Practical aspects and physicochemical evaluation of fluorene derivatives

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The work is dedicated to Professor Jan Epsztajn in occasion of celebration of his 75th year

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Abstract
A novel series of mono- and dialkylfluorene derivatives were synthesized by literature C-C coupling procedure (prepared by means of palladium-catalyzed Stille and Suzuki coupling reaction). The new compounds were tested as organic semiconductors in presence of toxic gases. The electropolymers thus obtained showed high stability under ambient conditions.

Keywords: Cross-coupling, heterocycles, metalations, palladium, Stille reaction, Suzuki coupling reaction, LB films, charge transfer complex, cyclic voltammetry, electropolymerization

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Introduction

The notion of π-conjugated polymer materials should possess interesting and useful electronic and optical properties, now well established in the scientific literature. Many of these expectations have been realized by the practical demonstration of electronic and optoelectronic devices in which conjugated polymeric materials are responsible for charge transport or light generation. The wide-ranging applications of electro active and photoactive conjugated polymers have attracted great interest in the development of functionalized polypyrroles, polythiophenes and polyfluorenes. These materials combine the excellent electrical, optical and sensor properties of many fields.[1]

In the past decade, polyfluorenes (PFs) have emerged as emitting materials suitable for use in LEDs (light emitting diodes) because of their highly efficient photoluminescence (Pl) and electroluminescence (El), their thermal and oxidative stability, and their good solubility. In the light of the above facts, we envisaged that poly(3,4-etylenedioxythiophene), which contains alkyl chain in fluorine ring, should possess high electrochromic contrast and thermal stability.[2]

A major support for the advancement in the design of functional molecular nano-objects is improving of ability to control their macromolecular structure in great detail often by using proper polymerization techniques or other deposition methods (Langmuir – Blodgett, LB). In the last two decades there has been an increasing interest in electro active molecules arranged in thin films, due to their capability for the development of electronic and sensor devices.[3]

In the last time charge transfer (CT) complexes also are under study to be utilized as conductive wires for nanoscale devices. One of the important features of molecular CT – complexes is the possibility of modifying their electronic properties by virtue of the coupled electronic and structural change of the molecular state.[4]

Recently, we have reported the synthesis, the electrochemical moieties of series well-defined mono- and dialkylfluorenes,[5] as well as carbazole derivatives prepared by Stille coupling of *N*-alkylcarbazole and sulfur-containing heterocycles.[6]

In context of continuing our previous efforts, in case of fluorine, the Stille or Suzuki coupling reaction is promising method for preparation the furane derivatives. It is surprising that pyridine units have been very incorporated into conjugated oligomers or polymer structures.

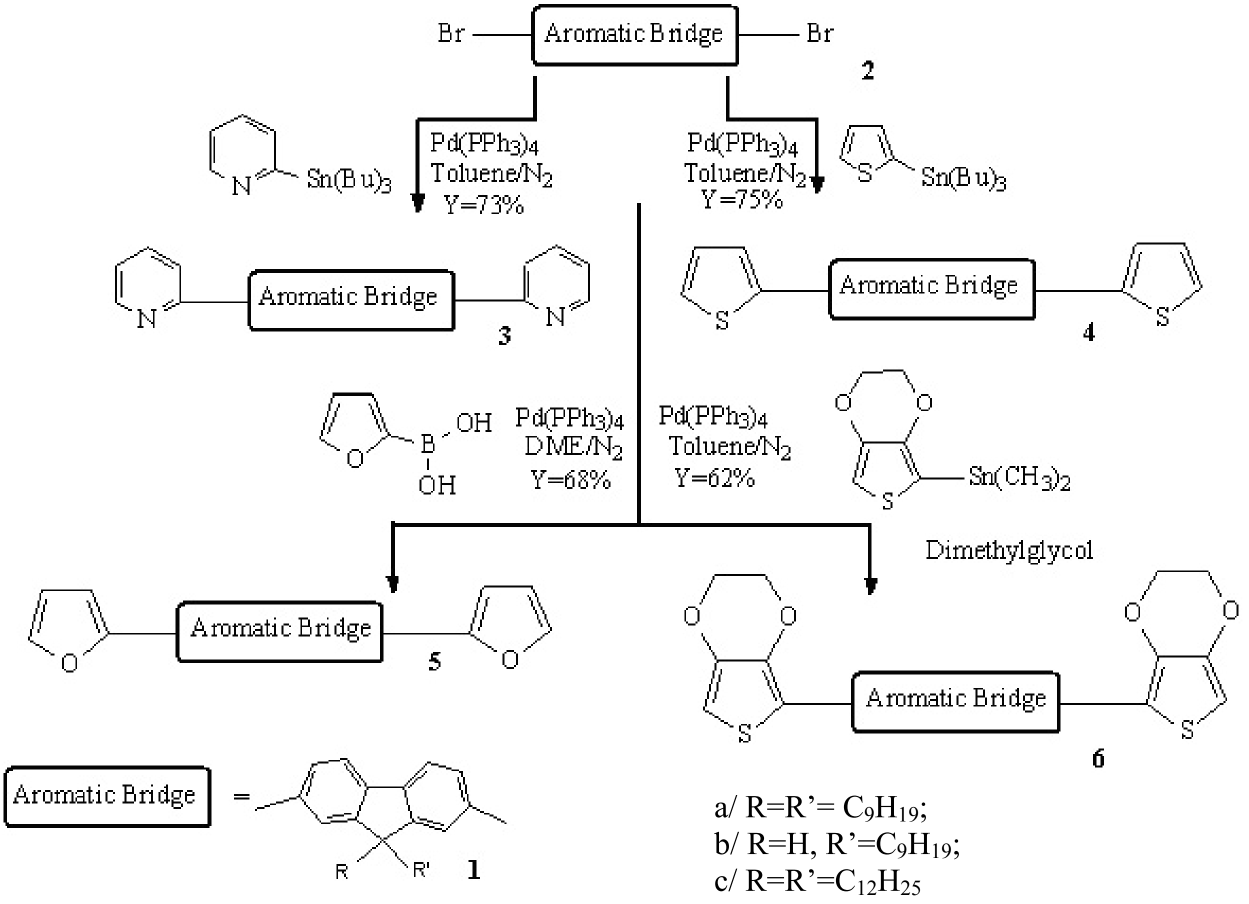
Our considerable interest in precursors of conducting and sensing materials chemistry[5] stimulate us also to present the results of research into the properties of Langmuir – Blodgett (LB) films containing CT complexes with tetracyanoquinodimethane (TCNQ). TCNQ as well as its derivatives focus on extensively use as electron acceptor molecules in a large number of organic conducting system, and many efforts have been centered on the preparation of LB films containing TCNQ complexes moieties.

