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CHEMICAL TECHNOLOGY

Synthesis and Optical and Electrochemical Properties of 5,6-Bis[9-(2-decyltetradecyl)-9*H*-carbazol-3-yl]naphtho[2,1-*b*:3,4-*b*']dithiophene as a Promising Building Block for Photovoltaic Applications

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Abstract—A new carbazole-containing naphthodithiophene heteroaromatic compound, 5,6-bis[9-(2-decyltetradecyl)-9*H*-carbazol-3-yl]naphtho[2,1-*b*:3,4-*b*']dithiophene (**M1**), was synthesized to be subsequently used as the weak donor structure for the construction of narrow bandgap D–A conjugated polymers in terms of the "weak donor–strong acceptor" concept. The composition and structure of **M1** were confirmed by the data of elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy. The optical and electrochemical characteristics of the product were measured. The compound **M1** was shown to have low-lying HOMO (–5.57 eV), which is favorable for high open-circuit voltage and to be suitable as a promising weak donor moiety in the D–A conjugated polymer for photovoltaic applications.

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In recent years, considerable attention has been devoted to organic semiconductors as promising materials for optoelectronic applications. Most of the studied organic semiconductors are based on the synthesis of π-conjugated structures such as oligothiophenes [1], oligofluorenes [2], polycyclic aromatic compounds [3], and fused heterocyclic aromatic structures [4]. A special place in the series of these compounds is occupied by fused thiophene derivatives, which are of interest from both scientific and practical standpoints. In view of the unusual electronic and optical features and high chemical and thermal stabilities, these compounds are tested as active layers for field effect transistors [5], light emitting diodes [6], and organic solar cells [7]. In particular, fused thiophene derivatives are studied owing to their planar geometry providing good π-stacking and highly ordered molecular structure promoting efficient charge transfer.

Among these promising classes of heteroaromatic compounds are naphthodithiophene (NDT) derivatives containing two thiophene rings fused with a naphthalene moiety and representing planar structures with a π-conjugated system favorable for strong intramolecular π-conjugation and intermolecular π-stacking [8]. Naphthodithiophene derivatives with clear-cut weak donor properties incorporated in conjugated D–A-copolymers lower the highest occupied molecular orbital (HOMO) level, which increases the open-circuit voltage, and, as a consequence, they increase the efficiency of polymeric solar cell [9]. Recently, Wong and co-workers [10] synthesized the D–A copolymer with a narrow bandgap (1.6 eV) and low-lying HOMO (–5.22 eV) based on 5,6-dialkoxynaphthodithiophene derivatives and employed this copolymer to design solar cells with a bulk heterojunction of 5.3% efficiency not inferior to world analogs. The low position of the HOMO led to high open-circuit voltage (V_{xx} = 0.68 V) and, hence, to higher efficiency [10]. You and co-workers [11] proposed one more novel naphthodithiophene-containing narrow bandgap polymer, approaching the "ideal polymer," with a band gap of 1.59 eV and low-lying HOMO (–5.35 eV) [11].

Here we developed and synthesized a new monomer, 5,6-bis[9-(2-decyltetradecyl)-9*H*-carbazol-3-yl]naphtho[2,1-*b*:3,4-*b*']dithiophene (**M1**), based on NDT containing carbazole moieties in the 5- and 6-positions (Scheme 1). As noted above, compounds of this type form highly ordered π-stacked structures, which enhances the hole conductivity.

