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New Fused Thiophene Derivatives as Promising Building Blocks for Optoelectronic Devices

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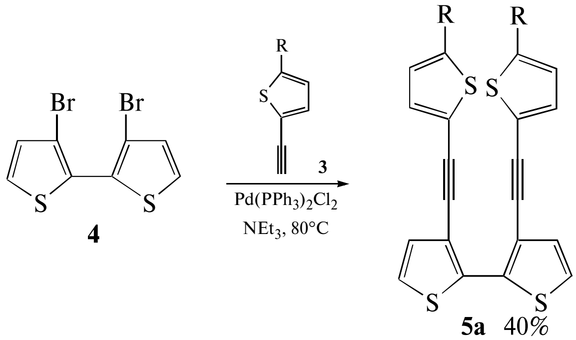
In recent two decades, much attention has been paid to organic semiconductors (OS), which are extremely attractive materials for application in optoelectronic devices due to their unique properties, such as low density, low cost, flexibility, and possibility to choose necessary physicochemical parameters. To date, the best-studied organic optoelectronic devices are the following: field-effect transistor [1], light-emitting diodes [2], and solar cells [3–6]. Their design is associated mainly with the synthesis of conjugated semiconducting polymers based on fused aromatic derivatives of thiophene, carbazole, furan, fluorene, etc. The coplanar structure of these compounds favors their self-organization to build ordered condensed molecular structures due to strong π–π interaction (stacking) [7], which facilitates efficient charge transfer [8].

This work deals with the search for efficient methods of synthesis of new fused benzothiophenes: 2,8-dibromo-4,6-bis(*n*-octylthien-2-yl)benzo[2,1-*b*:3,4-*b*':5,6-*c*'']trithiophene (**M1**) and 2,5-dibromo-8-pentadecyl-10H-bisthieno[2',3':6,7,3'',2'':4,5]indeno[1,2-*d*][1,3]thiazole (**M2**), which are promising donor monomers for preparing various photo- and electroactive polymers.

Monomer **M1** was initially prepared from 3,3'-dibromodithiophene (**4**) as a starting compound [9]. Preparation sequence included: (1) double cross-coupling of compound **4** with 2-ethynylthiophene **3** [10] under Sonogashira reaction conditions to give the corresponding diacetylene **5**, (2) rhodium-catalyzed intramolecular condensation of compound **5** in the presence of elemental sulfur, and (3) subsequent selective bromination of intermediate **6** with *N*-bromosuccinimide (NBS) at the two free C_2 positions of the benzothiophene fragment to form the target compound **M1** (Scheme 1).



5a 40%
5b 45%

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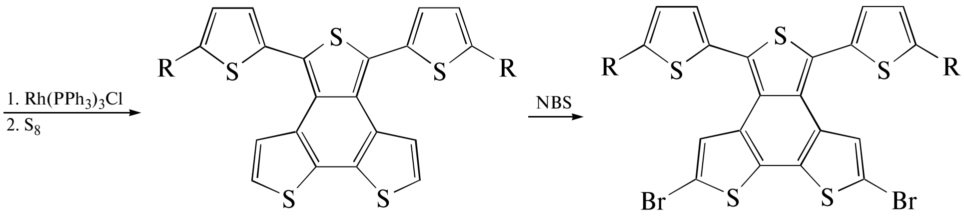
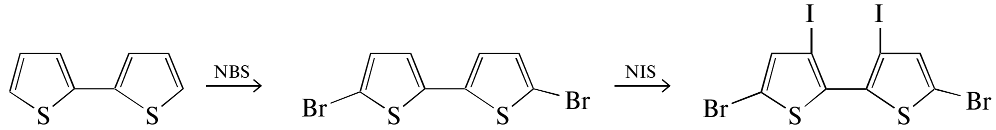


6a 60% **a**: R = 2-ethylhexyl **M1a** 55%

6b 62% **b**: R = *n*-octyl **M1b** 50%

Scheme 1.

Low yields of compound **5** (40–45%) at the stage of cross-coupling are caused by the incomplete transformation of initial dibromide **4** and the formation of a large number of unidentified byproducts. Unfortunately, all our attempts to optimize this process failed. Therefore, we developed an alternative strategy for preparing monomer **M1b** from 5,5'-dibromo-3.3'-diiodo-2,2'-bisthiophene **9** as a key intermediate. It synthesis was carried out in two stages by sequential halogenation of bisthiophene **7**, which considerably simplifies the known method recently reported by Müllen and co-workers [11] (Scheme 2).