Result and Discussion

Our approach is based on utilizing synthesis of fluorine derivatives. The mono alkyl and dialkylfluorene derivatives, substituted by pyridine, thiophene or furane for the present study (according our previous experience[6]) are reported. First of all, longer alkyl chains were introduced at the C9 position of each fluorine unit to improve solubility in classical organic solvents.[7]

The synthetic sequence leading to **3-6** from **2** is depicted in Scheme 1. Alkylation of the fluorine by alkylbromide led to the first compound of series **2,** while dibromo derivatives were obtained in classical bromination procedure[7]. Finally, palladium catalyzed Stille coupling of 2-trimethyltinthiophene, 2-pyridyl tributyl tin or 2-trimethyltin-3,4-ethylenedioxythiophene with 9,9-dialkyl-2,7-dibromofluorene or 9-monoalkyl-2,7-dibromofluorene provided the target molecules **3, 4** or **6** (Scheme 1). The general procedure for preparation of furane-arylidenefurane triblock (compound **5**) by Suzuki cross-coupling methodology was as follows on Scheme 1.

To obtain further scope about the packing structure and chemical properties of such CT type alternating π-conjugated copolymers, we have synthesized new furane-based alternating monomers **5**.



a/ R=R'= C_9H_{19};
b/ R=H, R'=C_9H_{19};
c/ R=R'=$C_{12}H_{25}$

Scheme 1

The key step for the synthesis of bis(furane)fluorene derivatives **5,** (Scheme 1) was a trifold Suzuki cross-coupling reaction[7-8], which was carried out in two-phase system of toluene or xylene and aqueous potassium carbonate solution. Our general synthetic strategy for monomers was based on step-by-step methodology using cross-coupling reactions leading to formation of **5** with yields near 70%. For the more reactive fluorene side-arms, the reactivity of Pd(PPh_3)$_4$ is sufficient.

In all cases a chromatographic purification of the crude products are performed to separate completely palladium traces incorporating the product and some by-products formed in course of the coupling reaction.

All these materials are soluble in common organic solvents and appear yellow. The molecular structures of monomers were confirmed by ^{1}H NMR and ^{13}C NMR, elemental analysis.

Properties of Langmuir – Blodgett Films built of charge transfer complex

The charge transfer complex of fluorine derivative with tetracyanoquinodimethane (TCNQ) was prepared by refluxing an equimolar solution of 9,9-dinonyl-2,7-bis(2-thiophene)fluorene (DNTF) and TCNQ in, respectively, chloroform and acetonitrile, until all of the TCNQ had reacted.

Then organic layers were deposited by LB technique onto a clean glass substrate pre-coated with an indium tin oxide (ITO) layer (300 nm thick) with a sheet resistance of ~ 20 Ω/square. All initially unmeasured under water films were deposited at the velocity lower than the draining rate of film of carboxylic acids i. e. 1.3 mm/min. After deposition films were stored in vacuum desiccator prior to use.

Langmuir monomolecular films, of 9,9-dinonyl-2,7-bis(2-thiophene)fluorene- DNTF (**4a**) – TCNQ complex was spread from $CHCl_3$ – CH_3CN (1:1) solution on high purity water at 293 K. Langmuir – Blodgett deposition was carried out with a KSV System 5000 LB through at a surface pressure of around 5 mN/m.

The preparation of gas mixtures, sample processing and all conductivity measurements were carried out at *ca*. 293 K. The current – voltage characteristics were measured both in ambient atmosphere, prior to the admission of the gas and for different partial pressures of NO_2, and were found linear over the entire voltage range covered by experiment.

We first investigated the LB film quality of DNTF – TCNQ complex deposited on ITO substrate (Figure 1). Atomic force microscopy (AFM) revealed homogenous films even with great magnifications, we can clearly observed layers texture of LB films. In homogenous matrix we observed dump flamed floats. Their main characteristic is that all of them have more or less the same size (film grain size of ~250 nm).

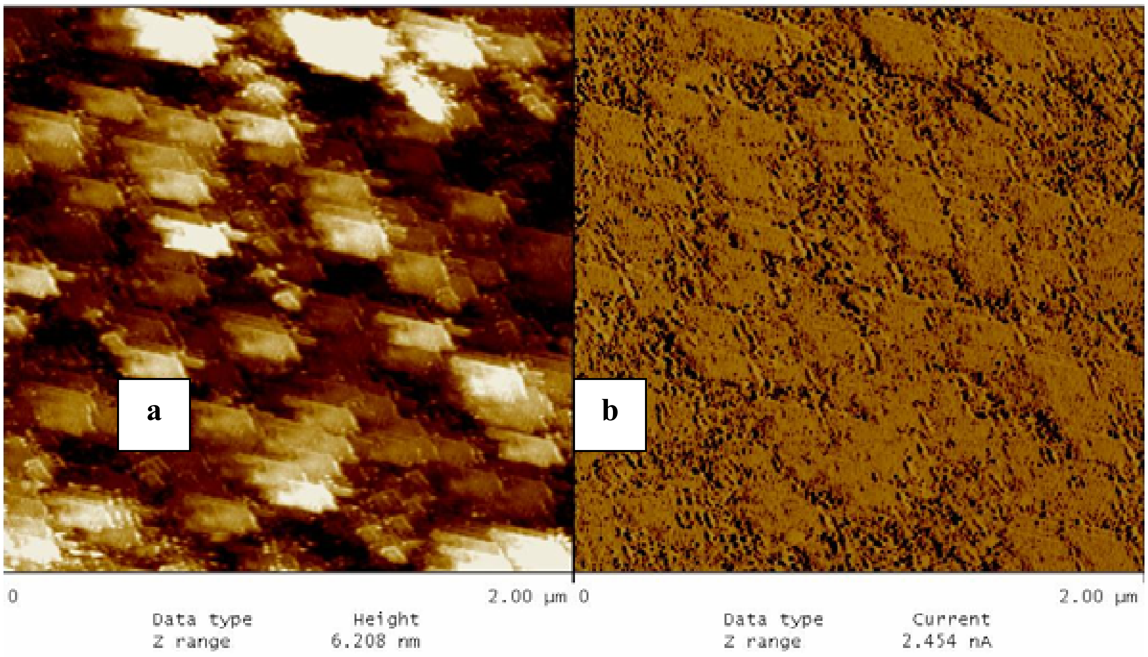


Figure 1. AFM photomicrographs of DNTF-TCNQ complex's LB Film deposited on ITO substrates; a/ real pictures of surface topography, b/ mathematical function of film architecture.

