Voltammetric and Spectroscopic Investigation of Electrogenerated Oligo-Thiophenes: Effect of Substituents on the Energy-Gap Value

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Featured Application: Redox and optical features of thiophene-based oligomers and polymers make them appealing in several technological fields, including light-emitting diodes, solar cells, electrochromic and electroluminescent devices. In this context, the evaluation of the energy gap can give useful suggestions on the effect of substituents on the behavior of the oligothiophenes chain, and on the extension of the electron density delocalization.

Abstract: Oligothiophenes are especially appealing due to their promising applications in different fields, including photosensitive devices. In this context, anchoring a selected substituent on the main structure of the starting material can induce changes in redox and spectroscopic features, according to the nature of the substituent and its position on central or terminal rings. Here, an electrochemical and spectroscopic comparison between 2,2′,5,2′′-terthiophene (2), 5-Br-terthiophene (3) and 5-ethynyl-terthiophene (5-ET) is reported, aimed at elucidating the effect of the nature of the substituent on the energy gap value of the terthiophene skeleton. Furthermore, in order to understand the influence of a selected substituent in varying its position on the terthiophene backbone, 5-ET is compared to the previously described 3′-ethynyl-terthiophene (3′-ET). Experimental results are confirmed by DFT calculations, showing a higher extension of the electron density in 5-ET compared to 2 and 3, as well as to 3′-ET. In addition, as a consequence of the presence of the unsaturated fragment on the C-5-position, the energy gap value of poly-5-ET (the electrogenerated film from 5-ET) appears significantly lower than poly-2 and poly-3. Finally, the higher conjugation effect of a terminal acetylene fragment compared to a central one is confirmed by the energy gap values of poly-5-ET and poly-3′-ET.

Keywords: oligothiophenes; conducting polymers; electrochemical synthesis

1. Introduction

Conducting polymers (CPs) are a well-known, wide class of compounds where the structural flexibility and the mechanical properties of “classical” polymers are coupled to the electronic and optical properties typical of inorganic semi-conductors. Since the Nobel Prize that was awarded to Heeger, McDiarmid, and Shirakawa in 2000, CPs have received a large attention from the scientific community due to their possible application in different technological fields such as sensors [1–6], photosensitive and electrochromic devices [7–13], rechargeable batteries [14–16], corrosion protection [17–19], and biomedicine [20,21]. In this context, polythiophenes (PTs) are especially appealing because of their structural versatility, as well as their environmental and thermal stability in the doped and undoped states, moderate band gap values, ease in p- and n-doping, and high conductivity [22]. CPs, including PTs, are often successfully achieved by electrochemical polymerization, with some interesting advantages to this methodology compared to the classical synthetic
The electrochemical synthesis of a conducting polymer allows for obtaining a polymer film on an electrode surface, tuning the thickness by the deposition charge, and monitoring the growth process by electrochemical or spectrophotometric techniques. Furthermore, the CP-modified electrode surface can be directly used in some specific applications, as in the case of sensors. Additionally, the electro-generated polymer can be firstly characterized on the same electrode surface where it is grown [23]. The features of the film can be controlled through an appropriate selection of the experimental conditions, namely electrode material, monomer concentration, solvent and supporting electrolyte, temperature, pH (in case of aqueous solutions), and the electrochemical technique of deposition. From a general point of view, the electrical and optical properties of PTs are due to the extended charge delocalization along the polymer backbone as a consequence of the overlapping of the π orbital of the thiophene rings, which tend to be coplanar. On the other hand, the rigidity of the structure causes insolubility of unsubstituted PTs, making their chemical characterization difficult. The insertion of flexible chains as substituents on the polymer skeleton increases the solubility of PTs but produces a twisting in the structure, and consequent changes in the properties of the polymer [24]. Furthermore, the presence of substituents in the β position of the heterocyclic ring facilitates α-α couplings rather than the α-β, leading mostly to stereoregular chains. In order to promote α-α couplings, as well as to reduce the value of the potential in electrochemical polymerization of thiophenes, chemically synthesized oligomers can be used as starting materials [25,26]. A combination of all these aspects influences the mean effective conjugation length of the polymer chain and, consequently, its band gap energy and conductivity values. However, the effect of using monomers/oligomers as starting materials on the properties of the electrogenerated conducting polymers is not totally defined. In 1986, Roncali et al. [25] proved that polythiophenes obtained by mono-, bi- and ter-thiophene showed an increasing doping potential moving from poly (thiophene) to poly (terthiophene), suggesting a decrease of the mean conjugation length when increasing the number of heterocyclic rings in the relative oligomer. On the other hand, Zotti and Schiavon [26] reported that polythiophenes obtained from bi- and ter-thiophene showed comparable conductivity, whereas the polymer obtained by thiophene monomer showed lower conductivity values, maybe because of overoxidation processes that generate degradation phenomena. However, the lower oxidation potential of bi- and ter-thiophene, compared to thiophene as it is, allows to avoid overoxidation phenomena on the growing polymer. Therefore, these oligomers are often used in the electrochemical synthesis of thiophene polymers.

