cdot 10^{-5}$ mol L^{-1}, λ_{exc} = 265 (**3b**), 315 (**4a**), and 412 nm (**4b**)). *b*. Fluorescence emission spectra of compounds **3b** and **4a—d** in CH_2Cl_2 ($c = 1 \cdot 10^{-5}$ mol L^{-1}, λ_{exc} = 350 nm).

spectra of polythiophenes **4a—d** in both the solvents consist of two bands. Such a spectral pattern has been observed earlier[26] for other polythiophenes. The more resolved emission spectra are explained by the fact that emitting molecules (in the excited state) are more planar and rigid than ground-state ones.

Electrochemical characteristics of compounds 3b and 4a—d. The oxidation potentials of the compounds studied are given in Table 2. The cyclic voltammograms of compounds **4a—c** are shown in Fig. 4. The CV curves of compounds **4c,d** coincide.

The oxidation potential E_p^{Ox} = 0.74 V is characteristic of styrylthiophenes.[24] The oxidation potentials of compounds **4a—d** are close to the literature data. We also found that the redox process of compound **3b** is irreversible.

To sum up, we synthesized polythiophene derivatives containing one or two crown-containing styryl fragments. We studied their optical properties and found that these compounds intensely absorb and fluoresce. The band position and shape in their spectra depends on the structure of the polythiophene. The character of the optical spectra is determined by electron transitions involving the O atoms of the crown-ether fragments. This means that the formation of complexes with metal cations through the crown-ether fragment will dramatically change the optical characteristics. The data for complex formation with crown-containing polythiophenes **3b** and **4a—d** will be published elsewhere.

Table 2. Electrochemical characteristics (oxidation peak potential E_p^{Ox} and half-wave potential $E_{1/2}$) of compounds **3b** and **4a—d** (from CV data)

Compound	E_p^{Ox}	$E_{1/2}$
	V	
3b	1.06*	—
4a	0.76/0.70	0.73
4b	0.70/0.62	0.66
4c	0.81**	—
4d	0.79**	—

* The irreversible process.

** The low solubility.

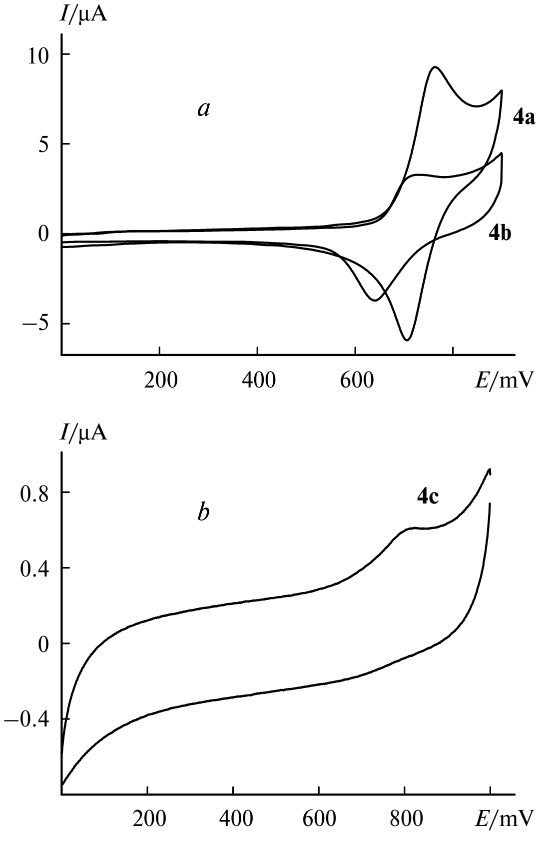


Fig. 4. Cyclic voltammograms of compounds **4a,b** (*a*) and **4c** (*b*) in MeCN—CH_2Cl_2 (1 : 1) in the presence of 1 *M* Bu_4NClO_4 (scan rate 250 mV s^{-1}).

