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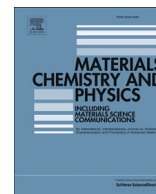
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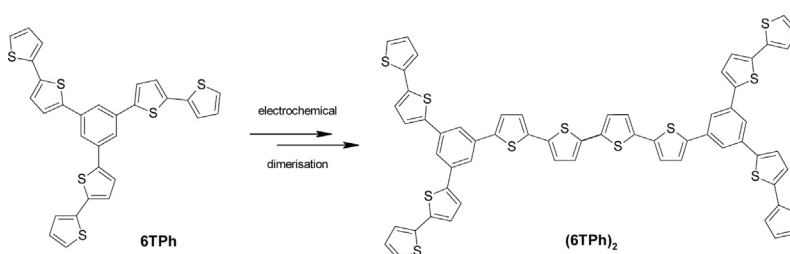
## Doping behaviour of electrochemically generated model bithiophene meta-substituted star shaped oligomer

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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  $\pi$ -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)<sub>2</sub>, whose  $\alpha,\omega$ -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  $\pi$ -conjugated system.

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## 1. Introduction

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

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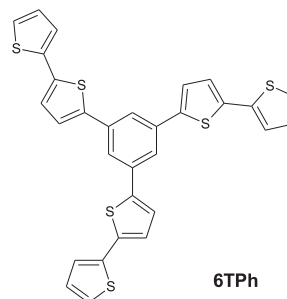
experiments, aimed at improving properties of such systems by modifications of their structure, have been conducted. One of the design concepts involves well-defined, branched or star-shaped macromolecular architectures, featuring properties distinct from their linear analogues [1,2]. A particularly 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  $\sigma$ -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.

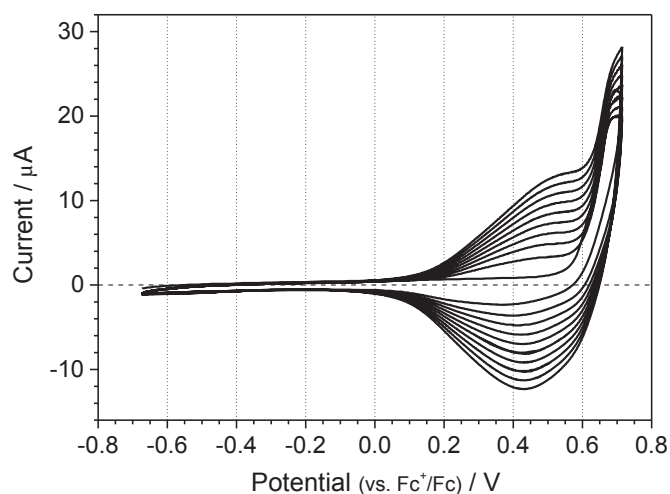
## 2. Experimental



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/ferrocenium 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<sub>4</sub>NBF<sub>4</sub> (Aldrich) in 99.8% pure dichloromethane (POCh, Poland) solutions under an argon flow blanket.

