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Bipolar properties of polythiophene derivatives with 1,3,5-triazine units

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ABSTRACT

Bipolar properties of model polythiophene derivatives with 1,3,5-triazine units are investigated. The conjugation length is controlled by the meta substitution. In situ spectroelectrochemical UV–Vis–NIR and ESR measurement recorded during electrochemical reduction and oxidation are presented. Spectroelectrochemistry recorded during reduction of polymers in the solid state is especially interesting. Most literature data of spectroelectrochemistry of solid state polymers has been obtained during oxidation which is due to poor stability of radical anions in reduced polymers. Cathodic reduction leads to the formation of stable radical anions in a certain potential range. Exceeding this range leads to overreduction. A similar effect is observed during electrooxidation. Obtained results indicate that not only oligomers with 1,3,5-triazine units but also respective polymers are worth considering during studies on new bipolar polymer materials to broad range of optoelectronic and photovoltaic applications.

1. Introduction

Organic π-conjugated materials are an issue of interest in numerous studies owing to their inherent optoelectronic properties and their potential applications such as organic light-emitting diodes (OLEDs) [1,2], light-emitting electrochemical cells (LECs) [3], photovoltaic cells [4–6], organic thin film transistors (OFETs) [7,8] and sensors [9]. Two types of organic semiconductor can be distinguished low and high molecular weight. Depending on application both types of materials have certain advantages [10].

Increasing popularity of compounds with donor and acceptor groups in one molecule as a promising materials for optoelectronic and photovoltaic applications is observed [11]. For example in bulk heterojunction organic solar cells the donor–acceptor configuration considerably improves photoinduced charge separation in the excited state [12]. In order to improve electron transport properties, this type of materials is used in OLEDs [13] and OFETs [6]. The most popular electron-accepting units are s-tetraazines [14], 1,3,5-triazines [15,16], naphthaleneimides [17], perylenediimides [18,19] and benzothiadiazoles [20,21].

1,3,5-Triazine is a strong electron-accepting unit with good thermal stability and luminescence properties [22,23]. Radical anion can be effectively stabilized at this moiety and hence reversible reduction of this type of materials is observed [24]. It was found that triazine derivatives exhibit high electron affinities and reach LUMO values in the range of −2.7 to −3.1 eV [25]. 1,3,5-Triazine is an important unit in low [26–28] and high molecular weight donor–acceptor conjugated molecules. The use of central 1,3,5-triazine core leads to the molecule with star-shaped architecture and C3-symmetry [29,30]. Molecules of this type were also tested as π-conjugated columnar liquid crystals with bipolar charge carrier transport [31,32].

Basic electrochemical properties of different star-shaped 1,3,5-triazines with thiophene derivative arms are described and show that electrochemical oxidation leads to the formation of a conjugated polymer [33]. The electrooxidation of star shaped monomers leads to the hyperbranched polymer with great electrochemical deviation from the linear analogues [34]. It was found that the combination of electron-rich thienyl group and the triazine-based system through the π-system can be an efficient strategy to design new materials with strengthened third-order nonlinear optical

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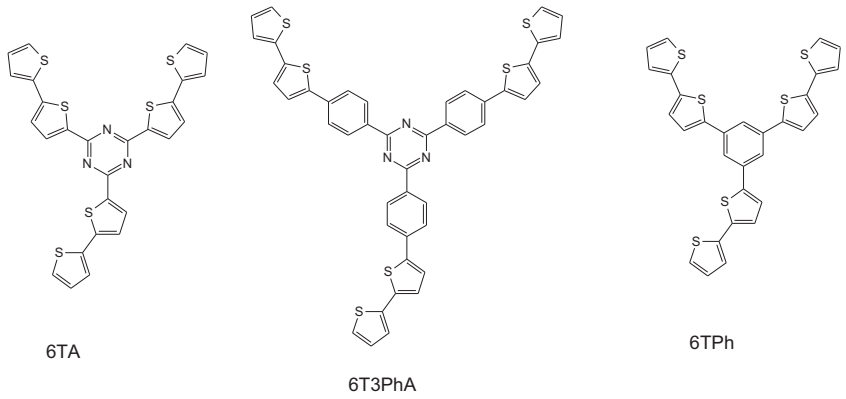

Fig. 1. Monomer structures.

properties [35]. The 1,3,5-triazine unit has also been incorporated into the polymer backbone in order to improve n-transport in OLEDs [36].