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400.13 and 100 MHz, respectively). Chemical shifts were measured to within 0.01 ppm; spin-spin coupling constants were measured to within 0.1 Hz. Mass spectra were recorded on Finnigan MAT-112S (EI, 70 eV, direct inlet probe) and Agilent 1100 Series LC/MSD Trap instruments (ESI). Electronic absorption spectra were recorded on Varian-Cary and Specord-M40 spectrophotometers connected to a PC; fluorescence spectra were recorded on a FluroLog (Jobin Yvon) spectrofluorimeter at 20±1 °C.

The quantum yields of fluorescence were determined for air-saturated acetonitrile solutions at 20±1 °C with respect to 9,10-diphenylanthracene in cyclohexane ($\varphi_{fl} = 0.9$). The wavelength of excitation light was 370 nm. To calculate the quantum yields, we used refined fluorescence spectra. Melting points were measured on a Mel-temp II instrument and are given uncorrected.

The course of the reaction was monitored and the purity of the products was checked by TLC on Kieselgel 60 F254 plates (Merck). Column chromatography was carried out on Kieselgel 200—600 nm (Merck). Elemental analysis was performed at the organic analysis laboratory of the Department of Chemistry of the M. V. Lomonosov Moscow State University.

CV studies were carried out on a BAS 100 potentiostat (Bioanalytical Systems) with the BAS100W software (v. 2.3). Oxidation potentials were measured in a three-electrode cell containing a platinum disk 1.6 mm in diameter and silver-chloride reference electrodes in 3 *M* NaCl. Tetrabutylammonium perchlorate (Fluka) was used as purchased. The concentration of Bu_4NClO_4 was 1 mol L^{-1}; the concentration of a test compound was 1 mmol L^{-1}. The scan rate was 250 mV s^{-1}.

All reagents and solvents (99% purity; Acros, Aldrich, and Merck) were used without additional purification. 2,5-Bis(tributylstannyl)thiophene (**5a**) and 5,5′-bis(tributylstannyl)-2,2′-bithiophene (**5b**) were prepared as described earlier.[27]

2-Bromo-5-bromomethylthiophene (1a). A solution of 2-methylthiophene (4 g, 0.041 mol) in CCl_4 (10 mL) was added to a suspension of NBS (14.2 g, 0.082 mol) in CCl_4 (30 mL). The stirred reaction mixture was refluxed for 8 h. On cooling, the precipitate was filtered off and the solvent was removed. Distillation gave dibromide **1a** (6.7 g, 63%), b.p. 88—90 °C (2 Torr), n_D^{20} 1.6413 (*cf.* Ref. 18: n_D^{20} 1.6406). ^1H NMR ($CDCl_3$), δ: 4.61 (s, 2 H, CH_2Br); 6.84, 6.87 (both d, 1 H each, H(3), H(4), $^3J = 3.5$ Hz). ^{13}C NMR ($CDCl_3$), δ: 26.12 (CH_2Br); 113.78 (C(2)); 128.22, 129.78 (C(3), C(4)); 142.01 (C(5)).

Diethyl [(5-bromo-2-thienyl)methyl]phosphonate (2a). Triethyl phosphite (4.65 g, 0.028 mol) and dibromide **1a** (6.64 g, 0.026 mol) were heated with stirring to 120 °C in a flask fitted with a short Liebig condenser. The vapor of ethyl bromide was collected in a cooled trap. Distillation of the reaction mixture gave phosphonate **2a** (6.66 g, 81%), b.p. 190 °C (15 Torr). ^1H NMR ($CDCl_3$), δ: 1.26 (t, 6 H, $CH_2C\underline{H}_3$, $^3J = 7.1$ Hz); 3.23 (d, 2 H, CH_2P, $^2J = 20.7$ Hz); 4.05 (d, 4 H, $C\underline{H}_2CH_3$, $^3J = 7.2$ Hz); 6.69, 6.86 (both d, 1 H each, H(3), H(4), $^3J = 3.6$ Hz). ^{13}C NMR ($CDCl_3$), δ: 16.29 ($CH_2\underline{C}H_3$); 28.28 (d, CH_2P); 62.36 ($\underline{C}H_2CH_3$); 110.70 (C(2)); 127.59, 129.67 (C(3), C(4)); 134.29 (C(5)).