## 3. Results

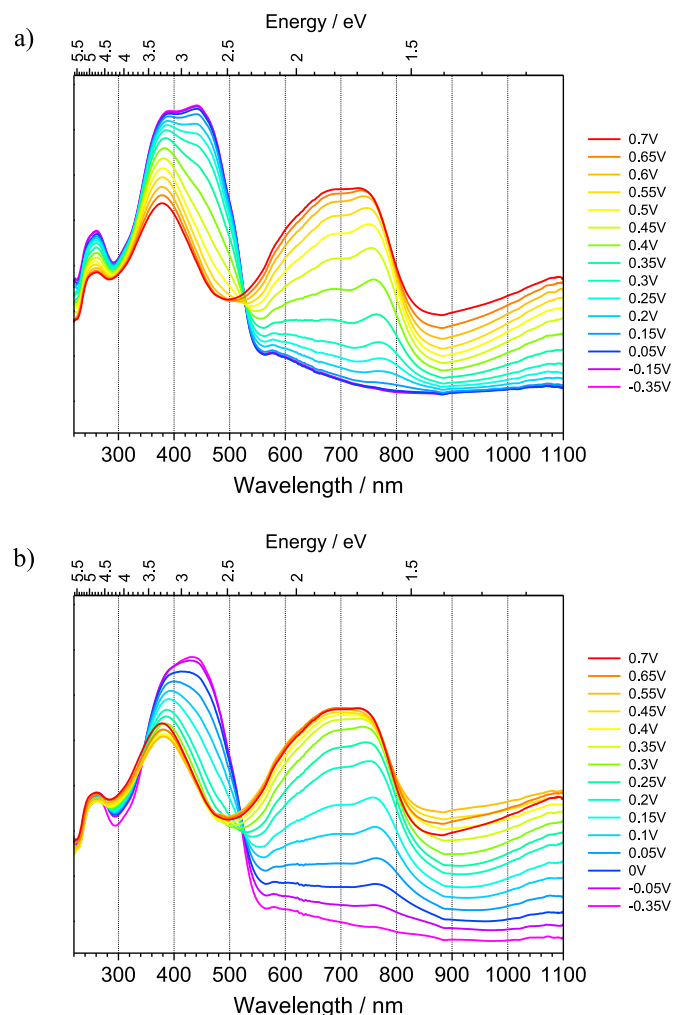
Upon application of an anodic potential, 6TPh exhibits a single, irreversible oxidation peak at 0.69 V in the first voltammetric cycle (Fig. 1). Upon successive potential cycling, a new redox system develops between 0.2 V and 0.6 V, accompanied by steady accumulation of a conductive electrodeposit at 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.



**Fig. 1.** Cyclic voltammogram of 0.3 mM 6TPh in 0.1 M solution of  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$ , at  $0.1 \text{ V s}^{-1}$ , showing steady accumulation of conducting film layer at the platinum electrode, upon repetitive electrooxidation of 6TPh.

UV–Vis–NIR absorption spectrum of the film at negative potentials, comprises two dominant, ill-resolved peaks at 380 nm and 440 nm (Fig. 2 – magenta (in the web version) line), the latter one permitting estimation of the spectroscopic band gap at 2.30 eV. This result is comparable to other polythiophenes (2.2–1.9 eV) [34]. Upon stepping the potential up, the lower energy component peak abates, concomitantly with incrementing absorption bands between 560–800 nm and 900–1100 nm. Attenuation of the peak at 300 nm together with its satellite at 260 nm takes place as well, though it appears that this decrease comes about only as a consequence of the decrease of the peak at 440 nm whose high energy tail overlaps with the former two. Only at highest potentials, these two bands appear to diminish, independently of waning absorbance changes at 440 nm. At the lower energy side of the spectrum, above 0.2 V, a concerted growth of the absorption bands between 560–800 nm and 900–1100 nm takes place, reminiscent of radical cation (polaron) transitions, until 0.65 V when the absorption rise at ca. 870 nm discloses a new component signal. Absorption in this region continues to grow even at first potential steps of the reduction half-cycle. Further decrease of potential reverses the spectral transformations observed upon oxidation, however the peak at 330 nm does not recover to its exact initial intensity in the pristine film.

