



Doping behaviour of electrochemically generated model bithiophene meta-substituted star shaped oligomer



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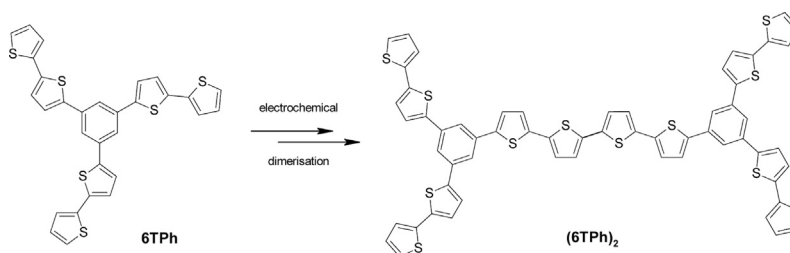
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HIGHLIGHTS

- Tris(bithiophene) meta-substituted benzene dimerises upon electrooxidation.
- The insoluble dimer features well developed electrochromic properties.
- Unreacted bithiophene groups activate during dimer doping.
- Reactivity of bithiophene groups narrows down the dimer's stable doping range.
- The paradox of concurrent dimer formation and overoxidation is disclosed.

GRAPHICAL ABSTRACT



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ABSTRACT

The redox processes accompanying electrochemical oxidation of 1,3,5-tris(bithiophene)benzene (6TPH) and its products have been investigated using a suite of spectroelectrochemical tools. Investigated tri-functional molecule, featuring reactive bithiophene units can be considered a model of numerous star shaped compounds – the building blocks of dense π -conjugated polymer networks. Accounting for conjugation disruption between the meta-arranged bithiophene groups, it is found that electrochromic films generated upon 6TPH electrooxidation comprise primarily dimers (6TPH)₂, whose α,ω -diphenylquaterthiophene units are the principal redox doping active species. Upon reaching a certain, electrochemically inconspicuous oxidation threshold, profound changes take place in the oligomer film, incurring irreversible changes to its electroactive properties, previously observed for these systems. An attempt is made to examine the nature of these changes and the impact they have on the doping behaviour of this intriguing π -conjugated system.

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1. Introduction

In recent years, organic π -conjugated materials have been an issue of interest in numerous studies. The photophysical properties of π -conjugated molecules depend on their structure. Numerous

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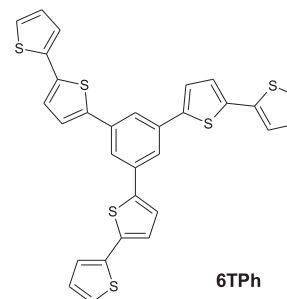
experiments, aimed at improving properties of such systems by modifications of their structure, have been conducted. One of the design concepts involves well-defined, branched or star-shaped macromolecular architectures, featuring properties distinct from their linear analogues [1,2]. A particularly large group of three-dimensional compounds with thiophene segments stands out among the different chemical moieties of this type due to their reported high hole mobility, broad absorption and good stability [3]. Owing to self-contained and, hence, relatively compact structure, their photophysical and electrical properties can be controlled effectively [4]. This makes them promising materials for applications in a broad range of organic optoelectronic applications such as light-emitting devices (LED), photovoltaics, field-effect transistors [5] and nonlinear optics [6]. These molecules were utilised in organic field-effect transistor [7–10], bulk heterojunction solar cell [11–14] and electrochromic [15] devices. Moreover, further application of these organic materials is prospected, on account of their other, interesting properties: solvatochromism [16], two-photon absorption [17], third-order nonlinear susceptibility [18], liquid-crystalline hole and electron charge transport [19], or water dispersibility with negligible self-aggregation [20]. The combination of different cores with thiophene arms can lead to unusual properties of electrogenerated polymers. For example, hydroxyl groups incorporated to benzene core enable coupling between selected, meta-positioned aryl arms [21], 1,3,5-triazine core yields donor-acceptor materials [22,23], triphenylamine endows the polymer with different colours, good switching times, contrast, and redox stability [24,25].