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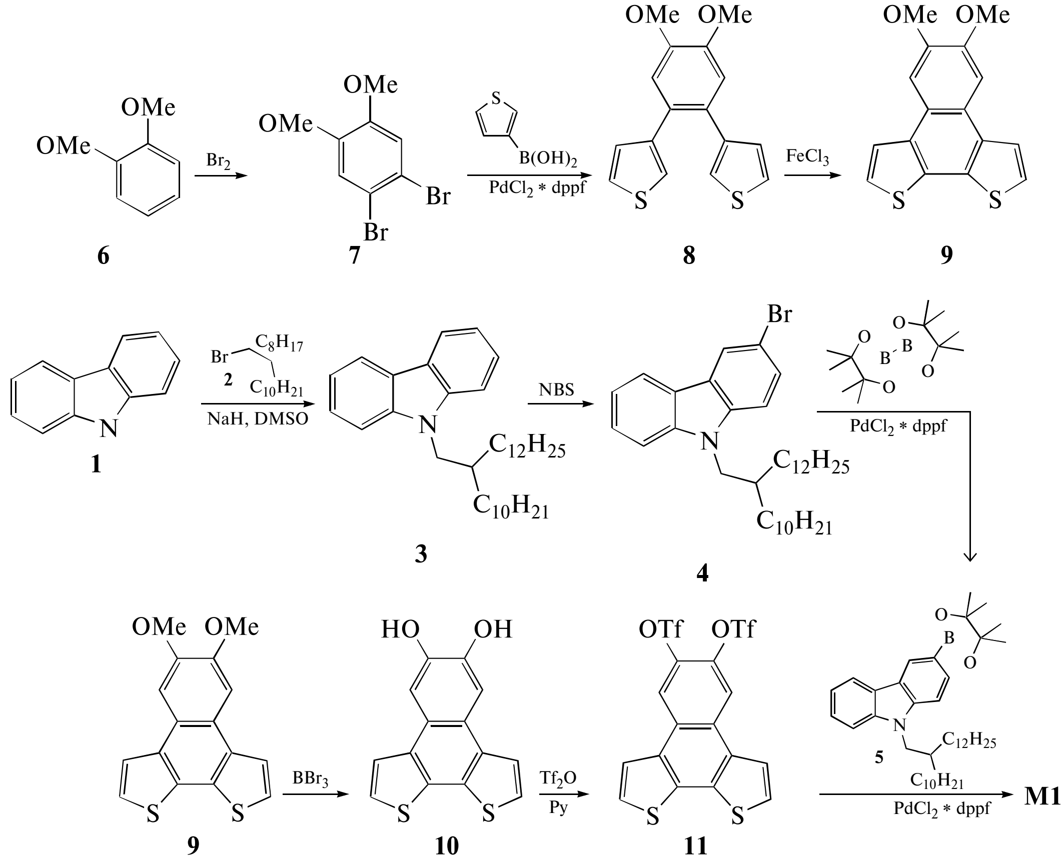
The naphthodithiophene monomer is a weak donor, which, being incorporated in D–A polymers, would promote a decrease in the HOMO level and an increase in the open-circuit voltage, and, as a consequence, would enhance the efficiency of a solar cell. It is noteworthy that in all known compounds, the 5- and 6-positions of NDT had alkyl or alkoxyl groups. Meanwhile, the use of carbazole moieties was not reported previously. Presumably, the introduction of carbazole moieties would induce additional conjugation with the NDT moiety, and this would reduce the bandgap width and enhance the light absorption. The presence of the N–H-group in carbazole would allow the introduction of alkyl substituents promoting good solubility in organic solvents.

We presented two synthetic routes to 5,6-bis[9-(2-decyltetradecyl)-9*H*-carbazol-3-yl]naphtho[2,1-*b*:3,4-*b*']dithiophene (**M1**).