The transference of LB film was Y – type in first deposition and Z – type in following ones. Then it seems that the TCNQ presence changes the hydrophilic/hydrophobic character of the film surface. The relationship between absorbance and number of layers and constant transfer ratio during the deposition indicate on constant architecture of LB film layers. The absorption spectrum of DNTF – TCNQ complex deposited film confirms also the formation of a CT complex. Figure 2 shows a characteristic CT band observed at 600 nm, while there was no significant absorption in the pristine TCNQ film.

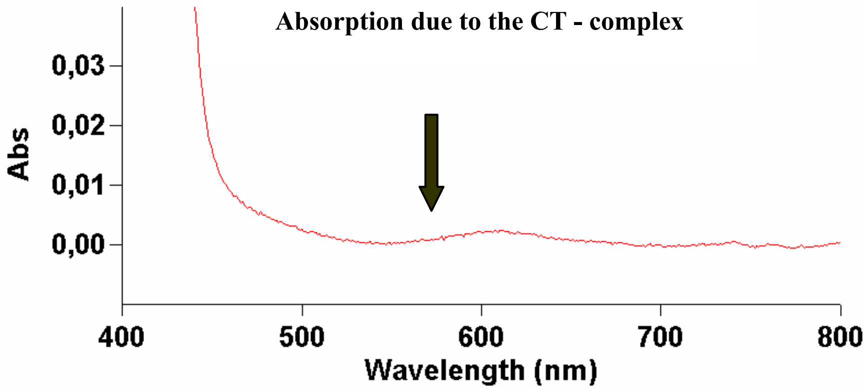


Figure 2. Absorption spectrum of DNTF-TCNQ complex in LB film (3 layers).

The major result of investigations was focused on measured dependence of the surface conductivity of LB films built of DNTF – TCNQ CT complex sensors exposed to air in ambient pressure, containing NO_2, against the concentration of the gas. The nominal concentration of gas ranged between 1 – 5 ppm of NO_2.

During the first gas admission we observed linear dependence conductivity on gas concentration (Figure 3 and Figure 4). After the series of measurements, a measuring box was opened to the air and recovery of conductivity was observed for a half an hour.

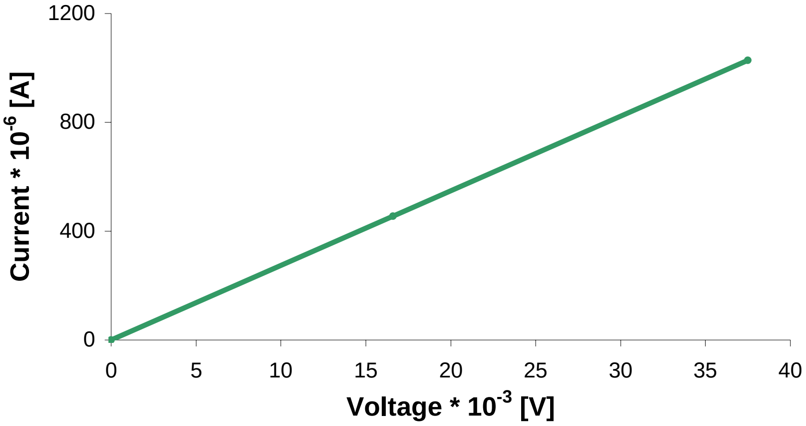


Figure 3. Conductivity response of 5 layer LB film of DNTF- TCNQ in presence of NO_2. The first admission of the gas.

The second and all consecutive admissions of gas resulted in the same character of the dependence of conductivity on gas concentration (Figure4).

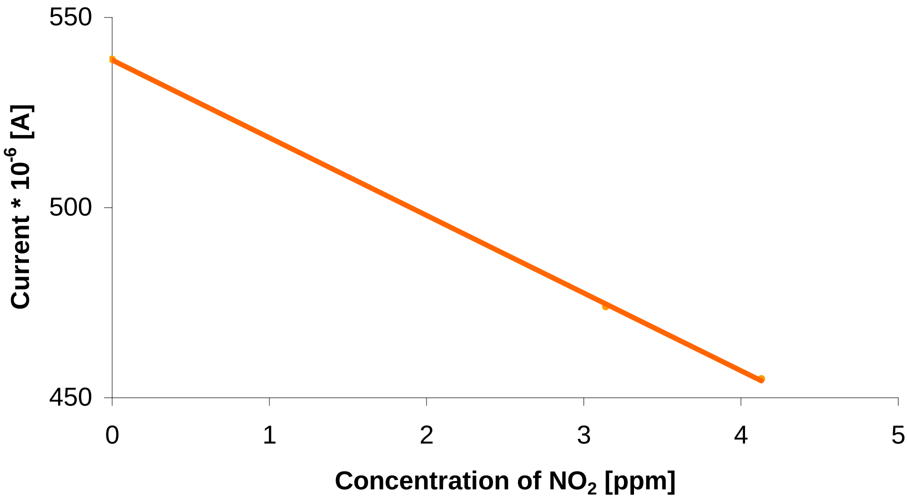


Figure 4. Conductivity response of 5 layer LB film on increasing NO_2 concentration in atmosphere surrounded the sample. U = 15 mV.

In all measuring cycles the response time of sensor was of the range of seconds and almost full recovery, at room temperature, was achieved within 20 minutes, or less, after the opening a measuring chamber. No heating was necessary for desorption of gas from the surface of sensor.

Relatively short response times and fair sensitivity at room temperatures make these materials a very promising candidates for gas sensing elements.

In the cause of CT complexes both types of gases (oxidative and reductive) engender an noticeable changes of conductivity. The electronic conduction in organic molecular – based compound of the TCNQ family arises from a charge transfer between the constituent acceptor (TCNQ) and donor molecules (9,9-dialkylfluorene derivatives).

Theoretical study of LB layer architecture

Theoretical study [9] of LB layers built of fluorene derivatives can be analyzed on two planes, hydrophilic-aromatic and hydrophobic-aliphatic part of molecule. Free rotation of aromatic rings causes bigger molecular area for aromatic molecular part (~108 Å^2), what is also confirmed by experimental π-A isotherms. Aliphatic chains influence on themselves only in hydrophobic plane.