In this context, the functionalization of terthiophene (Figure 1) on the C-3′ position is often adopted to assign new features to thiophene-based CPs.

![Figure 1. 2,2′:5′,2″-terthiophene.](image)

The synthesis of terthiophene oligomers with N-chelating moieties, connected to the central thiophene ring through a saturated or an unsaturated tether, has been previously reported [22,27,28]. Such arrangements allow to combine the polymerizing ability of the terthiophene to the coordinating ability of the N-ligand towards metal ions, mixing the conducting properties of the organic framework to the electronic and optical properties of the metal center. The resulting metal-containing species can be included in the so-called “outer-sphere metallopolymers” group [29]. In particular, an unsaturated (ethynyl) spacer between the polymerizing and coordinating units instead of a saturated (methoxy) one leads to a higher extension of conjugation, evidenced by a lower energy gap value. On the other hand, 5-substituted terthiophenes are reported as building blocks in photo-sensitive arrangements [30,31]. As in the case of 3′-ethynyl-terthiophene, the analogue 5-ethynyl
derivative could be properly modified to achieve a molecule with a double function, that is, a polymerizing and a coordinating one. In this last case, the resulting metallopolymer could be defined as “inner-sphere metallopolymer” [29], with conducting, electronic, and optical performances higher than in the case of outer-sphere materials. In this context, a comparison between 3′-ethynyl- and 5-ethynyl-terthiophene could give useful suggestions to predict the optical and electrochemical behavior of new species, including such fragments as building block. Unlike 3′-ethynyl-terthiophene, the behavior of the 5-ethynyl-analogue has been reported only as a part of organic [31] or metallorganic [32,33] compounds, but its electrochemical characterization has not so far been reported to the best of our knowledge. Hence, with the aim of studying the influence of the position of an ethynyl substituent on the properties of the monomers and the resulting polymers, here we report a voltammetric and UV-Vis characterization of 5-ethynyl-terthiophene and poly (5-ethynyl-terthiophene), as well as a comparison of the corresponding 3′-ethynyl-terthiophene species. The experimental results are compared to calculated data by DFT-approach.

2. Materials and Methods

5-bromo-2,2′-bithiophene, 2-thienylboronic acid, tetrakis (triphenyolphosphine) palladium (0) ([Pd(PPh3)4]), 1,1′-bis (diphenylphosphino) ferrocene dichloropalladium ([Pd(dppf)Cl2]), trimethylsilylethynylene (TMS), and N-bromo-succinimide (NBS) were from TCI Chemicals. 

1H NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0 MHz. Chemical shifts are given in ppm relative to residual solvent signal [34].

UV-Vis spectra of the monomers were recorded in CH2Cl2 or CH3CN solvent using a Hitachi U-2010 spectrophotometer. IR spectra were carried out with a JASCO FT/IR-489 Plus spectrophotometer using KBr disks in the range 4000–400 cm$^{-1}$.