7 **8** 80–85% **9** 85–90%

Scheme 2.

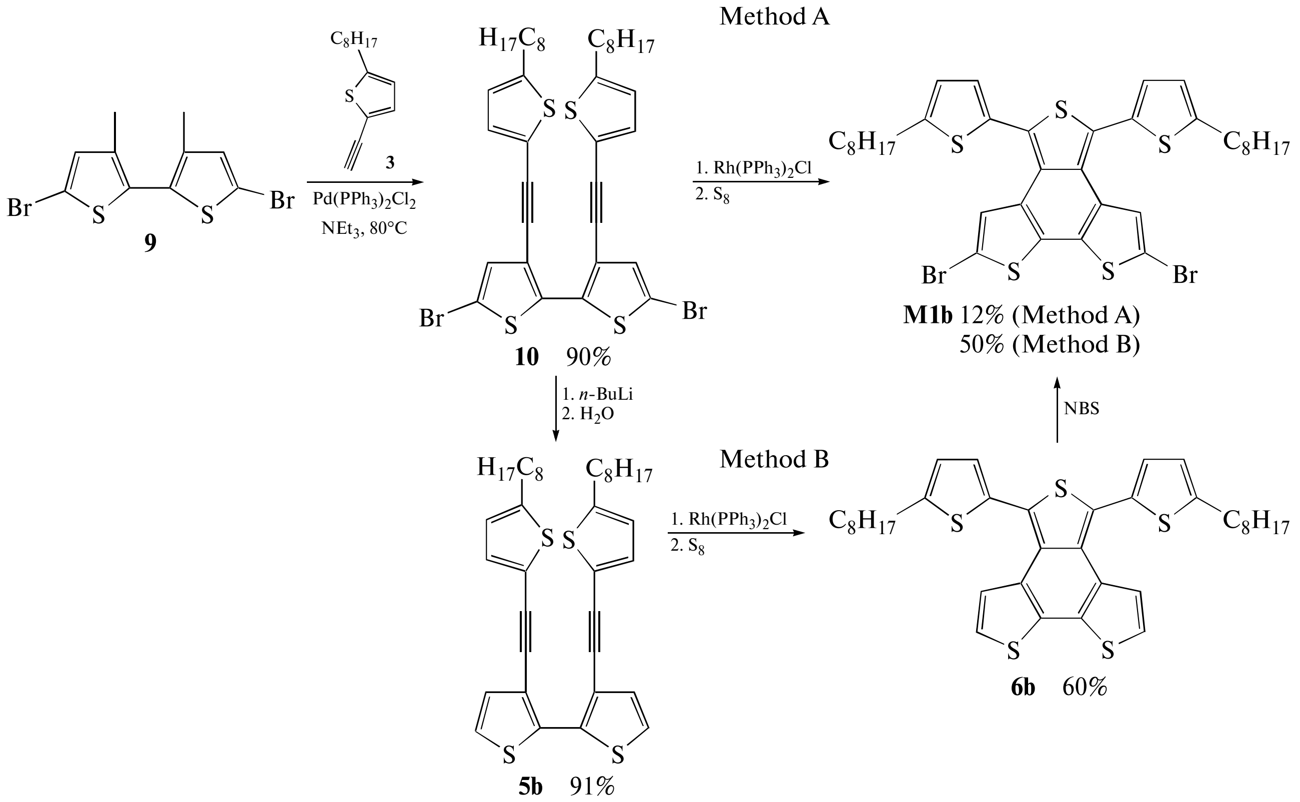
Both the intermediate and final compounds (**8** and **9**) were obtained in a pure state in high yields without using column chromatography. Both stages are easily adapted to the hundred-gram scale.

We found that compound **9** readily reacts with 2 equivalents of acetylene **3** at ambient temperature in the presence of catalytic amounts (5 mol %) of Pd(PPh$_3$)$_2$Cl$_2$ to give bis-ethynyl derivative **10** in yield up to 90% (Scheme 3), which is a brominated analog of compound **5b**.