According to this study, we can suggest periodic model of location amphiphilic molecules (bis(arene)fluorene derivatives) in LB film. In this case we can defined three types of LB architecture: a/ short dialkyl chain, b/ middle dialkyl chain, c/ long dialkyl chain – possibility of irregular structure of film (Figure 5).

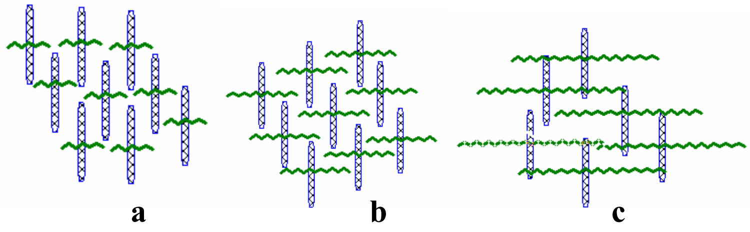


Figure 5. Three types of LB film architecture, aerial view.

Theoretical considering is pointed on stability of LB layers (Fig.6) obtained in mono- and binary systems what was also confirm by experiments. LB films of DNTF built in binary system with docosanoic acid well architecture films.

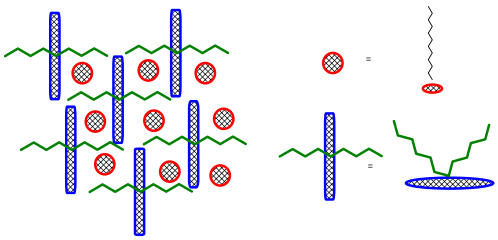


Figure 6. Proposed model for LB film topography in binary system.

Electrochemical polymerization

Compounds were electrochemically polymerized using cyclic voltammetry. For each of the electrochemical polymerizations, the reduction of the conductive polymer deposited on the electrode is observed upon scanning in the cathodic direction. Upon further cycling in the anodic direction, polymerization continues as observed by the increase in current response of the redox of the polymer (an increase in this electroactive species on the electrode surface).

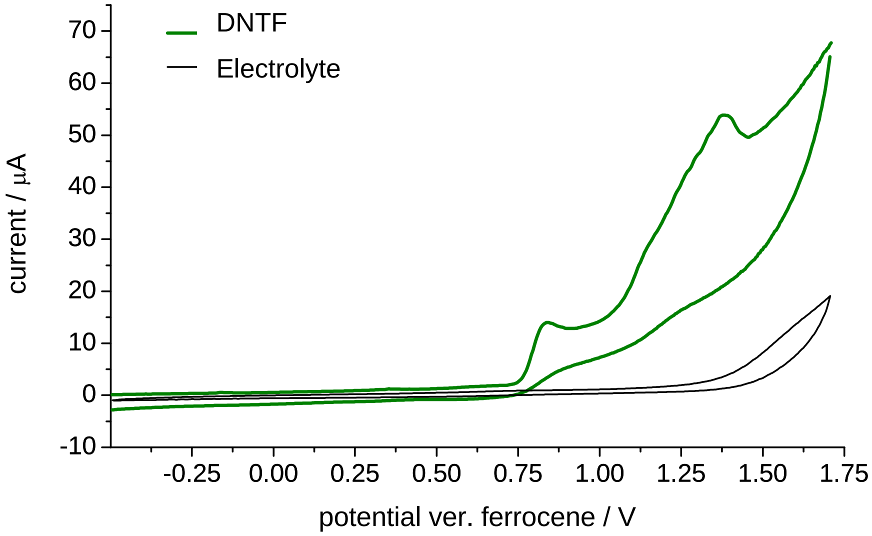


Figure7. Cyclic voltammogram of DNTF solution in 0.1M $(Bu)_4NBF_4$ in CH_2Cl_2 and CH_3CN mixture (1:1 vol.) at Pt electrode. Scan rate: 50 mV/s.

In this case a little dependence of electrochemical properties on kind of alkyl ligand of fluorene ring is observed. We found two oxidation peaks, whereas the first one for DNTF E_{p1} = 0.833 V, the second, much bigger - E_{p2} = 1.384 V. Experimental results suggest that monomer molecule undergoes non-reversible oxidation procedure in two steps, in first to radical cation and to dication in the second one. The high of the second oxidation peak and its complicated structure (Fig.7) let us to suppose, this process is connected also with electrochemical oxidation of condensed unstable radical cations of DNTF.

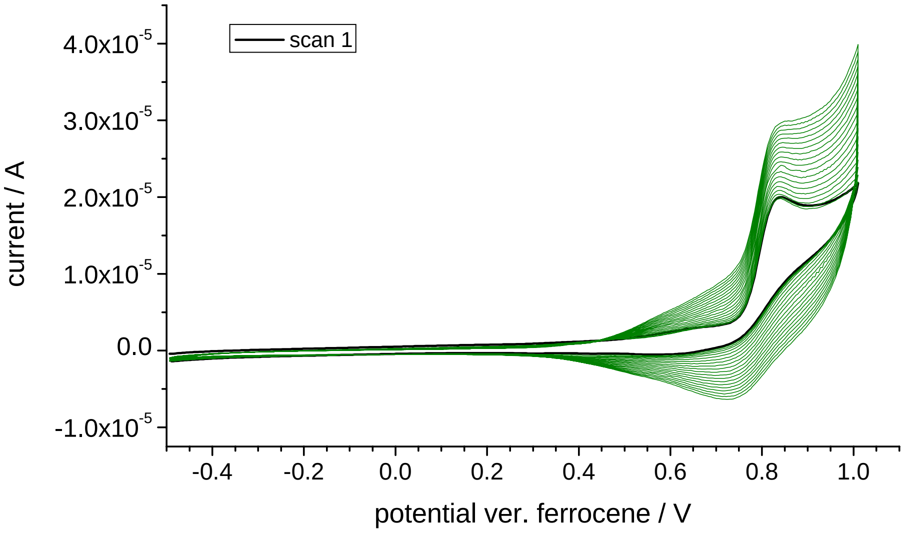


Figure 8. Cyclic voltammogram of DNTF solution in 0.1M $(Bu)_4NBF_4$ in CH_2Cl_2 and CH_3CN mixture (1:1 vol.) at Pt electrode. Scan rate: 50 mV/s.

The product of subsequent reactions of radical cations $DNTF^+$ is polymer. On Figure 8 we can observed example of cyclic voltammetry (CV) curves obtained during electrochemical polymerization process. Found, systematic growth of current in potential ranged between 0.4 - 0.75 V suggests regular layer of polymer deposited on electrode's surface. Important is fact that potential higher than 1.3V causes degradation of polymer film.