UV-Vis spectra of polymers were carried out on films electrodeposited on a ITO (indium-tin oxide) slide.

Electrochemical tests were performed with a AUTOLAB PGSTAT12 instrument, using the software GPES. The electrochemical synthesis and characterization were performed in a three-electrodes, single compartment cell using a Pt disk (2 mm diameter) as the working electrode, a graphite bar as the counter electrode, and Ag/AgCl equipped with a salt bridge containing the same solvent-supporting electrolyte system as the reference electrode. CH3CN or CH2Cl2 (99.8%, packaged under nitrogen), and 0.1 M tetraethylammonium hexafluorophosphate (TEAPF$_6$, puriss. electrochemical grade) were used as a solvent and supporting electrolyte, respectively. Before each experiment, the working electrode was polished with 1 and 0.3 µm alumina powder, then rinsed with distilled water in an ultrasonic bath. The monomer concentration in electrosynthesis and monomers characterizations was 2 × 10$^{-3}$ M. All the electrochemical experiments were performed under Ar atmosphere.

The energies of HOMO and LUMO were estimated by the voltammetric response according to Equations (1) and (2) [35]:

\[
\text{HOMO} = -e(E_{\text{onset,ox}} + 4.71) \text{ (eV)}
\]

\[
\text{LUMO} = -e(E_{\text{onset,red}} + 4.71) \text{ (eV)}
\]

where potential values are in Volts vs. Ag/AgCl and 4.71 is the potential (in Volts) of the redox couple Ag/AgCl versus vacuum, and taking into account that an electronvolt (eV) is defined as the energy gained by an electron moving along a potential of 1 V. The energy gap (Eg) values (difference between LUMO and HOMO) were calculated from the electrochemical data (Eg,ec), or from the UV-Vis spectra (Eg,opt) according to Equation (3):

\[
E_{\text{g,opt}} = \frac{1239.81}{\lambda_{\text{onset}}}
\]

where $\lambda_{\text{onset}}$ is the value of wavelength corresponding to 10% of maximum absorbance.

**DFT calculations.** DFT calculations were performed on PC GAMESS software [36], partially based on the GAMESS (US) source code [37] using the PBE0 functional [38] with
the basis set split-valence according to reference [39]. Concerning iodide, the corresponding pseudo-potential removing 28 core-electrons was adopted.

Harmonic analysis at PBE0/def2-SVP level was carried out on the equilibrium geometries of the substituted 2,2′:5′,2″-terthiophenes to confirm the nature of the minimum (i.e., the absence of imaginary frequencies) on the PES (Potential Energy Surface). The first 30 excited states were calculated from the equilibrium geometries at gas phase using the TD-DFT approach [40]. The resulting files were elaborated under Avogadro [41] and Gabedit software [42], released under GNU license.

Synthesis of 2,2′:5′,2″-terthiophene (2). 5-bromo-2,2′-bithiophene (1, 0.5827 g, 2.378 mmol) and [Pd(PPh₃)₄] (0.1644 g, 0.142 mmol) were dissolved in DME (15 mL). After 10 min, 2-thienylboronic acid (0.4473 g, 4.276 mmol) and [Pd(dppf)Cl₂] (0.1644 g, 0.142 mmol) were dissolved in DME (15 mL). After 10 min, 2-thienylboronic acid (0.4473 g, 4.276 mmol) and [Pd(dppf)Cl₂] (0.1644 g, 0.142 mmol) were dissolved in DME (15 mL). The reaction mixture was stirred at reflux temperature for 30 min and monitored by TLC (petroleum ether/dichloromethane 9:1 as eluent) until 1 disappeared, then cooled at room temperature and filtered. H₂O (20 mL) was added to the residue, the organic phase was extracted with ethyl acetate (3 x 30 mL) and washed with water (90 mL). Finally, the solution was treated with MgSO₄ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica, using petroleum ether/dichloromethane 9:1 as eluent, to give 2,2′:5′,2″-terthiophene (2, 0.5612 g, 2.259 mmol, yield 95%). ¹H NMR (CD₂Cl₂, ppm), δH: 7.29 (dd, 2H, H₅, 3J = 5.1 Hz, 4J = 1.0 Hz); 7.23 (dd, 2H, H₃, 3J = 3.6 Hz, 4J = 1.0 Hz); 7.14 (s, 2H, H₅+H₄); 7.07 (dd, 2H, H₄+H₅, 3J = 5.1 Hz, 4J = 3.6 Hz).