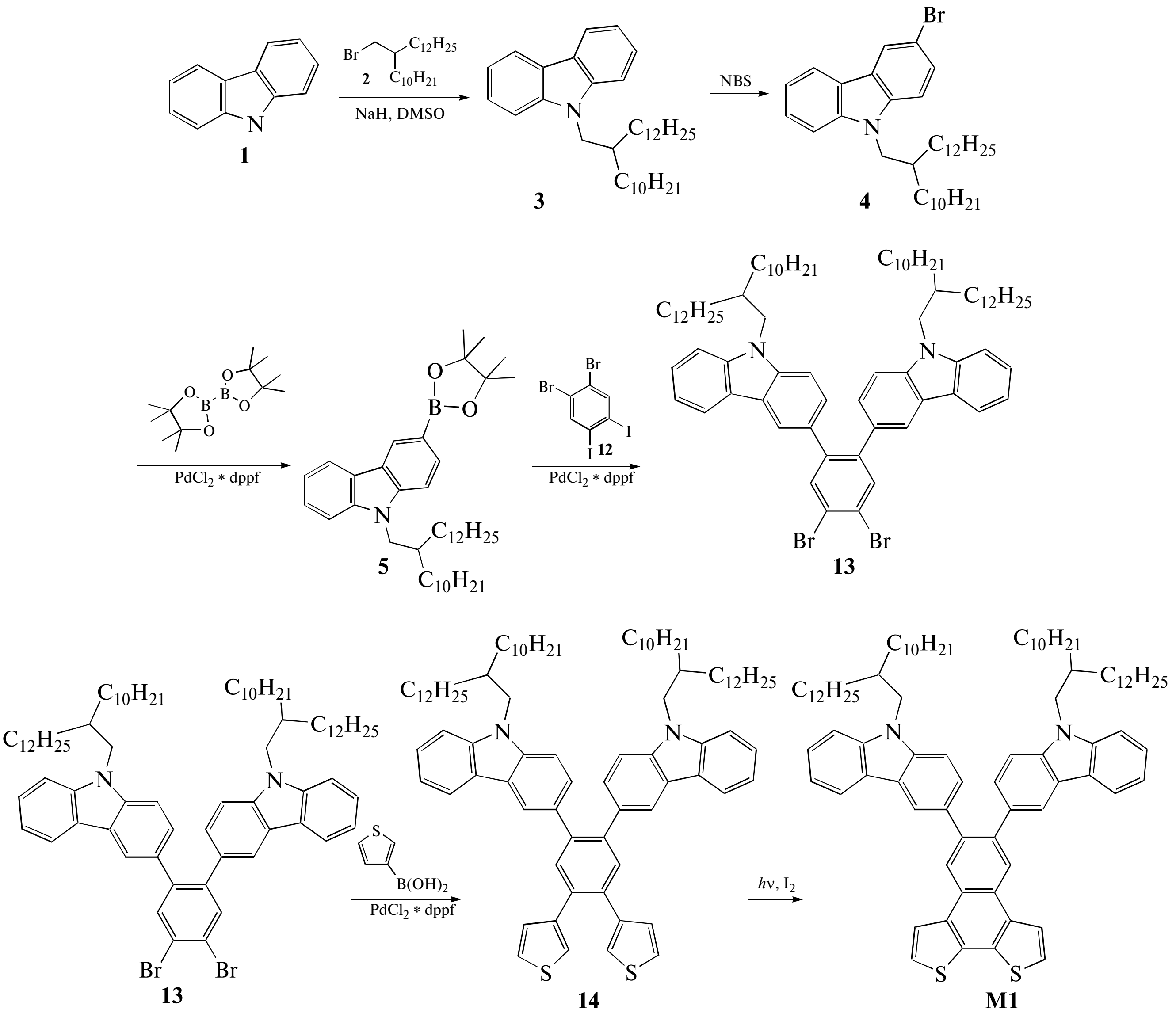
The first route (Scheme 1) consists of nine steps including bromination of 1,2-dimethoxybenzene (**6**) to give 1,2-dibromo-4,5-dimethoxybenzene (**7**) as large white crystals (92% yield), which then reacts with thiophene-3-boronic acid affording 1,2-bis(thiophen-3-yl)-4,5-dimethoxybenzene (**8**) in 85% yield. Successive treatment of compound **8** with anhydrous ferric chloride and BBr_3 induces oxidative cyclization giving first 5,6-dimethoxynaphtho[2,1-*b*:3,4-*b*']dithiophene (**9**) (49% yield) and then compound **10** in high yield (99%). Then, **10** is converted into bis(triflate) intermediate **11** in 72% yield. The last step is treatment of **11** with pinacol-boron carbazole derivative **5**, resulting in the formation of the target product **M1** in a good yield (60%). Compound **5**, 3-(1,3,2-dioxoborolan-2-yl)-9*H*-carbazole, was synthesized in three steps comprising the alkylation of carbazole (**1**) with 2-decyltetradecyl bromide (**2**) to give compound **3** in 92% yield, bromination of the alkylated product **3** with *N*-bromosuccinimide (formed in 64% yield), and reaction of 3-bromo-9-(2-decyltetradecyl)-9*H*-carbazole **4** with bis(pinacol)diborane to give **5** in 41% yield.