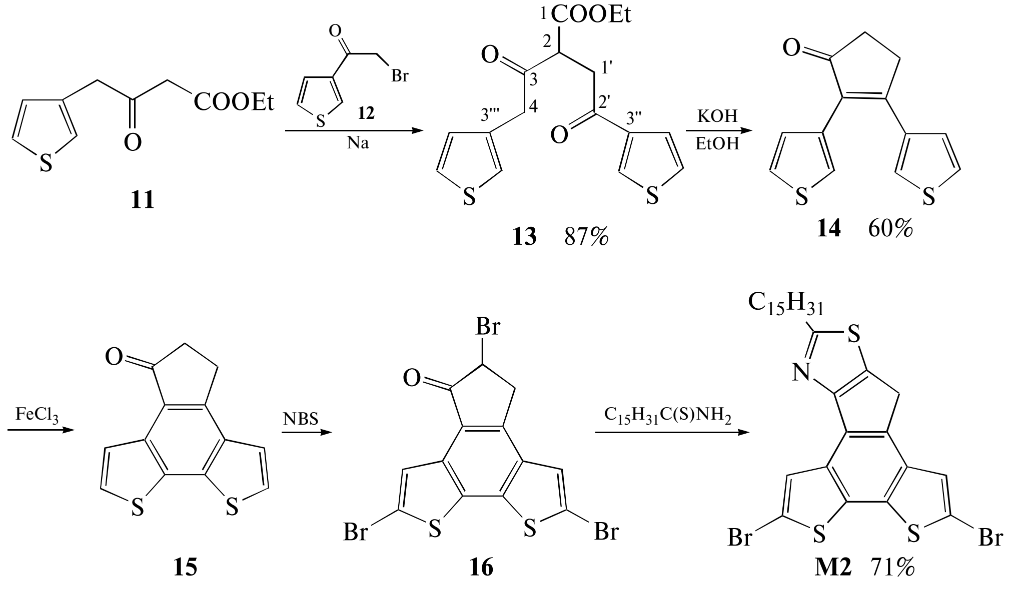
However, the subsequent intramolecular cyclization of compound **10** under the action of the Wilkinson complex (Rh(PPh$_3$)$_3$Cl) followed by addition of sulfur led to formation of the target compound **M1b** in only 12% yield (Scheme 3, Method A). At the same time, we revealed that compounds **5a** and **5b** containing no bromine atoms underwent cyclization under similar conditions to give the corresponding benzothiophenes **6a** and **6b** in good yields (Scheme 1). Therefore to increase the yield of desired monomer **M1b**, we carried out the dehalogenation of dibromide **10** under the action of *n*-butyllithium followed by hydrolysis and then performed cyclization and bromination of compound **6b** resulting in the target monomer **M1b** in enhanced total yield (Scheme 3, Method B).

The composition and structure of intermediate compounds **3**–**10**, as well as of target compound **M1**, were confirmed by elemental analysis data, ^{1}H and ^{13}C NMR spectroscopy. In particular, the proton spectrum of target product **M1** (Fig. 1a) shows one singlet and two doublets at 7.22, 7.09, and 6.89 ppm corresponding to aromatic protons of the thiophene fragment. The aliphatic region includes one triplet at 2.93 ppm typical for CH_2 group directly bound to thiophene ring. Signals related to other CH_2 groups of alkyl fragment are within 1.25–2.00 ppm. A triplet typical for CH_3 group of alkyl fragment is observed at 0.91 ppm. Integral intensity ratio for aromatic and aliphatic portions of target product molecule agrees well with the proposed structure. The downfield region of carbon spectrum of **M1** contains in the range 110–150 ppm ten signals that belong to 10 nonequivalent aromatic carbon atoms of thiophene fragment, while aliphatic portion shows eight resonances in the range 32–14 ppm that belong to eight different aliphatic carbon atoms (Fig. 1b).

Monomer **M2** was synthesized according to Scheme 4 via reaction of equimolar amounts of readily



Scheme 3.



Scheme 4.

available thiophenes **11** [12] and **12** [13] in the presence of sodium metal in anhydrous benzene resulting in ethyl 3-oxo-2-(2'-oxo-2'-thien-3''-ylethyl)-4-thien-3'''-ylbutanoate (**13**) in 87% yield.