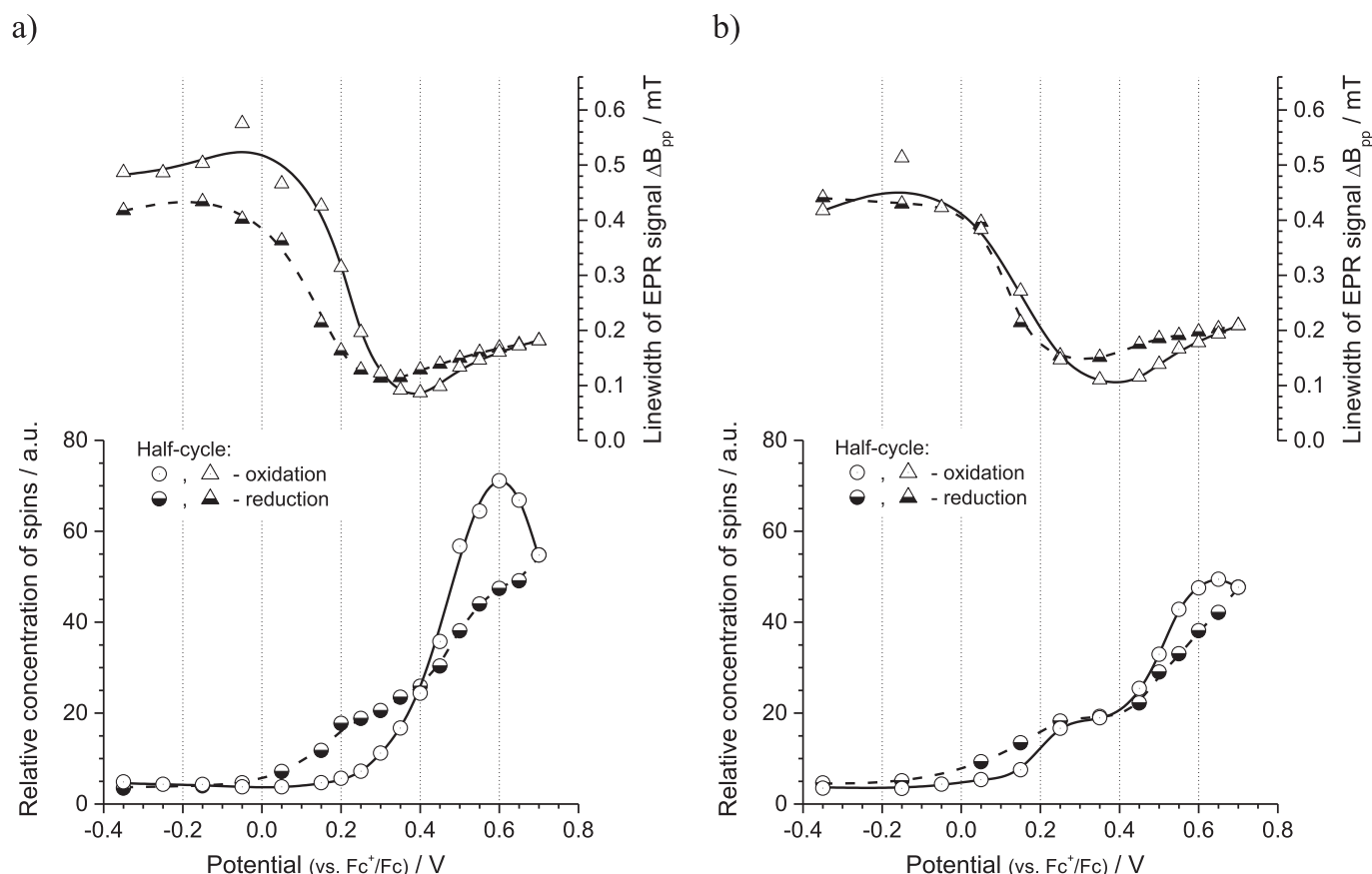
*In situ* EPR spectroelectrochemical studies show that at the oxidation onset, the concentration of paramagnetic species increases in the film, accompanied by a steep decrease of the EPR spectral linewidth (Fig. 3). The observed EPR spectrum is tall, isotropic and featureless, indicating fine delocalisation of the unpaired electron across the conjugated backbone. Between 0.6 V and 0.7 V peak concentration is attained, followed by a clear drop that coincides with growth termination of the 560–800 nm and 900–1100 nm UV–Vis–NIR bands. A minor increase of the EPR signal linewidth accompanies the above. The g-factor of the EPR line is almost potential invariant, spanning the range of 2.0027–28, thus indicating that the chemical environment of spins changes little with varying doping level. Upon dedoping, the spin concentration does not recover to its peak value recorded several potential steps earlier. Continuously decremending, in the range of 0.35 V–0.05 V, it surpasses the concentration observed in the oxidation half-cycle, however. This spin concentration profile endures almost unchanged in the subsequent, second oxidation half cycle as shown in Fig. 3b, with the EPR signal linewidth potential dependence



**Fig. 2.** UV–Vis–NIR spectra of films of oligo(6TPh) in 0.1 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$ , recorded *in situ* at progressively, a) incremented, and b) subsequently decremented potentials applied to the film.

following suit. Upon second time reduction of the film, the spin concentration and EPR signal linewidth become even less potential sensitive indicating that irreversible changes have taken place in the deposit.