Synthesis of 5-bromo-2,2′:5′,2″-terthiophene (3). NBS (0.3187 g, 1.790 mmol) was added drop by drop to a solution of terthiophene (2, 0.4922 g, 1.982 mmol) in DMF (6 mL). The additions were performed out of light, during 6 h, at −20 °C, under stirring. At the end of the additions, the reaction mixture was taken to room temperature, then the reaction was let to proceed further for 24 h. Finally, the mixture was poured into iced water (60 mL), and extraction with CH₂Cl₂ was performed. The organic phase was washed with H₂O, treated with MgSO₄ and filtered, and the solvent was evaporated under reduced pressure. The crude product was crystallized with hexane to give 3 (0.5107 g, 1.560 mmol), with 79% yield. ¹H NMR (CD₂Cl₂, ppm), δH: 7.30 (dd, 1H, H₅, 3J = 5.1 Hz, 4J = 1.0 Hz); 7.23 (dd, 1H, H₃, 3J = 3.6 Hz, 4J = 1.0 Hz); 7.13 (d, 1H, H₄, 3J = 3.8 Hz); 7.08 (d, 1H, H₅, 3J = 3.8 Hz); 7.07 (dd, H₄, 3J = 5.1 Hz, 4J = 3.6 Hz); 7.04 (d, 1H, H₅, 3J = 3.9 Hz); 6.98 (d, 1H, H₃, 3J = 3.9 Hz).

Synthesis of 5-(3-hydroxy-3-butyl-1-inyl)-2,2′:5′,2″-terthiophene (4). 5-bromo-2,2′:5′,2″-terthiophene (3, 0.2311 g, 0.707 mmol), [Pd(dppf)Cl₂] (0.0057 g, 0.007 mmol) and Cul (0.0442 g, 0.022 mmol) were dissolved in diisopropylamine (5 mL), and 2-methyl-3-butyn-2-ol (0.0663 g, 0.022 mmol) were dissolved in diisopropylamine (5 mL). The mixture was heated at reflux temperature for 30 min and monitored by TLC (petroleum ether/dichloromethane 9:1 as eluent) until the reaction mixture was taken to room temperature, then the reaction was let to proceed further for 24 h. Finally, the mixture was poured into iced water (60 mL), and extraction with CH₂Cl₂ was performed. The organic phase was washed with H₂O, treated with MgSO₄ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica, using petroleum ether/dichloromethane 9:1 as eluent, to give 2,2′:5′,2″-terthiophene (2, 0.5612 g, 2.259 mmol, yield 95%). ¹H NMR (CD₂Cl₂, ppm), δH: 7.29 (dd, 2H, H₅+H₃, 3J = 5.1 Hz, 4J = 1.0 Hz); 7.23 (dd, 2H, H₃+H₅, 3J = 3.6 Hz, 4J = 1.0 Hz); 7.14 (s, 2H, H₅+H₄); 7.07 (dd, 2H, H₄+H₅, 3J = 5.1 Hz, 4J = 3.6 Hz).
filtered. The solution was evaporated to dryness, and the crude residue was purified by column chromatography on silica, using petroleum ether/ethyl acetate 5/1 as eluent. The compound 5-ET was obtained (0.1845 g, 0.671 mmol, 84% yield) as a brown-reddish powder. \(^1\)H NMR (CD\(_2\)Cl\(_2\), ppm), \(\delta\): 7.30 (dd, 1H, \(\text{H}_5\), \(J = 5.1\) Hz, \(J = 1.0\) Hz); 7.24 (dd, 1H, \(\text{H}_3\), \(J = 3.6\) Hz, \(J = 1.0\) Hz); 7.23 (d, 1H, \(J = 3.6\) Hz); 7.15 (AB system, \(J_{AB} = 3.6\) Hz); 7.14 (AB system, \(J_{AB} = 3.6\) Hz); 7.09 \(\div\) 7.06 (m, 2H). IR (KBr, cm\(^{-1}\)): 3276 (C=\(\equiv\)C-H), 2094 (C\(\equiv\)C).