Previous papers focussing on oligothiophenes having star-shape architecture, reveal the ability of these compounds to undergo electropolymerisation giving electroactive polymer films [21,22]. Studies of electrochemical polymerisation process of 3,4-ethylenedioxythiophene derivatives reveal formation of stable, doubly charged σ -dimers [26]. Well defined, hyperbranched oligomers based on 1,3,5-benzene nodes, have been found to exhibit redox behaviour comprising at least two reasonably reversible redox couples, ascribed to the formation of radical cations and dications [27]. Furthermore, the conjugation arrangement afforded by the truxene structural unit has been shown to impart well-defined conjugation control between the oligothiophene arms of varying length [28]. Theoretical calculations led to identification of the geometries and frontier orbital spatial distributions [29], while time-dependent computations enabled simulation of the spectra of these compounds in their electroneutral and charged states [30]. One of the drawbacks of these star systems is their progressive loss of electroactivity over successive potential cycling. This phenomenon has not yet been the subject of study.

For perspective optoelectronic applications, elucidation of doping processes alongside material properties is crucial [31]. Upon doping, different charge carriers are envisaged, such as spin-bearing polarons and spinless bipolarons. The performance of a functional material is strongly dependent on which of these are the prevalent carriers. Redox charging, beside doping, can be also accompanied by irreversible side reactions such as formation of defects which degrade the redox performance of the electroactive material. Owing to their favourable oxidation potential, bithiophene moieties are being extensively employed nowadays in reactive precursor star systems, which, upon oxidative coupling, yield higher molecular weight conjugated structures. In this paper, we report upon the electrooxidation pathway of a model precursor system and the effects of electrochemical doping of its insoluble products. The electrochemical, optical and paramagnetic properties reveal the oligomeric nature of the electrooxidation product, whose oxidation involves a combination of doping and follow-up processes taking place in an apparently stable potential window. These

effects, perceived as a simple change of electrochemical properties, have often been observed for this class of systems. Heretofore, they have received little attention, much to the detriment of reliable determination of stable doping performance of this class of conjugated systems. It is our intent to investigate these issues in more detail, aiming to correlate the electrochemical oxidation process parameters of the selected model monomer molecule with the properties and doping behaviour of its electroactive films, obtained by this seemingly facile synthetic method.

2. Experimental



1,3,5-tris(2,2'-bithien-5-yl)benzene (6TPh), whose chemical structure is shown above, was synthesised in our group by Stille cross-coupling reaction, details of which are given in Ref. [32]. The synthetic procedure employed was a modification of the one reported by Cornacchio et al. [33]. Cyclic voltammetry was performed on a CH Instruments 620 potentiostat in a classic three-electrode cell with platinum wire working and counter electrodes and a silver quasi-reference electrode calibrated versus ferrocene/ferrocinium redox couple, relative to which all potentials in this work are cited. Using appropriate vessels adapted for electrochemical cells, spectroelectrochemical measurements were carried out on Hewlett Packard model 8453 UV–Vis spectrophotometer, JEOL JES-FA 200, X-band CW-EPR spectrometer and a Renishaw InVia Raman microscope equipped with an 830 nm laser. All electrochemical experiments were carried out in deaerated 0.1 M Bu_4NBF_4 (Aldrich) in 99.8% pure dichloromethane (POCh, Poland) solutions under an argon flow blanket.

3. Results

Upon application of an anodic potential, 6TPh exhibits a single, irreversible oxidation peak at 0.69 V in the first voltammetric cycle (Fig. 1). Upon successive potential cycling, a new redox system develops between 0.2 V and 0.6 V, accompanied by steady accumulation of a conductive electrodeposit at the electrode surface. The onset of its oxidation signal is located around 0.1 V and remains constant, irrespective of layer thickness, while its peak potential, obscured by an overlap with the monomer oxidation wave, clearly moves to higher potential values. At the same time, the monomer oxidation peak appears to shift to higher potentials, though not as pronouncedly as the oxidation peak of the deposit. Concurrently with its redox reactions, the deposit's electrochromism manifests itself in the form of a single switch from orange, in the reduced state, to deep green, in the oxidised state. This switch is reversible with the orange colour being restored at the cathodic potential boundary of the voltammetric measurement.

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