Using *in situ* Raman spectroelectrochemistry, an attempt at describing doping-induced carbon backbone changes of 6TPh film was made. In the reduced state, at potentials between 0 V and 0.2 V, except for the solvent signal at  $922 \text{ cm}^{-1}$ , low intensity signals from stretching vibrations of the thiophene aromatic ring were observed (Fig. 4a). Upon electrooxidation, signal intensities increase markedly, in connection with the resonance effect taking place [35]. Between 0.2 V and 0.6 V, the spectrum is dominated by bands typical to oligo or polythiophene systems [36] with only two potential insensitive signatures of the 1,3,5 symmetrically substituted benzene at  $993 \text{ cm}^{-1}$  and  $1587 \text{ cm}^{-1}$  [37]. Deconvolution of the Raman signal in the  $1300\text{--}1600 \text{ cm}^{-1}$  range reveals the presence of no less than seven components. Up to 0.6 V, mixed benzoid and quinoid  $\text{C}=\text{C}$  thiophene bands intensify, almost unchanged in position, with a steady growth of “defect” (oxidised) to “normal” (unoxidised) mode bands ( $1415/1449 \text{ cm}^{-1}$  and  $1495/1465 \text{ cm}^{-1}$ ) ratio. At 0.7 V and above, the defect bands shoot up well above the normal bands, accompanied by a significant increase of the fluorescence background. Upon dedoping, this band pattern is preserved. The ratio of bands between  $1495 \text{ cm}^{-1}$  and  $1415 \text{ cm}^{-1}$



**Fig. 3.** Relative concentration of paramagnetic centres and  $\Delta B_{pp}$  linewidth of first derivative EPR signal of oligo(6TPh) film as a function of applied potential during stepwise oxidation and reduction half-cycles in: a) first doping–dedoping cycle, b) second doping–dedoping cycle.

changes with decrementing potential together with the overall Raman signal intensity, until  $-0.2$  V, when the system returns to its dedoped state, albeit with persistently elevated background.

#### 4. Discussion

Obtained results present an interesting picture of the investigated model star-shaped conjugated system. The first curious observation concerns the electrochemical oxidation potential of 6TPh, which falls closer to terthiophene [38] rather than to bithiophene [39] one. This suggests conjugation of the bithiophene and benzene units [33,40] and delocalisation of the resultant radical cation over them [38]. Electron Paramagnetic Resonance studies of chemically generated  $\alpha,\omega$ -bis(phenyl) bithiophene radical cation directly confirm such delocalisation of uncompensated spin over the whole molecule [41]. Similar observations have been also made based on fluorescence spectra of analogous star shaped systems [42]. This is accountable, as the torsion angle between benzene and the adjacent thiophene ring is found to range from  $14^\circ$  to  $26^\circ$  in the solid state [33]. Theoretical gas-phase calculations, which would be expected to better model the solvated molecule, also return torsion angles between  $15^\circ$  and  $39^\circ$ , giving optimum molecule geometries featuring two of the bithiophene arms reasonably well aligned with the benzene ring [29,32]. Benzene–thiophene conjugation appears impaired, however, which can explain the intermediate oxidation potential value of 6TPh. With *meta*-arrangement of bithienyl arms precluding delocalisation of positive charge between them, the radical cation can be expected to stay confined to one phenyl-

bithiophene arm only [43]. On account of its conjugation length, the reactivity of this radical is intermediate between that of bithiophene and terthiophene. Upon inception, it engages in a follow up dimerisation reaction with a neighbouring counterpart radical cation molecule, yielding a doubly positively charged 6TPh  $\sigma$ -dimer [26]. With charge delocalised over the bithiophene and benzene rings, the oxidation potentials of the other four arms will be elevated, since a second positive charge would need to delocalise on an already positively charged benzene ring. For the same reason, the third arm should oxidise at even higher potential than the second arm, effectively grading the development of a reticulated polymer structure with respect of the maximum potential applied upon electrooxidation of 6TPh. Reversing the potential sweep right after 6TPh oxidation peak, reduction of the  $\sigma$ -dimer in the cathodic half-cycle takes place, bringing about its deprotonation [26] with subsequent rearomatisation of the two thiophene groups, thus yielding 6TPh dimer. Higher oligomer structures can form in small yield, accounting for the thermodynamic distribution of oxidation potentials of remaining bithiophene arms. Owing to its molecular weight, the oligomers precipitate out of the electrolyte solution [26] in the form of a deposit observed at the electrode surface.