15-[2-(5-Bromo-2-thienyl)vinyl]benzo-15-crown-5 (3a). A solution of phosphonate **2a** (6.6 g, 21 mmol) and 15-formylbenzo-15-crown-5 (6.22 g, 21 mmol) in benzene (25 mL) were added to a mixture of 50% NaOH (16.5 mL) and aliquat 336 (1.3 mL) in benzene (15 mL). The reaction mixture was refluxed for 1 h and cooled. The organic phase was separated, washed with water, and dried with $MgSO_4$. The solvent was removed and the residue was recrystallized from light petroleum—ethyl acetate (1 : 1). The yield of compound **3a** was 7.5 g (78%), m.p. 113—114 °C. Found (%): C, 52.75; H, 5.09. $C_{20}H_{23}BrO_5S$. Calculated (%): C, 52.46; H, 5.08. ^1H NMR ($CDCl_3$), δ: 3.74 (s, 8 H, H(5), H(6), H(8), H(9)); 3.90 (m, 4 H, H(3), H(11)); 4.14 (m, 4 H, H(2), H(12)); 6.71 (d, 1 H, $C\underline{H}=CH$, $^3J =$ 15.4 Hz); 6.73 (d, 1 H, H(3′), $^3J = 3.5$ Hz); 6.81 (d, 1 H, H(17), $^3J = 8.8$ Hz); 6.90 (d, 1 H, H(4′), $^3J = 3.9$ Hz); 6.92 (d, 1 H, $CH=C\underline{H}$, $^3J = 15.4$ Hz); 6.95 (d, 1 H, H(16), $^3J = 8.9$ Hz); 6.96 (s, 1 H, H(14)). ^{13}C NMR ($CDCl_3$), δ: 68.99, 69.21, 69.54, 69.60, 70.50, 70.55 (C(3), C(5), C(6), C(8), C(9), C(11)); 71.08, 71.10 (C(2), C(12)); 110.46 (C(2′)); 111.69, 113.91 (C(14), C(17)); 119.48, 120.33, 125.54, 128.62, 130.40 (C=C, C(3′), C(4′), C(16)); 130.16 (C(15)); 144.77, 149.3, 149.36 (C(5′), C(13a), C(17a)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 376 $[M + 1]^+$ (100), 454 $[M - 1]^+$, 368 (19), 366 (19), 243 (21), 219 (47), 187 (46), 171 (25), 115 (23), 86 (19), 45 (53). UV (MeCN), λ_{max}/nm: 349.

2-Bromomethylthiophene (1b). A solution of 2-methylthiophene (2.0 g, 0.02 mol) in CCl_4 (5 mL) and benzoyl peroxide (0.15 g) were added under argon to a suspension of NBS (3.6 g, 0.02 mol) in CCl_4 (15 mL). The reaction mixture was refluxed with stirring for 4 h. On cooling, the precipitate was filtered off and the solvent was removed. Distillation gave bromide **1b** (2.2 g, 50%), b.p. 77—79 °C (2 Torr), n_D^{20} 1.6055 (*cf.* Ref. 18: n_D^{20} 1.6050). ^1H NMR ($CDCl_3$), δ: 4.75 (s, 2 H, CH_2Br); 6.94 (dd, 1 H, H(4), $^3J = 3.5$ Hz, $^3J = 5.1$ Hz); 7.11 (dd, 1 H, H(3), $^3J = 3.4$ Hz, $^4J = 1.1$ Hz); 7.31 (dd, 1 H, H(5), $^3J = 5.2$ Hz, $^4J = 1.1$ Hz).