3. Results and Discussion

3.1. Synthesis

The synthesis of 5-ethynyl-2,2′:5′,2″-terthiophene has been reported [31] as a combination of Stille and Sonogashira–Hagihara couplings. In this approach, 2,2′:5′,2″-terthiophene obtained by the reaction of 2,5-dibromothiophene with 2-(tributylstannyli)thiophene reacts with NBS to give the bromo-substituted derivative. The coupling reaction between the halo-thiophene and trimethylsilylacetylene (TMS) provides the TMS-ethynyl-terthiophene that is finally deprotected, leading to the ethynyl-derivative.

As an alternative, the synthetic route reported here can be successfully adopted. According to previous results [22], the synthesis of the ethynyl-terthiophene derivative 5-ET (Scheme 1) involves a Sonogashira–Hagihara coupling reaction between the corresponding Br-derivative (3) and 2-methyl-3-butyn-2-ol, followed by treatment with KOH. The synthesis of 3 was first attempted using a classical Suzuki-type coupling between the 5-bromo-2,2′-dithiophene 1 and 5-bromo-2-thiopheneboronic acid, but it resulted in quite low yields (about 20%), ascribed to homo-coupling reactions of the bromo boronic acid. For this reason, 2-thiynylboric acid was employed instead of 5-bromo-2-thiopheneboronic acid, and its coupling with the Br-derivative 1 allowed to obtain the unsubstituted terthiophene 2 with very good yields (95%). Then, 2 underwent a selective bromination on the C-5 by reacting with NBS [43], and 3 was obtained with a significative increase in yields (75% on the whole). The reaction of the halo-thiophene 3 with 2-methyl-3-butyn-2-ol as the ethynyl synthon gave the intermediate product 4. Finally, the deprotection of 4 with KOH allowed to obtain the target product 5-ET in good yields (84%).

Scheme 1. Synthetic route for 5-ethynyl-terthiophene 5-ET. (i) [Pd(PPh\(_3\))\(_4\)], DME, 1 M NaHCO\(_3\); (ii) NBS; (iii) [Pd(dppe)Cl\(_2\)], CuI, diisopropylamine, 2-methyl-3-butyn-2-ol; (iv) KOH, toluene/methanol 1/1.

3.2. Characterization of Monomers

The electrochemical behavior of 2,2′:5′,2″-terthiophene (2), 5-bromo-2,2′:5′,2″-terthiophene (3), and 5-ethynyl-2,2′:5′,2″-terthiophene (5-ET) was investigated by cyclic voltammetry both in CH\(_2\)Cl\(_2\) and in CH\(_3\)CN as solvent, using 0.1 M TEAPF\(_6\) as the supporting electrolyte. The cyclic voltammetry response of 2 in CH\(_2\)Cl\(_2\) (Figure 2a) shows a two-step anodic process, located at +1.13 V and at +1.18 V, with an associated process in the backward scan at +0.64 V. Both the second anodic process and the backward one evidence a sharp shape, suggesting adsorbing/desorbing phenomena on the electrode surface, according to investigations in different experimental conditions reported previously [25,44].
Using CH$_3$CN as solvent in electrochemical investigations, a similar behavior is observed, with a double anodic system at lower potential values than in CH$_2$Cl$_2$ (+1.05 and +1.09 V) and an associated backward peak (+0.82 V), the shape of the more anodic peak being reasonably attributed to the occurrence of absorptions (and corresponding desorptions) of oligomeric species on the electrode surface.