The cyclization of compound **13** into dithiophene-containing cyclopentenone **14** was conducted in 7% KOH solution in EtOH–H_2O mixture (1 : 1) in 60% yield. The treatment of compound **14** with iron chlo-

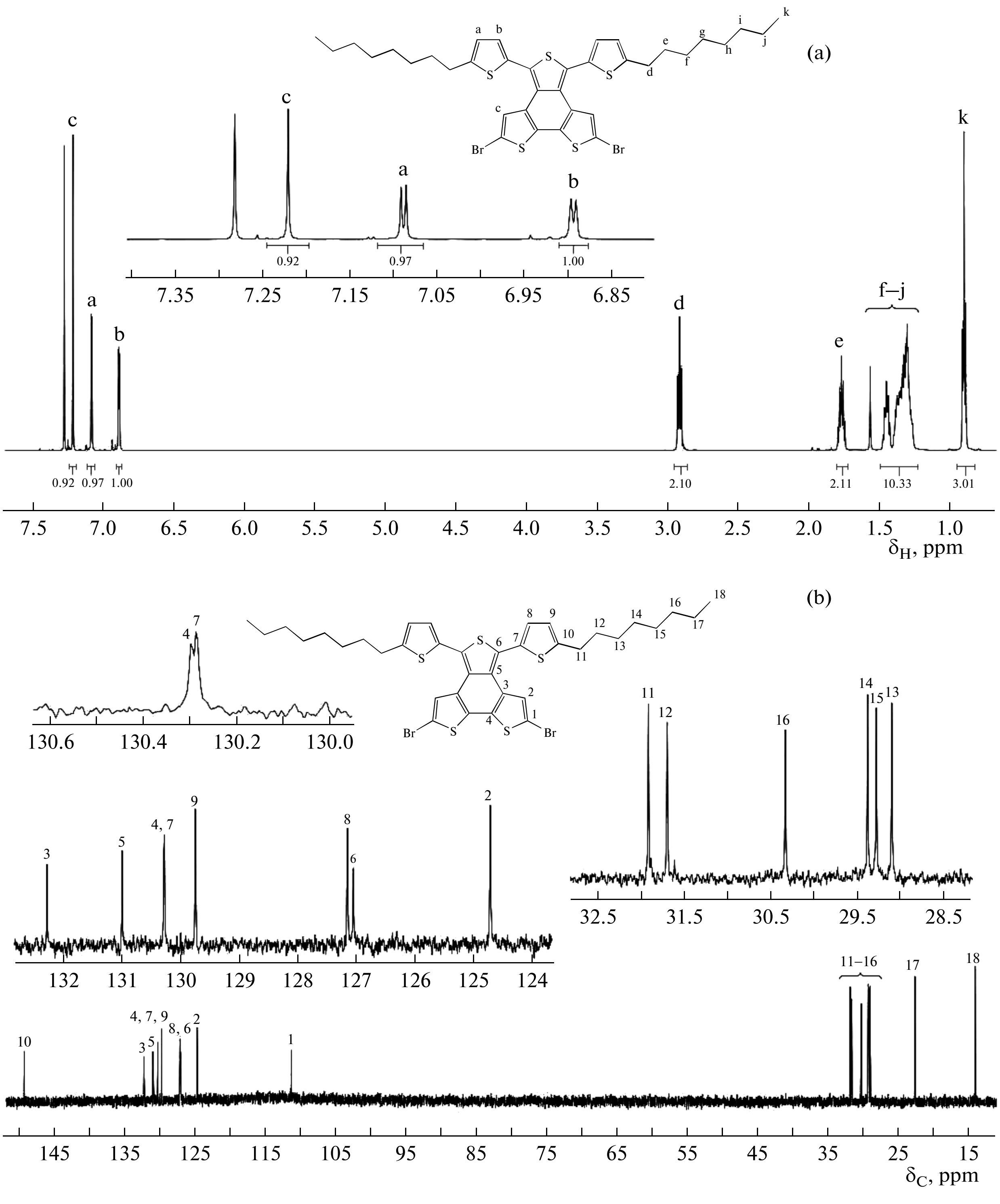


Fig. 1. ^{1}H (a) and ^{13}C (b) NMR spectra of monomer **M1b**.

ride resulted in benzodithiophene **15** whose bromination followed by condensation with aliphatic thioamide led to desired compound **M2** in 71% yield.