Diethyl [(2-thienyl)methyl]phosphonate (2b). Triethyl phosphite (2.1 g, 0.012 mol) and bromide **1b** (2.2 g, 0.012 mol) were heated with stirring to 130 °C in a flask fitted with a short Liebig condenser. The vapor of ethyl bromide was collected in a cooled trap. Distillation of the reaction mixture gave phosphonate **2b** (1.8 g, 64%), b.p. 160 °C (13 Torr), n_D^{20} 1.4930. ^1H NMR ($CDCl_3$), δ: 1.26 (t, 6 H, $CH_2C\underline{H}_3$, $^3J = 7.0$ Hz); 3.35 (d, 2 H, CH_2P, $^2J = 20.7$ Hz); 4.05 (d, 4 H, $C\underline{H}_2CH_3$, $^3J = 7.1$ Hz); 6.93 (dd, 1 H, H(4), $^3J = 3.7$ Hz, $^3J = 5.0$ Hz); 6.97 (dd, 1 H, H(3), $^3J = 3.4$ Hz, $^4J = 0.9$ Hz); 7.16 (dd, 1 H, H(5), $^3J = 5.0$ Hz, $^4J = 1.1$ Hz).

15-[2-(2-Thienyl)vinyl]benzo-15-crown-5 (3b). A solution of phosphonate **2b** (1.1 g, 4.7 mmol) and 15-formylbenzo-15-crown-5 (1.5 g, 4.7 mmol) in benzene (5 mL) was added to a mixture of 50% NaOH (3.6 mL) and aliquat 336 (0.3 mL) in benzene (3 mL). The reaction mixture was refluxed for 45 min and cooled. The organic phase was separated, washed with water, and dried over $NaSO_4$. The solvent was removed and the residue was recrystallized from light petroleum—ethyl acetate (1 : 1). The yield of compound **3b** was 1.3 g (76%), m.p. 128—130 °C. Found (%): C, 63.81; H, 6.43. $C_{20}H_{24}O_5S$. Calculated (%): C, 63.64; H, 6.49. ^1H NMR ($CDCl_3$), δ: 3.75 (s, 8 H, H(5), H(6), H(8), H(9)); 3.92 (m, 4 H, H(3), H(11)); 4.16 (m, 4 H, H(2), H(12)); 6.81 (d, 1 H, H(17), $^3J = 8.0$ Hz); 6.82 (d, 1 H, $C\underline{H}=CH$, $^3J = 15.7$ Hz); 6.97 (d, 1 H, H(16), $^3J = 8.3$ Hz); 6.98 (dd, 1 H, H(4′), $^3J = 3.9$ Hz, $^3J = 5.0$ Hz); 7.00 (s, 1 H, H(14)); 7.01 (d, 1 H, H(3′), $^3J = 3.5$ Hz); 7.06 (d, 1 H, $CH=C\underline{H}$,

^3J = 15.8 Hz); 7.14 (d, 1 H, H(5′), ^3J = 5.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 69.06, 69.20, 69.59, 69.63, 70.53, 70.57 (C(3), C(5), C(6), C(8), C(9), C(11)); 71.10, 71.12 (C(2), C(12)); 111.74, 114.03 (C(14), C(17)); 120.14, 120.18, 123.82, 125.42, 127.51, 128.15 ($\underline{\mathrm{C}}$=$\underline{\mathrm{C}}$, C(3′), C(4′), C(5′), C(16)); 130.63 (C(15)); 143.09 (C(2′)); 149.11, 149.28 (C(13a), C(17a)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 376 [M^+] (100), 288 (16), 244 (65), 188 (8), 171 (10), 160 (8), 122 (7), 115 (4), 86 (5), 45 (18).