The presence of an electron-withdrawing -Br substituent on the C-5 position (compound 3) causes a shift of the process towards more anodic values, both in CH$_2$Cl$_2$ and on CH$_3$CN solvents. In particular, an anodic peak at +1.21 V (with an associated backward process at about +0.7 V), followed by a shoulder at 1.35 V is observed in CH$_2$Cl$_2$ (Figure 2b). The voltammetric response in CH$_3$CN again shows two anodic processes (+1.13 and +1.23 V, respectively), where the second one increases in current intensity at subsequent scans.

The behavior of compound 5-ET, where an ethynyl substituent is present in place of -Br, evidences a single anodic process at +1.15 V, with a backward associated signal at +0.73 V in CH$_2$Cl$_2$ (Figure 2c). Changing the solvent to CH$_3$CN, an anodic process at +1.12 V is observed.

Electrochemical data of 2, 3, and 5-ET are reported in Table 1, as well as 3’-ethynyl-2,2′,5′,2″-terthiophene (3’-ET, [22]) as a comparison, where the ethynyl substituent is on the central ring of the terthiophene structure rather than on a peripheral ring. HOMO values were referred to the CH$_3$CN solutions according to the analogous evaluation on the corresponding polymer species (Section 3.3).

**Table 1.** Electrochemical data of the terthiophene derivatives in CH$_3$CN/0.1 M TEAPF$_6$ and CH$_2$Cl$_2$/0.1 M TEAPF$_6$ solvent system.

| Compound                        | $E_{ox}$ (V) | $E_{ox, onset}$ (V) | HOMO (eV) |
|---------------------------------|--------------|---------------------|-----------|
|                                 | CH$_2$Cl$_2$/TEAPF$_6$ 0.1 M | CH$_3$CN/TEAPF$_6$ 0.1 M | CH$_2$Cl$_2$/TEAPF$_6$ 0.1 M | CH$_3$CN/TEAPF$_6$ 0.1 M |          |
| 2,2′,5′,2″-terthiophene (2)     | 1.13         | 1.05                | 0.97      | 0.95      | −5.66   |
| 5-Br-terthiophene (3)           | 1.21         | 1.13                | 0.99      | 0.92      | −5.63   |
| 5-ethyl-terthiophene (5-ET)     | 1.15         | 1.12                | 0.93      | 0.91      | −5.62   |
| 3′-ethyl-terthiophene (3’-ET)   | 1.26         | 1.19                | 1.00      | 1.01      | −5.72   |

Potential values referred to Ag/AgCl. HOMO values referred to electrochemical responses in CH$_3$CN/0.1 M TEAPF$_6$.

Table 1 evidences that an ethynyl substituent on the central ring makes the terthiophene structure more stable, whereas (Br- or ethynyl-) functionalization on the external ring does not meaningfully influence the voltammetric parameters and the corresponding HOMO values.

Compounds 2, 3, and 5-ET were also investigated by UV-Vis spectroscopy, both in CH$_2$Cl$_2$ and CH$_3$CN, and spectroscopic data were again compared to 3′-ET. In all cases, $\lambda_{max}$ values are always in the range 340–390 nm, and are ascribed to $\pi$-$\pi^*$ transitions on the terthiophene [44,45], as confirmed by theoretical calculations (Table 2).
Table 2. Experimental $\lambda_{\text{max}}$ and $E_g$ values compared to calculated values.

|                  | $\lambda_{\text{max}}$ (nm) |          |          |          | $E_g$ (eV) |          |          |
|------------------|------------------------------|----------|----------|----------|-----------|----------|----------|
|                  | CH$_2$Cl$_2$ | CH$_3$CN | Calculated | CH$_2$Cl$_2$ | CH$_3$CN | Calculated |
| 2,2':5':2''-terthiophene (2) | 355  | 358  | 364  | 3.10  | 3.10  | 3.41  |
| 5-Br-terthiophene (3)       | 359  | 359  | 374  | 3.04  | 3.04  | 3.32  |
| 5-ethynyl-terthiophene (5-ET) | 383  | 379  | 388  | 2.88  | 2.88  | 3.20  |
| 3'-ethynyl-terthiophene (3'-ET) | 352  | 348  | 375  | 2.90  | 2.95  | 3.31  |