Scheme 1.

The first route is lengthy, consists of nine steps, and the overall yield of **M1** is low, being only ~4%; therefore, this method is not efficient. Therefore, we proposed an alternative route (Scheme 2). This route is shorter and consists of only six steps, in particular, the reaction of 1,2-dibromo-4,5-diiodobenzene (**12**) with

9-(2-decyltetradecyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl)-9*H*-carbazole (**5**) to give 1,2-bis(9-(2-decyltetradecyl)-9*H*-carbazol-3-yl)-4,5-dibromobenzene (**13**) in a good yield (68%). The subsequent Suzuki reaction of compound **13** with an excess of thiophene-3-boronic acid furnishes 1,2-bis(9-(2-decyltetradecyl)-9*H*-carbazol-3-yl)-4,5-bis(thiophen-3-yl)benzene (**14**) in 77% yield. The oxidative cyclization of **14** induced by UV light gives rise to the target compound **M1**. After column chromatography, the yield of **M1** is 90%, and the overall yield is 11.4%.



Scheme 2.

The composition and structure of the intermediate compounds and the target compound **M1** were confirmed by the data of elemental analysis and ^1H and ^{13}C NMR spectroscopy. In particular, the aromatic region of the ^1H NMR spectrum of the **M1** monomer (Fig. 1a) exhibits one singlet, two triplets, and seven doublets. The doublet at 8.29 ppm (d, $J = 1.20$ Hz) corresponds to the H^a protons of the carbazole rings. The signal at 7.27 ppm (dd, $J_1 = 8.45$ Hz, $J_2 = 1.36$ Hz) refers to the H^g proton. The latter is vicinal to the H^f, which is responsible for the doublet at 7.14 ppm ($J = 8.49$ Hz). The H^b, H^c, H^d, and H^e proton signals are observed at 8.09 (d, $J = 7.62$ Hz), 7.23 (t, $J = 7.56$ Hz), 7.46 (t, $J = 7.99$ Hz), and 7.40 (d, $J = 8.10$ Hz) ppm. The two doublets at 7.56 and 8.11 ppm have spin–spin coupling constants of ~5.25 Hz and can be assigned to the H^i and H^j protons of the thiophene moieties. The singlet at 8.59 ppm corresponds to the H^h protons of