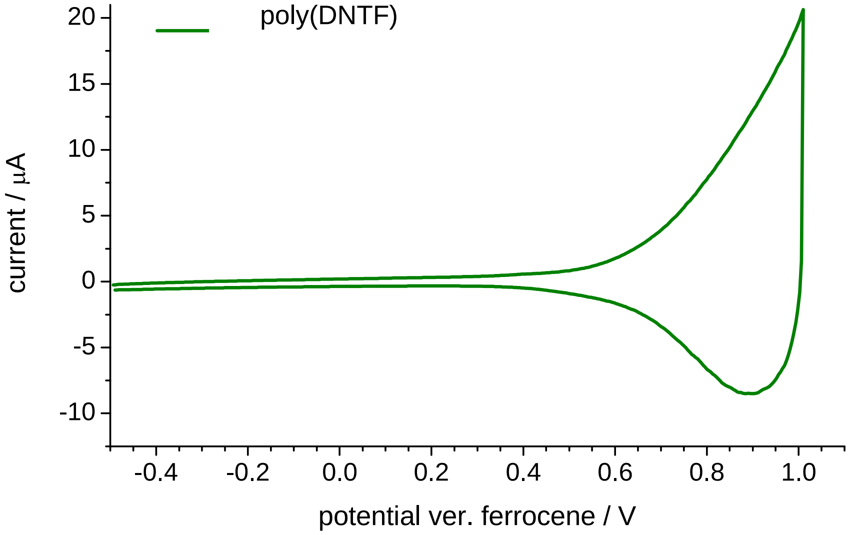


Figure 9. Cyclic voltammogram of film of poly(DNTF) in 0.1M $(Bu)_4NBF_4$ in CH_2Cl_2 and CH_3CN mixture (1:1 vol.) at Pt electrode. Scan rate: 50 mV/s.

Figure 9 shows response of poly(DNTF) in 0.1 M $(Bu)_4NBF_4$ in CH_2Cl_2 and CH_3CN mixture. Polymer oxidizes in relative high potential but in CV curve there is no distinct oxidation peak, polymer achieved in this process is rather stable and colourful.

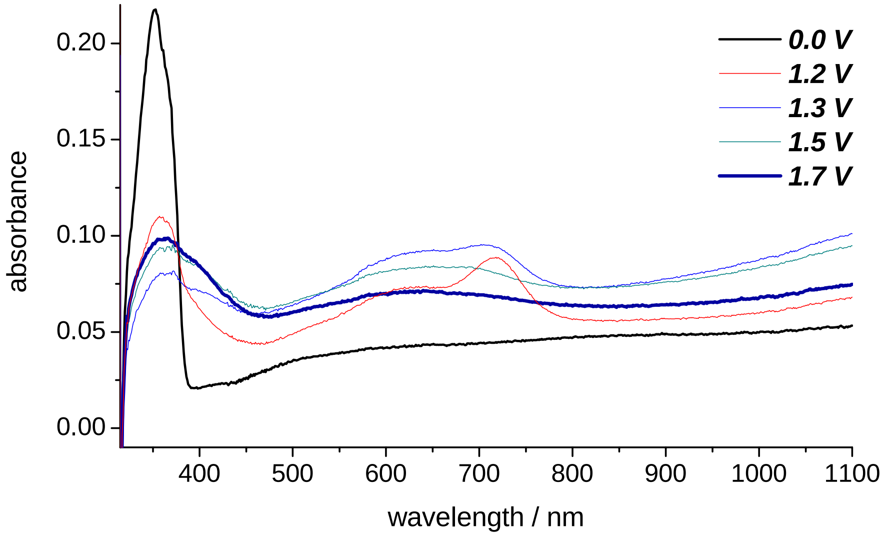


Figure10. UV – Vis spectrum recorded during electrochemical oxidation of DNTF solution in 0.1M $(Bu)_4NBF_4$ in CH_2Cl_2 and CH_3CN mixture (1:1 vol.) on ITO electrode.

On figure 10 one can find examples of UV-Vis spectra registered *in situ* during electrochemical polymerization process. Observed two clear absorption peaks near 620 and 717 nm are characteristic for radical cation $DNTF^+$. In this connection, experimental results suggest that electrochemical polymerization processing with relative stable $DNTF^+$, which in next step is condensed to insoluble polymer.

Conclusions

We are reported the synthesis, electrochemical characterization of new fluorene-based alternating π-conjugated compounds.

Mono- and dialkyldisubstituted fluorenes are synthesized as a building blocks for electrochemical processing (conductive electropolymers) and surface electrochemistry (LB films, CT – complexes exhibit conductive behaviour in presence of toxic gases).

In the course of provided by us reactions, it was found that the palladium–catalyzed coupling reaction between mono- and dialkylfluorenes (**2**) and 2-metalled thiophene, pyridine and ethylenedioxythiophene derivatives run, in general, without difficulties, as well as Suzuki coupling in case of bis(furane)derivatives of fluorene. They give rise to the formation of the coupling products **3**, **4, 5** and **6** with relatively high or moderate yield (60-80%).

We believe that materials obtained with synthesized derivatives of fluorene may lead to a further increase of the field-effect mobility and thus make these materials attractive for applications in organic sensors, electronic and electrochromic devices. [10]

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Experimental Section

General Procedures. Melting points are uncorrected. All NMR spectra were acquired a Brucker VXR-300 at 300 (^{1}H) and 75 (^{13}C) MHz in $CDCl_3$ using TMS as internal standard. Column chromatography was carried out on Merck Kiesel silica gel 60. Dry THF was used immediately after distilling from a solution containing benzophenone-sodium. Other starting materials, reagents and solvents were used as received from suppliers.

The purity of the products was checked by thin layer chromatography, and their molecular structures were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy as well as by the elemental analysis and UV-Vis spectroscopy.

Synthesis

The procedure for preparation of 9-alkyl-2,7-dibromofluorene (2a-2c)

9-alkylfluorene were converted to dibromofluorene derivatives in presence of bromine in acetic anhydride and ethyl acetate, starting from 2.55g of **1a-1c**.

S*elected data for* **2a.** Y = 71% (2.49g), oily [12] ^{1}H NMR ($CDCl_3$) δ: 7.50 (d, *J* = 6.4 Hz, 2H, arom. H), 7.46-7.43 (m, 4H, arom. H), 1.91 (q, *J* = 8.2 Hz, 4H, CH_2), 1.31-1.05 (m, 24H, CH_2), 0.87 (t, *J* = 6.5 Hz, 6H, CH_3), 0.60 (s, 4H, CH_2). ^{13}CNMR ($CDCl_3$) δ: 152.5, 139.1, 130.1, 126.2, 121.4, 121.1, 55.7, 40.2, 31.9, 29.9, 29.8, 29.6, 23.6, 22.7, 14.1.