15,15′-{2,2′-Dithienyl-5,5′-bis[(*E*)-ethene-2,1-diyl]}bis-1,4,7,10,13-pentaoxabenzocyclopentadecane (4a). Bromide **3a** (0.22 g, 0.49 mmol), bis(pinacolato)diboron (0.14 g, 0.54 mmol), and potassium acetate (0.14 g, 1.5 mmol) were dissolved in anhydrous DMF (7 mL). The resulting solution was degassed by three sequential freeze—pump—thaw cycles. The reaction vessel was filled with dry argon, charged with $PdCl_2$(dppf) (0.012 g, 0.015 mmol), and heated while stirring the reaction mixture at 75 °C for 2 h. On cooling, bromide **3a** (0.44 g, 1 mmol), $PdCl_2$(dppf) (0.012 g, 0.015 mmol), and Na_2CO_3 (0.26 g, 2.44 mmol) in water (1.2 mL) were added under argon and the mixture was heated at 75 °C for 10 h. The major part of the solvent was removed and the resulting suspension was filtered. The precipitate was washed with acetone and ether, dissolved in CH_2Cl_2, washed with water, and dried over $MgSO_4$. Evaporation gave the target product **4a** (0.35 g, 70%) as a bright yellow solid, m.p. 242—243 °C. Found (%): C, 63.98; H, 6.17. $C_{40}H_{46}O_{10}S_2$. Calculated (%): C, 64.01; H, 6.05. ^{1}H NMR ($CDCl_3$), δ: 3.73 (s, 8 H, H(5), H(6), H(8), H(9)); 3.89 (m, 4 H, H(3), H(11)); 4.16 (m, 4 H, H(2), H(12)); 6.79 (d, 1 H, C$\underline{\mathrm{H}}$=CH, ^3J = 16.2 Hz); 6.84 (d, 1 H, H(17), ^3J = 8.1 Hz); 6.92 (d, 1 H, H(4′), ^3J = 3.8 Hz); 7.00 (d, 1 H, H(16), ^3J = 8.1 Hz); 7.01 (s, 1 H, H(14)); 7.02 (d, 1 H, CH=C$\underline{\mathrm{H}}$, ^3J = 16.2 Hz); 7.04 (d, 1 H, H(3′), ^3J = 3.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 68.80, 68.96 (1 C each), 69.45, 70.37, 70.96 (2 C each, CH_2O); 111.30, 113.66 (C(14), C(17)); 119.86, 120.26, 123.94, 126.67, 128.13 ($\underline{\mathrm{C}}$=$\underline{\mathrm{C}}$, C(3′), C(4′), C(16)); 130.35, 135.69, 142.08 (C(2′), C(5′), C(15)); 149.07, 149.23 (C(13a), C(17a)). MS (ESI), *m/z* (I_{rel} (%)): 789 $[M + K]^+$ (100), 773 $[M + Na]^+$ (28), 768 $[M + NH_4]^+$ (59), 751 $[M + 1]^+$ (46). UV (MeCN), $\lambda_{\max}$/nm: 432.

Synthesis of compounds 4b—d (general procedure). Tetrakis(triphenylphosphine)palladium (1 mol.% with respect to the amount of **5a,b**) was added under argon to a solution of the starting compounds in an appropriate dry solvent (30—40 mL per millimole of **3a**). The reaction mixture was stirred for a period of time specified in Table 1; the reaction was accompanied by the formation of a precipitate. The major part of the solvent was removed and the resulting suspension was filtered. The precipitate was washed with acetone and ether, dissolved in chloroform or dichloromethane, washed with water, and dried over $MgSO_4$. Evaporation gave the target product as crystals.