In the second voltammetric cycle, the dimer – (6TPh)<sub>2</sub> molecule undergoes oxidation at the broad oxidation peak between  $0.1$  V and  $0.6$  V, as expected from previous literature reports [44]. Delocalisation of the resultant radical cation along the most extensively conjugated  $\alpha,\omega$ -bisphenylquaterthiophene unit makes the benzene rings positively charged, once again. This elevates the oxidation potentials of the other four bithiophene arms, though less

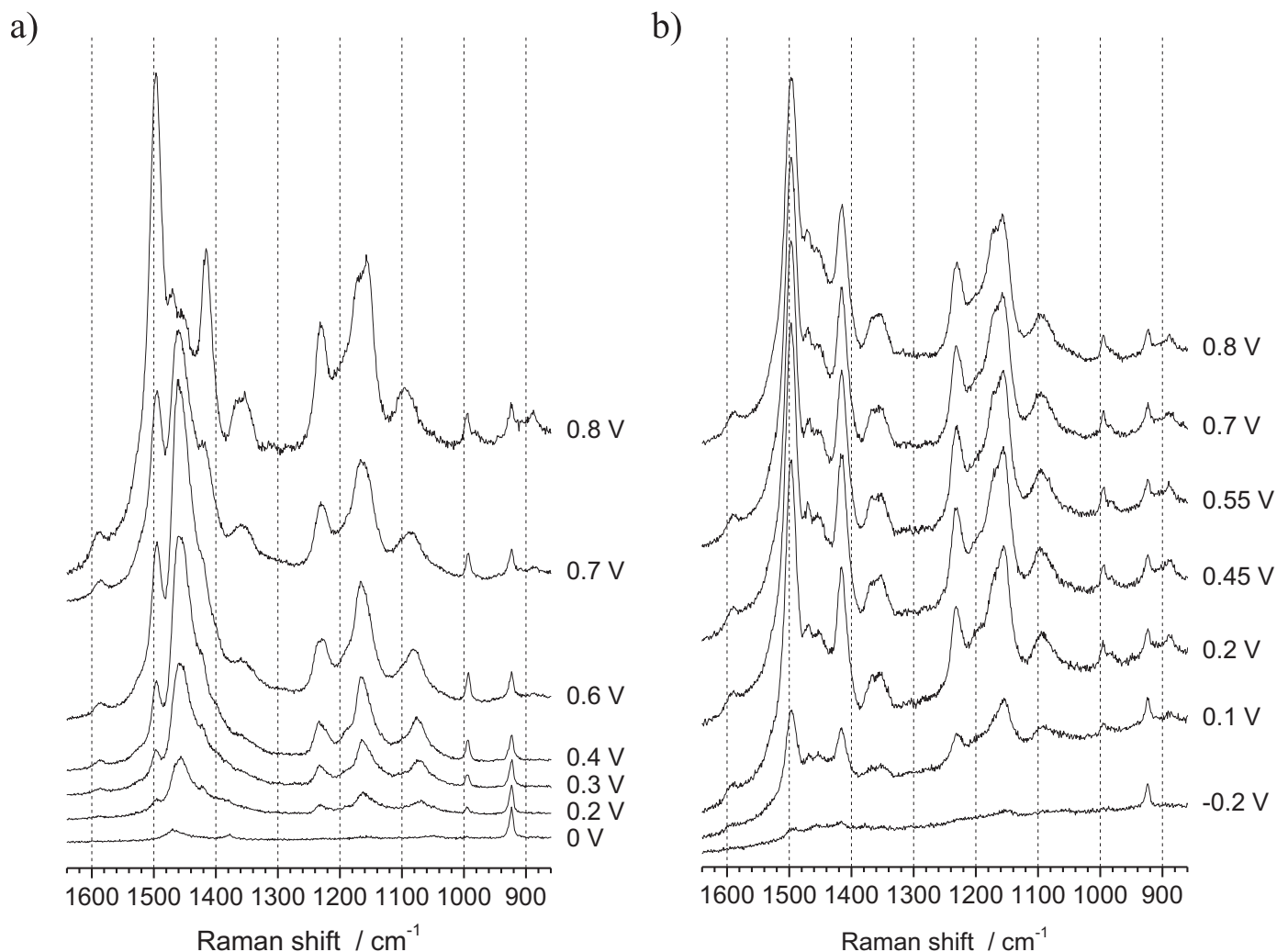


adversely compared to the conjugation broken 6TPh  $\sigma$ -dimer. Reactivity of (6TPh)<sub>2</sub> in the solid state is much weaker, effectively thwarting its further reactions with freshly generated 6TPh radical cations in solution, thus hindering the development of reticulated polymer structure. In the cathodic half-cycle, reduction of oxidised (6TPh)<sub>2</sub> overlaps the 6TPh  $\sigma$ -dimer reduction potential range, broadening the observed voltammetric reduction peak. The current build-up observed in subsequent cycles indicates that the oxidised (6TPh)<sub>2</sub> deposit is conductive. Acting as a surrogate electrode surface, it supports recurrence of monomer oxidation and  $\sigma$ -dimer reduction reactions in each subsequent voltammetric cycle, resulting in unobstructed accumulation of the (6TPh)<sub>2</sub> deposit. The observed, gradual increase in the oxidation potentials of 6TPh and (6TPh)<sub>2</sub> can be attributed to mounting resistivity of this growing film. Despite its oligomeric nature, the subsequent spectroelectrochemical results show that (6TPh)<sub>2</sub> is conjugated extensively enough, to account for the observed electroactive behaviour of the obtained electrode deposit.

Starting from the negative potential limit, oxidation of (6TPh)<sub>2</sub> commences at about 0.15 V with concurrent evolution of the visible and near infrared bands and a rise in spin concentration. All spectral signatures point to uninterrupted generation of radical cations taking place at the  $\alpha,\omega$ -bisphenylquaterthiophene unit. The UV–Vis band of the neutral (undoped) (6TPh)<sub>2</sub> at 440 nm [45] diminishes