The structure of target monomer **M2** was confirmed by the data of elemental analysis, IR spectroscopy, and ^{1}H and ^{13}C NMR. In particular, the proton spectrum of monomer **M2** shows two singlets at 8.16 and 7.39 ppm typical of the protons of thiophene ring, singlet (3.90 ppm) and triplet (3.17 ppm) corresponding to the CH$_2$ protons in the five-membered carbon

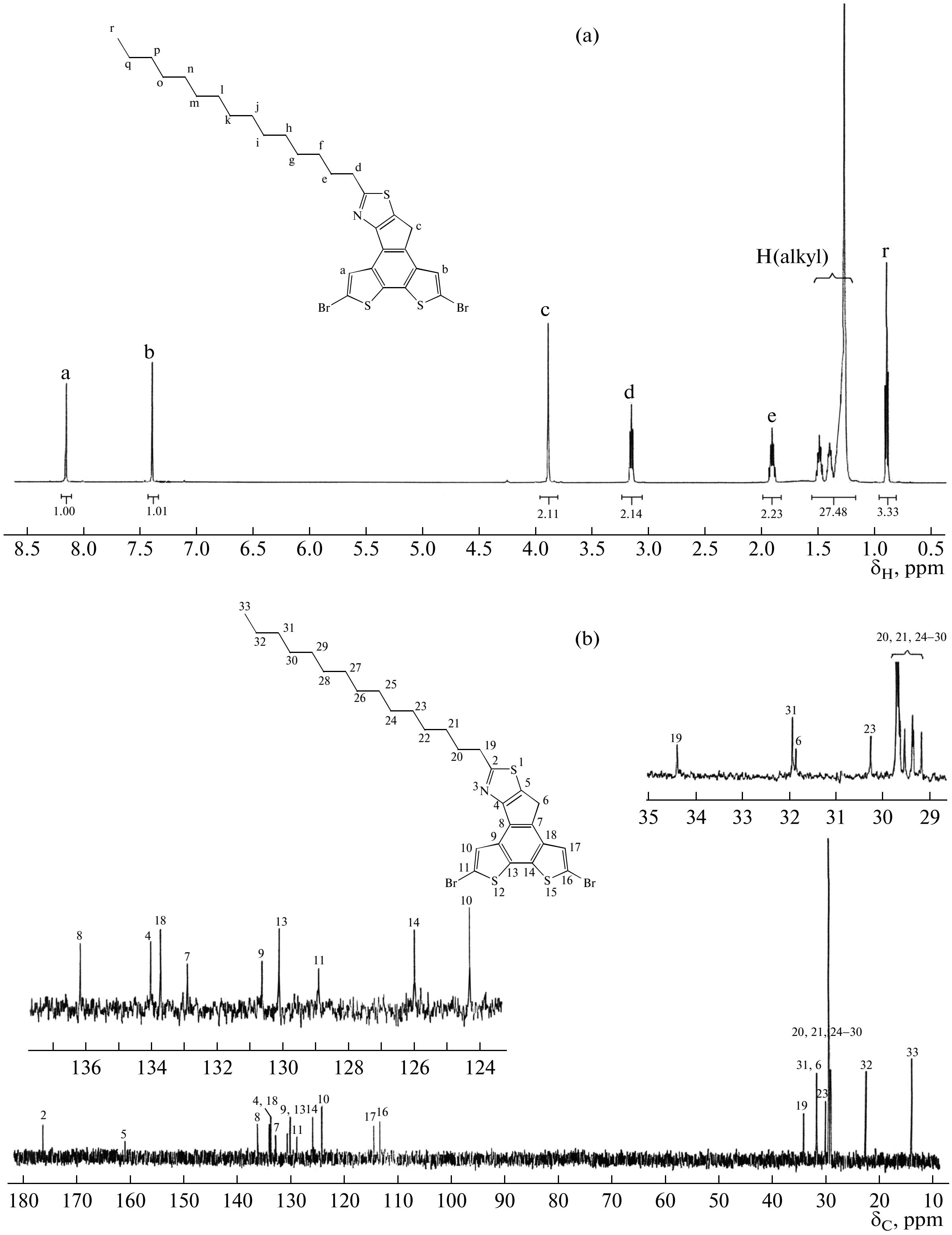


Fig. 2. ^1H (a) and ^{13}C (b) NMR spectra of monomer **M2**.

ring and in the alkyl group directly bound to the thiazole ring. The spectrum displays a multiplet at 2.01–1.40 ppm related to the aliphatic protons of the alkyl groups and a triplet of the CH_3 group at 0.90 ppm (Fig. 2a). The aromatic-to-aliphatic integrated intensity ratio corresponds to the suggested structure. The aromatic portion of carbon spectrum of compound **M2** exhibits 13 signals corresponding to 13 non-equiv-