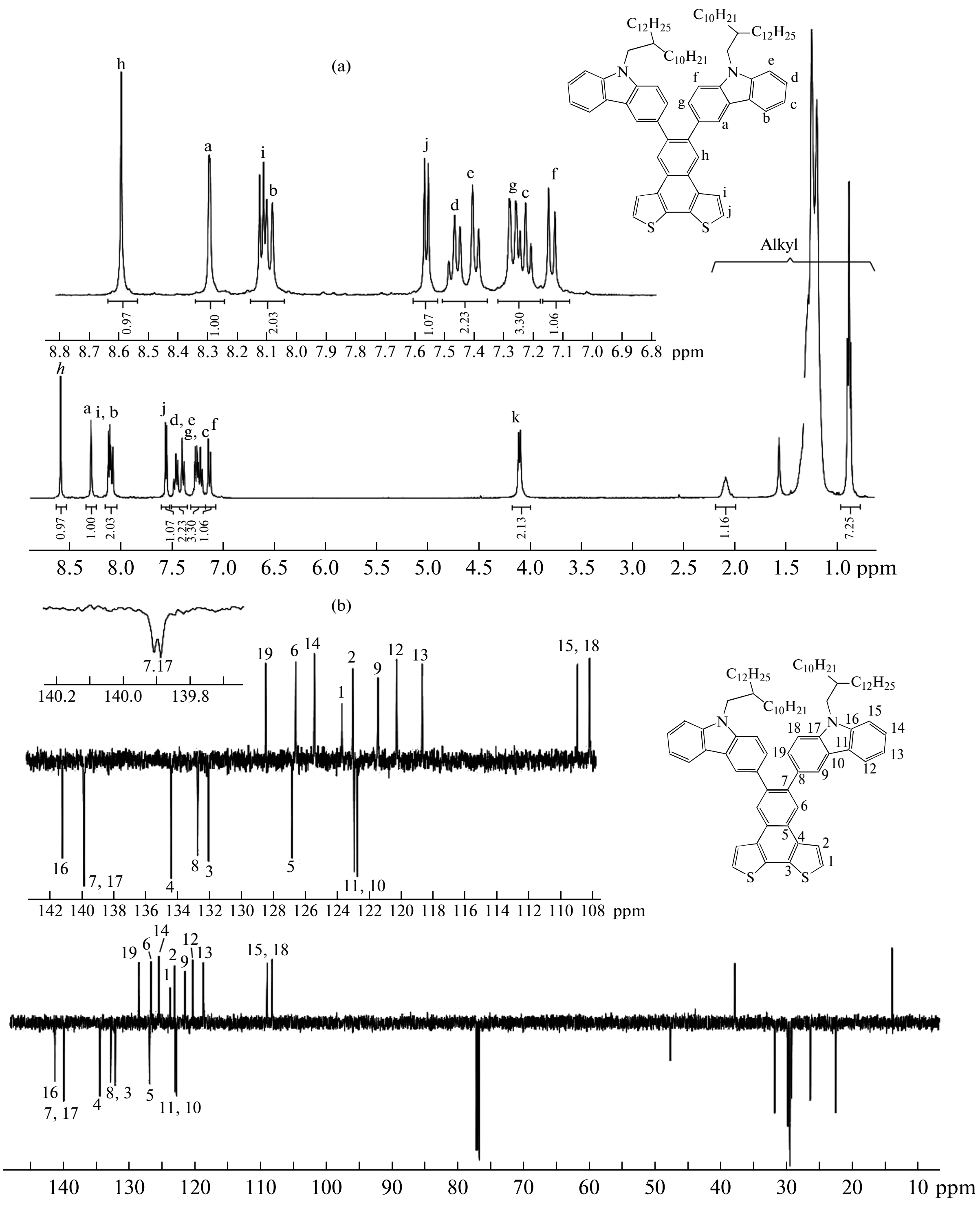


Fig. 1. (a) ^{1}H and (b) ^{13}C NMR spectra of the **M1** monomer.

the naphthodithiophene moiety. The ^{1}H NMR spectrum of **M1** is fairly complex; however, the aliphatic to aromatic integrated intensity ratio is in line with the proposed structure. The aromatic region of the carbon spectrum of **M1** exhibits 19 signals, nine of which refer to quaternary carbon atoms. The signals at 50–10 ppm correspond to aliphatic carbon atoms of the alkyl chains (Fig. 1b).

The UV absorption spectra of **M1** in solution and in the film are shown in Fig. 2. The absorption peaks of **M1** occur at 310 and 360 nm with absorption edge