concomitantly with the growth of high energy (600–800 nm) and low energy (ca. 1100 nm) radical cation bands. The Raman spectra intensify following a known oligothiophene pattern; the spin concentration goes up, whereas the EPR signal linewidth decreases, reflecting intensified relaxation processes in a growing spin population in a solid state film. First signs of departure from this trend can be traced from ca. 0.5 V. Spin concentration growth wanes, EPR signal linewidth broadens noticeably and NIR absorption at 880 nm rises independently of stabilising neighbouring bands, all of which could be ascribed to the commencement of the second oxidation step of the  $\alpha,\omega$ -bisphenylquaterthiophene fragment to spinless dication.

At 0.6 V a turning point comes about, indiscernible on the oligomer CV, when the concentration of spins declines steeply and the Raman spectrum undergoes profound transformation. We consider this to be the outcome of the oxidation onset of (6TPh)<sub>2</sub> unreacted bithiophene units, whose reactive radical cations engage in solid state follow-up reactions. One could be the self-coupling to  $\alpha,\omega$ -bisphenylquaterthiophene units, cross linking the (6TPh)<sub>2</sub> oligomers into a rigidified network. This not only augments the number of quaterthiophene segments but also makes the conjugated segments fixed relative to one another, preserving the doped state intermolecular architecture. This would explain the positive spin concentration hysteresis



**Fig. 4.** The Raman spectra of oligo(6TPh) film at Pt electrode in 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> recorded *in situ* at progressively incremented potentials in a) oxidation, and b) subsequent reduction half-cycle. Laser excitation wavelength: 830 nm.

observed in (6TPh)<sub>2</sub> reduction half cycle portrayed on Fig. 3a. Substitution to one of the exposed benzene ring sites [33], giving electroactive *para*- or *ortho*-bis(bithiophene)benzene units [46] or detrimental coupling with charged, spin bearing  $\alpha,\omega$ -bisphe-nylquaterthiophene units [47], may account for the observed spectral traits too. Looking at the Raman spectra of (6TPh)<sub>2</sub> reduction, shown in Fig. 4b, a remarkable lock-up of the Raman bands structure can be seen, reflecting the setting of polymer structure by these cross-linking reactions [48]. Furthermore, the Raman spectrum at 0.8 V (Fig. 4a) discloses considerable elevation of its background. Such background elevation effects have been associated with molecular structure disordering [49]. One has to be cautious to observe this effect however, as computational correction by elaborate background correction algorithms of modern advanced Raman spectrometers' software often remove it inconspicuously.