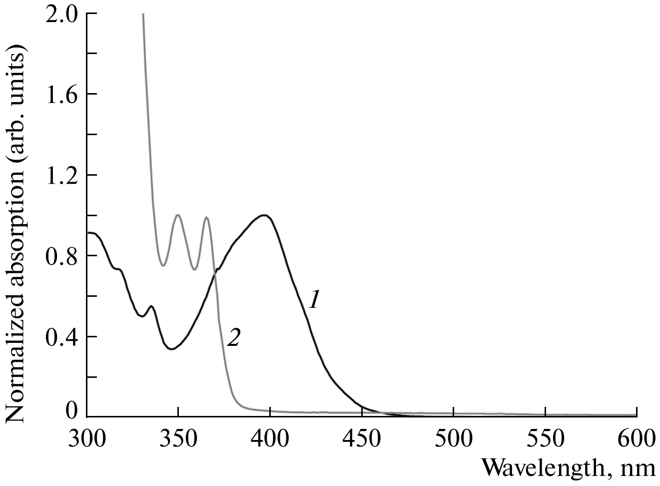


Fig. 3. Absorption spectra of compounds **M1** (*1*) and **M2** (*2*) in chloroform ($c = 1 \times 10^{-5}$).

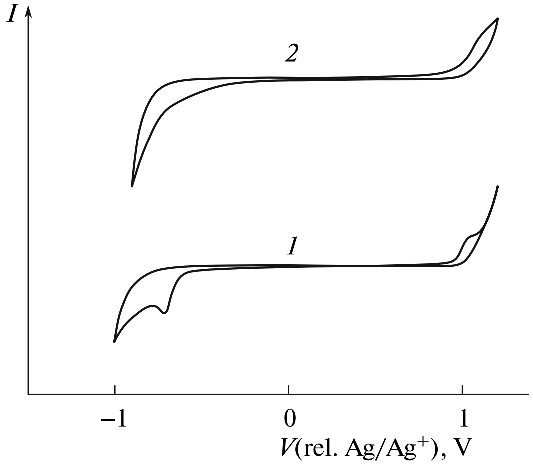


Fig. 4. Cyclic voltammograms of monomers **M1** (*1*) and **M2** (*2*) in 0.1 M lithium perchlorate solution in acetonitrile at scan rate 50 mV/s.

alent aromatic carbon atoms of thiophene fragment. The aliphatic portion of the spectrum includes signals of carbon atoms of CH_2 groups within 36–18 ppm and a signal at 14.15 ppm typical for CH_3 group.

Compounds **M1** and **M2** display absorption spectra with several maxima inherent in flat conjugated systems. Absorption spectra of these compounds show maxima at 350, 362, and 400 nm with absorption edges at 385 and 455 nm, respectively (Fig. 3). Band gap width corresponding to the position of absorption edges of these derivatives is within 2.83–3.44 eV.

The electrochemical properties of the monomers were studied by cyclic voltammetry. Cyclic voltammogram (Fig. 4) shows one reduction peak in negative region and one oxidation peak in the positive voltage region. Cathode reduction peak is likely to be due to formation of anion radicals of thiophene unit, while anode oxidation peak corresponds to cation radicals of thiophene fragment. HOMO and LUMO and band gap width of compounds **M1** and **M2** were calculated from the onset oxidation potential (E_{ox}^{onset}) and onset reduction potential (E_{red}^{onset}) of the monomers according to equations

$$\text{HOMO} = -e(E_{ox}^{onset} + 4.48)\ (\text{eV}), \quad (1)$$

$$\text{LUMO} = -e(E_{red}^{onset} + 4.48)\ (\text{eV}), \quad (2)$$

$$E_g^{ec} = e(E_{ox}^{onset} - E_{red}^{onset})\ (\text{eV}). \quad (3)$$

The HOMO and LUMO energies determined from onset oxidation potential and onset reduction potential according to Eqs. (1) and (2) are –5.43, –5.46 and 3.86, 3.80 eV, respectively. The energy gap width (E_g^{ec}) for the monomers determined by cyclic voltammetry, according to Eq. (3) is within 1.57–1.66 eV and insufficiently agrees with the band gap width (E_g^{opt}) determined by optical method. It was found that the obtained compounds have low-energy HOMO close to ideal value (5.4 eV), which provides a possibility to reach high open-circuit voltage in polymeric solar cells.

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