15,15′-{2,2′:5′,2″-Trithienyl-5,5″-bis[(*E*)-ethene-2,1-diyl]}bis-1,4,7,10,13-pentaoxabenzocyclopentadecane (4b), brick-colored crystals, m.p. 252 °C. Found (%): C, 63.01; H, 5.83. $C_{44}H_{48}O_{10}S_3$. Calculated (%): C, 63.44; H, 5.81. ^{1}H NMR ($CDCl_3$), δ: 3.75 (s, 8 H, H(5), H(6), H(8), H(9)); 3.91 (m, 4 H, H(3), H(11)); 4.15 (m, 4 H, H(2), H(12)); 6.78 (d, 1 H, C$\underline{\mathrm{H}}$=CH, ^3J = 15.4 Hz); 6.81 (d, 1 H, H(17), ^3J = 8.3 Hz); 6.89 (d, 1 H, H(3′), ^3J = 3.8 Hz); 6.97 (m, 2 H, H(14), H(16), ^3J = 8.9 Hz); 7.00 (d, 1 H, CH=C$\underline{\mathrm{H}}$, ^3J = 15.4 Hz); 7.01 (d, 1 H, H(4′), ^3J = 3.8 Hz); 7.05 (s, 2 H, H(3″), H(4″) of thiophene). ^{13}C NMR ($CDCl_3$), δ: 68.89, 69.07 (1 C each), 69.57, 70.48, 70.07 (2 C each, CH_2O); 111.41, 113.75 (C(14), C(17)); 119.81, 120.31, 124.24 (2 C), 125.98, 126.66 (C=C, C(3′), C(4′), C(14), C(16), C(17)); 130.35 (C(2″), C(5″)); 133.80, 135.21, 142.29 (C(2′), C(5′), C(15)); 149.18, 149.23 (C(13a), C(17a)). MS (ESI), *m/z*: 871 $[M + K]^+$, 855 $[M + Na]^+$. UV (MeCN), $\lambda_{\max}$/nm: 451.

15-[(*E*)-2-(2,2′:5′,2″-Tetrathienyl-5-yl)vinyl]-1,4,7,10,13-pentaoxabenzocyclopentadecane (4c), red crystals, m.p. 294 °C. Found (%): C, 61.89; H, 5.05. $C_{28}H_{28}O_5S_3$. Calculated (%): C, 62.20; H, 5.22. ^{1}H NMR ($CDCl_3$), δ: 3.76 (s, 8 H, H(5), H(6), H(8), H(9)); 3.92 (m, 4 H, H(3), H(11)); 4.17 (m, 4 H, H(2), H(12)); 6.84 (d, 1 H, C$\underline{\mathrm{H}}$=CH, ^3J = 15.4 Hz); 6.99—7.29 (m, 11 H, H arom., H of thiophene, CH=C$\underline{\mathrm{H}}$). MS (ESI), *m/z*: 579 $[M + K]^+$, 563 $[M + Na]^+$, 558 $[M + NH_4]^+$, 541 $[M + H]^+$. UV (MeCN), $\lambda_{\max}$/nm: 422.

15,15′-{2,2′:5′,2″:5″,2‴-Tetrathienyl-5,5‴-bis[(*E*)-ethene-2,1-diyl]}bis-1,4,7,10,13-pentaoxabenzocyclopentadecane (4d), dark red crystals, m.p. 273 °C. Found (%): C, 62.93; H, 5.38. $C_{48}H_{50}O_{10}S_4$. Calculated (%): C, 63.00; H, 5.51. ^{1}H NMR ($CDCl_3$), δ: 3.75 (s, 8 H, H(5), H(6), H(8), H(9)); 3.91 (m, 4 H, H(3), H(11)); 4.16 (m, 4 H, H(2), H(12)); 6.81 (d, 1 H, C$\underline{\mathrm{H}}$=CH, ^3J = 15.4 Hz); 6.83 (d, 1 H, H(17), ^3J = 7.9 Hz); 6.92 (d, 1 H, H(3′), ^3J = 3.4 Hz); 6.99 (m, 2 H, H(14), H(16), ^3J = 8.9 Hz); 7.01 (d, 1 H, CH=C$\underline{\mathrm{H}}$, ^3J = 15.6 Hz); 7.02 (d, 1 H, H(4′), ^3J = 3.2 Hz); 7.07 (m, 4 H, H(3″), H(4″) of thiophene). MS (ESI), *m/z*: 937 $[M + Na]^+$, 488 $[M + Na + K]^{2+}$, 480 $[M + 2 Na]^{2+}$. UV (MeCN), $\lambda_{\max}$/nm: 458.

This work was financially supported by the INTAS (Grant 03-51-4696) and the Russian Foundation for Basic Research (Project No. 07-03-00724).

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Received January 24, 2007