Regardless of their exact identity, the side reactions impact the electroactivity of the oligomer film as portrayed by the spin concentration and EPR linewidth profiles registered in the subsequent, second voltammetric cycle. Upon repeated oxidation, the potential profiles of these two spectral parameters do not return to their original, first half-cycle shape, signifying irreversible changes had taken place in the film, once the spin concentration peak potential was traversed. Decrease of CV current magnitudes recorded before and after the spectroelectrochemical measurements of (6TPh)<sub>2</sub> film also support this inference. Such a subtle yet gradual decay of current has been regularly observed during repetitive cycling of such films, howbeit, its significance was usually depreciated on account of its minor contribution to the CV shape. The time span of spectroelectrochemical measurements performed here is much longer, running even into hours, giving time for these slow reactions to take place in the solid film making their effects perceptible. It is also important to note that repeated application of 0.8 V potential in the second doping half-cycle, resulted in a further decrease of spin concentration magnitudes, indicating that at these potentials the film is indeed electrochemically unstable. Such unfavourable reactions could equally well take place in the incipient polymer layers during electrosynthesis of poly(6TPh), when sufficiently high potentials are employed to oxidise each and every bithiophene arm of the monomer molecule. These observations point to an unsettling conclusion that a paradox, similar to the one observed for unsubstituted thiophene [50], operates for the investigated meta arranged conjugated systems, whereby application of electro-polymerisation conditions necessary for activation of reactive monomer moieties, entails degradation of the electroactive properties of the nascent polymer layer. One way to resolve this intricacy would be to assist the electrochemical oxidation with an addition of boron trifluoride diethyl etherate [51,52]. It would be prudent, though, to perform an independent study, in order to descry the catalytic effects of boron trifluoride on the different chemical moieties of the monomer molecule, in particular, the benzene ring itself. Another approach, would be employ well established chemical coupling reactions like Suzuki [53,54], Kumada [55,56] or Negishi [57]. These reactions elude the pitfalls of oxidative coupling methods, opening the way for preparation of high molecular weight, truly three-dimensional polymer structures, by taking full advantage of the multi-functional character of the investigated monomers.

## 5. Conclusions

Electropolymerisation and redox doping processes of a model, tri-functional meta-substituted molecule – 1,3,5-tris(bithiophene)benzene (6TPh) have been studied using a set of

spectroelectrochemical techniques. Analysis of obtained results, supplemented with the available literature data, suggests that the oxidation process of this molecule proceeds stepwise, with oxidation of each bithiophene moiety taking place at progressively higher potentials. Effecting the electrooxidation of this molecule at the lowest possible potential affords insoluble electroactive film at the electrode surface, whose spectral signatures suggest it predominantly comprises dimer molecules, whose  $\alpha,\omega$ -bisphe-nylquaterthiophene segment accounts for the observed p-doping spectral traits. Spectroelectrochemical investigations disclose an irreversible deterioration of the electroactive properties of the dimer film, at potentials, close to the first oxidation potential of the monomer molecule. Such close overlap of the two contradictory phenomena is found accountable for the observed gradual loss of electroactive properties of the oligomer film, observed upon prolonged electrochemical redox cycling. This can be considered the reason for notable dependence of the voltammetric responses of these films on the applied maximum anodic electrooxidation potential, observed in the literature. Consequently a paradox phenomenon postulate is put forward, whereby electrooxidation of conjugated, thiophene meta-substituted benzenes takes place concurrently with electroactivity impairing overoxidation reactions, complicating the electrochemistry of these conjugation-defined systems and impacting the perspectives of their oxidatively synthesised films in organic electrochromic applications.

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