The objective of this study is to clarify the n- and p-doping processes taking place in conjugated polymers based on polythiophenes as well as to elucidate the role of 1,3,5-triazine units. Such donor–acceptor systems gain attention, however mainly as low molecular weight oligomers. The spectroelectrochemical properties of this type of conjugated polymers in the solid state have not been investigated in details so far. In this paper we characterize two polythiophene derivatives with 1,3,5-triazine core by electrochemical and spectroelectrochemical techniques. Moreover, we compare the electrochemistry of these polymers with benzene analogue.

2. Experimental

2.1. Materials

The synthesis, structures and basic properties of monomers have been characterized in one of our previous papers [37]. They are triazines: 2,4,6-tris(2,2′-bithiophen-5-yl)-1,3,5-triazine (6TA), 2,4,6-tris[p-(2,2′-bithiophen-5-yl)-phenyl]-1,3,5-triazine (6TtPhA) and benzene analogue 1,3,5-tris(2,2′-bithiophen-5-yl)-benzene (6TPh). Structures are shown in Fig. 1.

2.2. Measurements

Electrosynthesis and studies on polymer films were performed on CH Instrument Electrochemical Analyzer model 600. Measurement was carried out in dichloromethane (CH_2Cl_2; Sigma Aldrich ≥99.9%) or acetonitrile (CH_3CN; Sigma Aldrich ≥99.8%) containing 0.1 M tetrabutylammonium hexafluorophospate (Bu_4NPF_6; Sigma Aldrich 98%) as a supporting electrolyte. The target polymer films were synthesized on the platinum wire or indium–tin-oxide (ITO) coated quartz electrode at a scan rate of 50 mV/s. An Ag pseudo-reference electrode was used and its exact potential was calibrated versus ferrocene/ferrocinium redox couple. Platinum wire served as a counter electrode. Appropriate vessels adapted for electrochemical cells were used. Spectral measurements were carried out using UV–vis Hewlett Packard spectrophotometer 8453 as well as JEOL JES-FA 200, X-band CW-EPR spectrometer, operating at 100 kHz field modulation. Concentration of paramagnetic species was estimated by double integration of the first-derivative ESR spectra. All electrochemical and spectroelectrochemical experiments were carried out in deaerated solutions and an additional argon cushion was maintained above the solutions.

3. Results and discussion

3.1. Electrochemical properties

All investigated polymers were obtained by cyclic voltammetry. To elucidate the role of 1,3,5-triazine unit in the polymer backbone, electrochemical properties of this type of polymer were compared with its benzene analogue.

All monomers polymerize at potentials related to the first oxidation peak. Fig. 2 presents the voltammogram recorded during electropolymerization of 6T3PhA. The first oxidation peak is located at approximately 0.65 V. In second scan at lower potentials a new peak appears, which increases with every subsequent scan. This indicates the formation of a conductive film on the electrode surface and the formation of products with higher conjugation, probably conjugated polymers. Similar results were obtained for electropolymerization of 6TA and 6TPh.

Electrochemical properties of the studied polymers were investigated by cyclic voltammetry in a monomer free electrolyte solution. Measurements were made in broad range, in order to register reduction and oxidation peaks (Fig. 3). The value of onset oxidation potential is only slightly different from approximately 0.17 V for poly(6TPh) to approximately 0.26 V for 1,3,5-triazine derivatives. This is related to the oxidation of quaterthiophene segments.

Larger differences are observed in the case of cathodic curves. The first reduction peak of poly(6TA) is located at approximately −1.5 V and the second at −1.95 V. After changing the potential sweep direction only one oxidation peak at −1.74 V is observed.

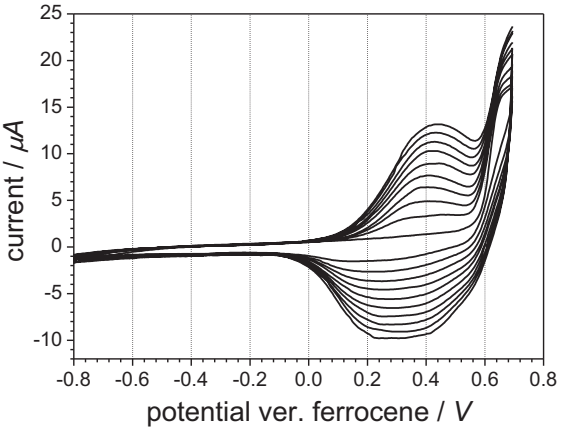

Fig. 2. Cyclic voltammetry of 6T3PhA; potential sweep rate 50 mV/s; 1 mM monomer solution in 0.1 M Bu_4NPF_6 in CH_2Cl_2.