For $C_{31}H_{44}Br_2$, Calcd C, 64.59; H, 7.69. Found C, 64.45; H, 7.65.

2b. Y = 82% (3.22g), white crystals mp. 64 ^{0}C, ^{1}H NMR ($CDCl_3$) δ: 7.26-7.20 (m, 4H, arom. H), 6.67 (d, *J* = 6.7 Hz, 2H, arom. H), 3.74 (t, *J* = 7.0 Hz, 1H, CH), 1.72 (q, *J* = 7.4 Hz, 2H, CH_2), 1.41-1.24 (m, 14H, CH_2), 0.87 (t, *J* = 6.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 144.1, 130.0, 129.6, 129.4, 116.6, 114.6, 47.5, 31.8, 29.4, 29.1, 26.7, 26.5, 22.6, 22.6, 14.1.

For $C_{22}H_{26}Br_2$, Calcd C, 58.69; H, 5.82; Found C, 58.45; H, 5.65.

2c. Y = 79% (2.76.g), white crystals, mp. 52-53 ^{0}C (lit. 51-52 ^{0}C [13]), ^{1}H NMR ($CDCl_3$) δ: 7.53-7.50 (m, 2H, arom. H), 7.46-7.43 (m, 4H, arom.H), 1.99-1.08 (m, 4H, CH_2), 1.31-1.05 (m, 36H,

CH_2), 0.87 (t, J = 6.5 Hz, 6H, CH_3), 0.61-0.59 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 152.6, 139.1, 130.2, 126.2, 121.5, 121.2, 55.7, 40.2, 31.9, 30.0, 29.9, 29.6, 29.5, 29.3, 29.2, 23.6, 22.7, 14.1.

The procedure for preparation of 9-alkyl-2,7-bis(2-pyridine)fluorene (3a-3c)

Monomers were synthesized according to our previous method [8] by a coupling reaction of 9-alkyl-2,7-dibromofluorene (**2a-2c)** with 2-pyridyl tributyl tin, starting from 1g of **2a-2c**.

Selected data for **3a.** Y = 75% (0.75g), mp. 105 ^{0}C, ^{1}H NMR ($CDCl_3$) δ: 8.81 (s, 2H, arom. H), 8.60 (d, J = 4.5 Hz, 2H, arom. H), 8.13 (d, J = 8.5 Hz, 2H, arom. H), 7.83-7.68 (m, 4H, arom. H), 7.41 (d, J = 8.6 Hz, 2H, arom. H), 7.15 (d, J = 6.0 Hz, 2H, arom.), 2.13 (t, J = 7.0 Hz, 4H, CH_2),1.29-0.94 (m, 24H, CH_2), 0.87 (t, J = 7.4 Hz, 6H, CH_3), 0.80-0.72 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 152.6, 139.1, 130.5, 126.2, 121.5, 121.1, 124.7, 122.3, 55.7, 40.1, 31.8, 29.9, 29.3, 29.1, 23.6, 22.6, 14.1.

Anal. Calcd for $C_{41}H_{52}N_2$: C, 85.95.; H, 9.15; N, 4.89. Found, C, 85.79; H, 9.05; N, 4.75.

3b. Y = 74 % (0.73g), mp. 75 ^{0}C, ^{1}H NMR ($CDCl_3$) δ: 8.80 (s, 2H, arom. H), 8.60 (d, J = 4.7 Hz, 2H, arom. H), 8.13 (d, J = 8.5 Hz, 2H, arom. H), 7.83-7.66 (m, 4H, arom. H), 7.41 (d, J = 8.6 Hz, 2H, arom. H), 7.15 (d, J = 6.0 Hz, 2H, arom. H), 4.13 (t, J = 7.2 Hz, 1H, CH), 1.75 (q, J = 7.4 Hz, 2H), 1.46-1.22 (m, 13H, CH_2), 0.82 (t, J = 6.9 Hz, 4H, CH_3). ^{13}C NMR, ($CDCl_3$) δ: 144.0, 129.0, 128.0, 125.0, 124.7, 124.1, 122.3, 115.4, 47.6, 32.8, 31.8, 29.7, 29.5, 29.2, 26.9, 22.7, 14.1.

For $C_{32}H_{34}N_2$ Calcd C, 86.05.; H, 7.67; N, 6.27; Found C, 86.00; H, 8.05; N, 6.12.

3c. Y= 73% (0.73g), yellow oil. ^{1}H NMR ($CDCl_3$) δ: 8.84 (s, 2H, arom. H), 8.6 (d, J = 4.5 Hz, 2H, arom.H), 8.13 (d, J = 8.5 Hz, 2H, arom. H), 7.83-7.68 (m, 4H, arom. H), 7.41 (d, J = 8.4 Hz, 2H, arom. H), 7.15 (d, J = 6.0 Hz, 2H, arom. H), 2.15-2.12 (m, 2H, CH_2), 1.29-0.99 (m, 38H, CH_2), 0.88 (t, J = 7.2 Hz, 6H, CH_3), 0.73-0.71 (m, 4H, CH_2). ^{13}C NMR, ($CDCl_3$) δ: 144.0, 129.0, 128.0, 125.0, 124.7, 124.1, 122.3, 115.4, 55.3, 40.4, 31.9, 30.0, 29.6, 29.5, 29.3, 29.2, 24.6, 23.7, 22.7, 14.1.

Anal. Calcd for $C_{47}H_{64}N_2$: C, 85.92; H, 9.82; N, 4.26. Found, C, 85.70; H, 9.75; N,4.15.

The procedure for preparation of 9-alkyl-2,7-bis(2-thiophene)fluorene (4a-4c)

Monomers were synthesized according to our previous method [6] by a coupling reaction of 9-alkyl-2,7-dibromofluorene **(2a-2c)** with 2-tributhyltin-thiophene, starting from 1g of **2a-2c**.