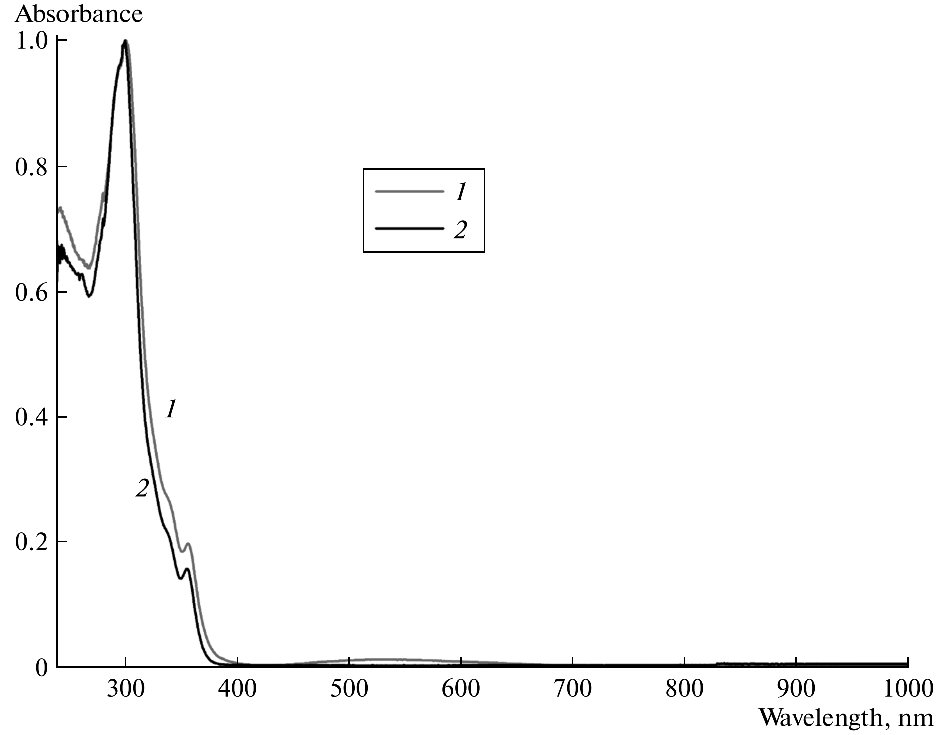


Fig. 2. Absorption spectra of **M1** in (*1*) film and (*2*) chloroform ($c = 10^{-5}$ M).

at 380 nm (Fig. 2). The optical bandgap width corresponding to the absorption edge is 3.26 eV. The absorption spectrum of **M1** in the film is somewhat red-shifted with respect to that in solution. This is apparently due to more ordered structure existing in the solid state.

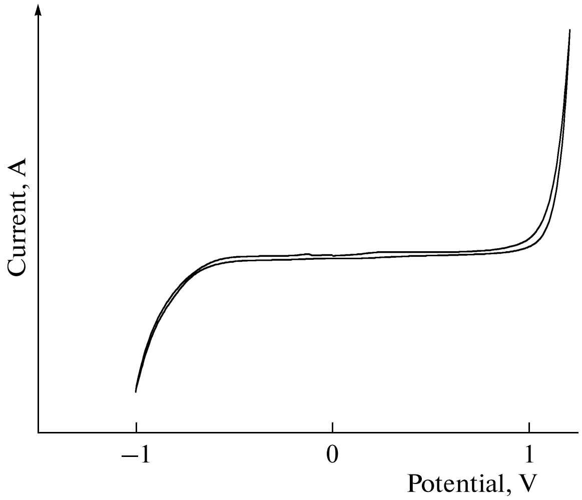


Fig. 3. Cyclic voltammogram of **M1** in a 0.1 M solution of lithium perchlorate in acetonitrile at a sweep rate of 50 mV/s.

The electrochemical properties of **M1** were studied by cyclic voltammetry. The cyclic voltammogram (Fig. 3) has one reduction peak in the negative potential region and one oxidation peak in the positive region. The cathodic reduction peak refers apparently to the formation of radical anions of the thiophene derivative, while the anodic oxidation peak corresponds to the radical cations of the thiophene moiety. The oxidation and reduction onset potentials in the cyclic voltammogram were used to calculate the HOMO and LUMO levels of **M1** by the following equations (*e* is the electron charge)

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

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

The HOMO and LUMO levels found from the oxidation and reduction onset potentials using Eqs. (1) and (2) are –5.57 and –3.88 eV, respectively. Compound **M1** has a low-lying HOMO level, which provides a high open-circuit voltage in polymeric solar cells and endows **M1** with good air stability.

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