The analysis of UV-Vis data suggests that the presence of -Br as a substituent on the C-5 atom of the terthiophene skeleton slightly affects the maximum absorbance wavelength, whereas an -ethynyl fragment on the same position of the ring results in a red shift in the $\lambda_{\text{max}}$ value, as well as a decrease in the $E_g$ value. Furthermore, the comparison between 3'-ET and 5-ET suggests a slight lowering in $E_g$ when the ethynyl substituent is in a peripheral position instead of on the central thiophene ring.

Experimental results were compared with theoretical calculations using the TD-DFT approach. Initially, a level RHF/STO-3G was tested to obtain an equilibrium geometry of the reference molecules that is the quaterthiophene [46]. Then, different functional/basis set couples were adopted and compared, as reported in Table 3. According to such a preliminary study, PBE0 functional with split-valence (def2-SVP) basis set shows the strongest agreement with the proposed structure, although the time required is quite long. Therefore, the PBE0/def2-SVP level was selected to calculate the singlet excited states.

Table 3. Computing time and percent average error (AE%) at different functionals and basis sets.

|          | PBE96 | OLYP  | B3LYP5 | B3PW91 | BHHLYP | O3LYP5 | PBE0  |
|----------|-------|-------|--------|--------|--------|--------|-------|
| 3-21G    |       |       |        |        |        |        |       |
| Time (min) | 85.6  | 123.8 | 94.9   | 100.2  | 91.1   | 99.1   | 82.9  |
| % AE (dist) | 2.65  | 2.49  | 2.31   | 2.02   | 1.91   | 1.76   | 1.85  |
| % AE (ang) | 3.06  | 21.24 | 3.47   | 3.63   | 4.69   | 3.46   | 1.68  |
| % AE (all) | 2.70  | 4.83  | 2.45   | 2.22   | 2.26   | 1.97   | 1.83  |
| 6-31G    |       |       |        |        |        |        |       |
| Time (min) | 150.2 | 167.1 | 113.3  | 166.1  | 137.4  | 113.9  | 148.3 |
| % AE (dist) | 2.63  | 2.49  | 2.33   | 2.01   | 1.70   | 1.77   | 1.87  |
| % AE (ang) | 1.74  | 15.22 | 4.63   | 5.95   | 5.84   | 4.75   | 3.85  |
| % AE (all) | 2.52  | 4.08  | 2.61   | 2.50   | 2.22   | 2.14   | 2.12  |
| MC       |       |       |        |        |        |        |       |
| Time (min) | 269.4 | 392   | 360.9  | 348.2  | 255.9  | 311.9  | 320.6 |
| % AE (dist) | 2.54  | 2.37  | 2.23   | 1.89   | 1.70   | 1.63   | 2.13  |
| % AE (ang) | 4.78  | 20.95 | 8.76   | 10.09  | 9.15   | 8.56   | 6.57  |
| % AE (all) | 2.82  | 4.69  | 3.05   | 2.92   | 2.63   | 2.49   | 2.69  |
| def2-SVP  |       |       |        |        |        |        |       |
| Time (min) | 445.9 | 476.2 | 382    | 435.3  | 523.9  | 455.4  | 470.6 |
| % AE (dist) | 1.28  | 1.14  | 1.01   | 0.72   | 0.34   | 0.70   | 0.63  |
| % AE (ang) | 5.53  | 12.93 | 5.19   | 6.67   | 7.69   | 5.41   | 4.77  |
| % AE (all) | 1.81  | 2.62  | 1.54   | 1.47   | 1.26   | 1.29   | 1.15  |

% AE: percent average error.