Selected data for **4a.** Y = 75% (0.76g), mp. 105 ^{0}C, ^{1}H NMR ($CDCl_3$) δ: 7.68 (d, J = 7.9 Hz, 2H, arom. H), 7.62-7.56 (m, 4H, arom. H), 7.38 (dd, ^4J = 3.6 Hz, ^3J = 2.5, Hz, 2H, arom. H), 7.30 (dd, ^4J = 5.1 Hz, ^3J = 0.95 Hz, 2H, arom. H), 7.11 (dd, ^4J = 5.0, ^3J = 3.60 Hz, 2H, arom. H), 2.02 (q, J = 8.2 Hz, 2H, CH_2), 1.36-1.05 (m, 26H, CH_2), 0.80 (t, J = 7.4 Hz, 6H, CH_3), 0.80-0.72 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 152.6, 139.2, 130.2, 126.9, 126.2, 121.2, 55.6, 40.2, 31.8, 29.8, 29.4, 29.2, 23.7, 22.6, 14.1.

Anal. Calcd for $C_{39}H_{50}S_2$: C, 80.35; H, 8.65. Found: C, 80.25; H, 8.56.

4b. Y = 75% (0.76g), mp. 75 ^{0}C, ^{1}H NMR ($CDCl_3$) δ: 7.39-7.36 (m, 2H, arom. H), 7.23-7.19 (m, 4H, arom. H), 7.31-7.29 (m, 2H, arom. H), 7.04 (dd, ^4J = 3.6 Hz, ^3J = 8.5 Hz, 2H, arom. H), 7.09-7.07 (m, 2H, arom. H), 4.13 (t, J = 7.2 Hz, 1H, CH), 1.75 (q, J = 7.4 Hz, 2H), 1.46-1.22 (m, 14H, CH_2), 0.82 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR, ($CDCl_3$) δ: 150.1, 139.2, 129.0, 126.9, 126.2, 121.2, 55.6, 40.2, 31.8, 29.8, 29.4, 29.2, 23.7, 22.6, 14.1.

For $C_{30}H_{32}S_2$ Calcd C, 78.90; H, 7.06. Found C, 78.74; H, 6.89.

4c. Y= 75% (0.76g), green oil. ^{1}H NMR ($CDCl_3$) δ: 7.70 (d, J = 7.3 Hz, 2H, arom. H), 7.67-7.65 (m, 4H, arom. H), 7.43 (dd, ^4J = 6.5 Hz, ^3J = 1.9 Hz, 2H, arom. H), 7.33 (d, J = 5.0 Hz, 2H, arom. H), 7.16 (d, J = 5.0 Hz, 2H, arom. H), 2.10 (d, J = 8.0 Hz, 4H, CH_2), 1.34-1.00 (m, 36H, CH_2), 0.95 (t, J = 7.4 Hz, 6H, CH_3), 0.89-0.77 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 144.0, 129.0, 128.0, 125.0, 124.7, 124.1, 122.3, 115.4, 55.3, 40.4, 31.9, 30.0, 29.6, 29.5, 29.3, 29.2, 24.6, 23.7, 22.7, 14.1.

For $C_{45}H_{62}S_2$ Calcd C,81.02; H, 9.37. Found C, 81.00; H, 9.06

The procedure for preparation of 9-alkyl-2,7-bis(2-furane)fluorene (5a-5c)

Under a nitrogen atmosphere, furane-2-boronic acid (2.68g, 24 mmol) was added to a mixture of dihalogenearene **2a-2c** (10 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.69g, 0.60 mmol, 6 mol%) in 1,2-dimethoxyethane (80 ml). A solution of sodium bicarbonate (60 ml, 1M) was added immediately and the combined mixture was cooled to room temperature, filtered and evaporated. Water, (100 ml) was added to the residue and the suspension was extracted with ether. The combined ether phases were worked up in the standard manner to give **5**.

Selected data for **5a.** Y = 73% (4.02g), green oil. ^{1}H NMR ($CDCl_3$) δ: 7.69 (d, J = 7.9 Hz, 4H, arom. H), 7.63-7.57 (m, 2H, arom. H), 7.40 (dd, ^4J = 3.6 Hz, ^3J = 0.7 Hz, 2H, arom. H), 7.30 (dd, ^4J = 5.0 Hz, ^3J = 0.7 Hz, 2H, arom. H), 7.12 (dd, ^4J = 5.0, ^3J = 3.6 Hz, 2H, arom. H), 2.03 (q, J = 8.1 Hz, 2H, CH_2), 1.27-1.06 (m, 26H, CH_2), 0.86 (t, J = 6.6 Hz, 6H, CH_3), 0.69 (s, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 152.5, 139.1, 130.2, 126.9, 126.2, 121.2, 55.5, 40.2, 31.8, 29.8, 29.4, 29.2, 23.7, 22.6, 14.1.

Anal. Calcd for $C_{39}H_{50}O_2$: C, 85.04; H, 9.15. Found: C, 84.80; H, 9.05.

5b. Y = 85% (3.61g), green oil. ^{1}H NMR ($CDCl_3$) δ: 7.39-7.36 (m, 4H, arom. H), 7.23-7.19 (m, 2H, arom. H), 7.31-7.29 (m, 2H, arom. H), 7.04 (dd, ^4J = 3.6 Hz, ^3J = 8.5 Hz, 2H, arom. H), 7.09-7.07 (m, 2H, arom. H), 4.13 (t, J = 7.2 Hz, 1H, CH), 1.75 (q, J = 7.4 Hz, 2H), 1.46-1.22 (m, 13H, CH_2), 0.82 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR, ($CDCl_3$) δ: 152.3, 129.0, 128.0, 125.0, 124.7, 124.1, 122.3, 121.4, 55.1, 40.6, 31.8, 29.7, 29.5, 29.2, 26.9, 22.7, 14.1.

For $C_{30}H_{32}O_2$ Calcd C, 86.87; H, 7.60. Found C, 71.34; H, 6.50; N, 3.02

5c. Y= 82% (5.21g), green oil. ^{1}H NMR ($CDCl_3$) δ: 7.68 (d, J = 7.3 Hz, 2H, arom. H), 7.63-7.57 (m, 4H, arom. H), 7.40 (dd, ^4J = 2.0 Hz, ^3J = 6.6 Hz, 2H, arom.H), 7.31 (d, J = 5.1 Hz, 2H, arom. H), 7.12 (d, J = 5.0 Hz, 2H, arom. H), 2.05 (d, J = 8.0 Hz, 4H, CH_2), 1.27-1.06 (m, 36H, CH_2), 0.86 (t, J = 7.4 Hz, 6H, CH_3), 0.80-0.69 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 151.7, 145.2, 140.0, 128.0, 125.0, 124.7, 122.3, 115.4, 55.2, 40.4, 29.6, 29.5, 29.3, 29.2, 28.7, 26.9, 24.6, 23.5, 22.7, 14.1.

Anal. Calcd for $C_{45}H_{62}O_2$: C, 85.12; H, 9.84. Found, C, 85.01; H, 9.75.

The procedure for preparation of *9*-alkyl-2,7-bis(2-(3,4-ethylenedioxythiophene))fluorene (6a-6b)

Compound **2a-2b (**1.0 g**,** 2 mmol) 2-trimethyltin-3,4-ethylenedioxythiophene and Pd(PPh_3)$_4$ (0.29g, 0.4 mmol) were added to DMF (100 ml); the mixture was stirred at 90 ºC overnight. The DMF was evaporated, residue was purified by column chromatography (eluent hexane/chloroform 3:1) to give the product as a brown oil **(6a-6b),** 6a 0.93 g (75%).

Selected date for **6a.** Y = 81% (1.13g), brown-green oil. ^{1}H NMR ($CDCl_3$) δ: 8.02 (d, *J* = 2.2 Hz, 2H, arom. H), 7.46 (dd, ^4J = 8.7 Hz, ^3J = 1.9 Hz, 2H, arom. H), 7.18 (d, *J* = 8.7 Hz, 2H, arom. H), 6.26 (s, 2H, arom. H), 4.12-1.10 (m, 8H, O-CH_2-CH_2-O), 1.72 (q, *J* = 7.4 Hz, 2H, CH_2), 1.27 (s, *J* = 7.5 Hz, 2H, CH_2), 1.24-1.16 (m, 24H, CH_2), 0.87 (t, *J* = 7.3 Hz, 6H, CH_3), 0.80-0.74 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 152.6, 141.8, 139.1, 130.2, 126.2, 121.2, 99.7, 64.7, 55.7, 40.2, 31.9, 29.9, 29.5, 29.2, 23.7, 22.7, 14.1.

Anal. Calcd for $C_{43}H_{54}S_2O_4$: C, 73.88; H, 7.79. Found, C, 73.65; H, 9.65.

6b. Y= 75% (0.85g) brown oil, ^{1}H NMR ($CDCl_3$) δ: 8.02 (d, *J* = 2.2 Hz, 2H, arom. H), 7.46 (dd, ^4J = 8.7 Hz, ^3J = 1.9 Hz, 2H, arom. H), 7.18 (d, *J* = 8.7 Hz, 2H, arom. H), 6.26 (s, 2H, arom. H), 4.12-1.10 (m, 9H, O-CH_2-CH_2-O, CH), 1.74-1.60 (m, 2H, CH_2), 1.24-1.16 (m, 14H, CH_2), 0.87 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 152.6, 141.8, 139.1, 130.2, 126.2, 121.2, 99.7, 64.7, 55.7, 40.2, 31.9, 29.9, 29.5, 29.2, 22.7, 14.1.

Anal. Calcd for $C_{36}H_{40}S_2O_4$: C, 76.01; H, 7.09. Found, C, 75.95; H, 6.95.

Oxidative polymerization

Electrolyte solution was prepared by dissolving tetrabutylammonium tetrafluoroborate Bu_4NBF_4 (Janssen Chimica, 99 %) in acetonitrile (CH_3CN for DNA synthesis and peptides) and dichloromethane (CH_2Cl_2 for spectroscopy, stab. amylene, POCh, Gliwice, Poland) 1:1 vol. mixture. The measurements were carried out at room temperature. Concentration of the compound was 1 mM and the measurements were done in three – electrode cell, using 2 mL sample solution. CV of electrodeposited film was taken in monomer–free solutions of the same supporting electrolyte as used for polymerization.

Electrosynthesis and studies of polymer films were performed on Ecochemie AUTOLAB potentiostat – galvanostat model PGSTAT20. Results were analyzed using GPES program (*General Purpose Electrochemical System*). Cyclic voltammetry (CV) was used for electrochemical measurements. Polymer film was synthesized directly on the Pt electrode, which was used as a working electrode. Ag/Ag+ wire served as a pseudoreference electrode and platinum spiral was employed as an auxiliary electrode.

References

1. Hughes, G.; Wang, Ch.; Batsanow, A. S.; Fern, M.; Frank, S.; Bryce, M. R.; Perepichka, I. F.; Monkmen, P.; Lyons, B. P. *Org. Biomol. Chem.* **2003**, *1*, 3069.

2. Dong, J. H.; Meng, W. D.; d Qing, F. L. *Arkivoc* **2004**, *(ix)*, 9.
3. Hirano, C.; Imae, T.; Fujima, S.; Yanagimoto, Y.; Takaguchi, Y. *Langmuir* **2005**, *21*, 272.
4. Robles-Martinez, J. G.; Salmeron-Valverde, A.; Zehe, A. *Cryst. Res. Technol*. **2003**, *38*, 94.
5. Cabaj, J.; Sołoducho, J.; Nowakowska, A.; Chyla, A. *Electroanalysis Journal* **2006**, *18*, 801.
6. (a) Asawapirom, U.; Gunther, R.; Forster, M.; Farrell, T.; Scherf, U. *Synthesis* **2002,** *9,* 1136. (b) Cabaj, J.; Idzik, K.; Sołoducho, J. *Tetrahedron* **2006**, *62*, 758.
7. (a) Anemian, R.; Mulatier, J-C.; Andraud, C.; Stephan, O.; Vial, J-C. *Chem. Comm.* **2002**, 1608. (b) Jin, Y.; Ju, J.; Kim, J.; Lee, S.; Kim, J. Y.; Park, S. H.; Son, S.; Lee, K.; Suh, H. *Macromolecules* **2003**, *36,* 6970.
8. Silcoff, E. R.; Asadi, A. I.; Sheradsky, T. *J. Polymer Chem.* **2001**, *39*, 872.
9. Sonntag, M.; Kreger, K.; Hanft, D.; Strohrielgl, P. *Chem. Mat.* **2005,** *17,* 3031.
10. Sapp, A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.***1998***, 10*, 2101.
11. Sołoducho, J.; Chyla, A. *Bull. Pol. Pat*. **2004**, *6,* 48.
12. Mongin, O.; Porres, L.; Katan, C.; Pons, T.; Mertz, J.; Blanchard-Desce, M. *Tetrahedron Lett.* **2003**, *44*, 8121.
13. Yang, N. C.; Lee, S. M.; Yoo, Y.; M., Kim, J. K.; Suh, D. H. *J. Polym. Sci.: Part A: Polym. Chem.* **2004,** *42,* 1058.