The second step was the choice of the proper structure of terthiophene for the relative position of heteroatoms (i.e., cis-cis, cis-trans, or trans-trans). From a general point of view, the structure of 2,2':5':2''-terthiophene has a conformational variability due to the free rotation of aromatic rings. For this reason, a tridimensional map has been calculated to observe the changing energies as a function of dihedral angles S-C-C-S in 2,2':5':2''-terthiophene (Figure 3). The map evidences a symmetric behavior with respect to the diagonal, suggesting an equivalence of the external aromatic rings. Moreover, the trans-trans configuration (with 180° dihedral angles) shows the lowest energy. Hence, although the situation in a solution phase is certainly more dynamic, the trans-trans configuration was selected for the optimizations adopted here.
Table 3. Computing time and percent average error (AE%) at different methods.

| Method     | Computing Time (min) | AE% (dist) | AE% (ang) |
|------------|----------------------|------------|-----------|
| def2-SVP   | 269.4                | 1.28       | 4.78      |
| PBE96      | 392                   | 1.14       | 20.95     |
| B3LYP      | 360.9                 | 1.01       | 8.76      |
| B3PW91     | 348.2                 | 0.72       | 10.09     |
| O3LYP      | 255.9                 | 0.34       | 9.15      |
| PBE0       | 311.9                 | 0.70       | 8.56      |
| APE (dist) | 320.6                 | 0.63       | 6.57      |

On these bases, the singlet excited states were calculated (Table 2) evidencing that all $\lambda_{\text{max}}$ values are in a narrow range (360–390 nm), being ascribable to $\pi-\pi^*$ transitions on the common terthiophene skeleton of the investigated species. Experimental and theoretical $\lambda_{\text{max}}$ values are in good agreement, as well as $E_{\text{g,opt}}$ values, showing a 15% maximum difference between the calculated and experimental data. The red-shift in $\lambda_{\text{max}}$ and the corresponding lowering in $E_{\text{g,opt}}$ argue a more extended conjugation in the terthiophene framework, due to the presence of an unsaturated fragment on the C-5 atom instead of on the C-3′ position.

3.3. Electrochemical Polymerization and Polymer Characterization

Electrochemical polymerization of 2, 3, and 5-ET was performed on a Pt disk as a working electrode by cyclic voltammetry (Figure 4), as well as, when successful, by chronocoulometry on a $2 \times 10^{-3}$ M solution of each monomer in CH$_2$Cl$_2$/TEAPF$_6$.

Figure 4. Cyclic voltammetry polymerization of 2 (a), 3 (b) and 5-ET (c) on a Pt disk electrode in CH$_2$Cl$_2$/TEAPF$_6$ 0.1 M solvent system. Potential scan rate: 100 mV s$^{-1}$.

The potentiodynamic polymerization of terthiophene 2 by cycling the potential between 0 and 1.3 V evidences an increase in the current intensity when increasing the scan number. After 10 scans, a homogeneous deep-red polymer film was observed on the electrode surface.

A film of poly-2 obtained by potentiostatic polymerization proved to be scarcely stable on the electrode surface, maybe due to the absorption/desorption processes mentioned in the previous section, as well as to a possible partial solubility of low-molecular-weight oligomer species.

The polymerization behavior of the Br-derivative 3 was similar to the unsubstituted terthiophene 2, and a red polymer film of poly-3 was obtained only by cyclic voltammetry, whereas the potentiodynamic polymerization was unsuccessful.

Lastly, the polymer form of 5-ethylthiophene (poly-5-ET) was initially obtained by cyclic voltammetry, scanning the potential from 0 and +1.25 V for 10 cycles. The potentiostatic approach was also successful in the polymerization of 5-ET, being performed...
at +1.12 V for 300 s, then neutralizing the film at 0 V for 60 s. In both cases, a stable brown-red film of poly-5-ET formed on the electrode surface.

To compare the electrochemical behavior of the polymer species here reported and poly-3'-ET [22], the voltammetric characterization of poly-2, poly-3 and poly-5-ET was performed in CH\textsubscript{3}CN/TEAPF\textsubscript{6} 0.1 M solution (Figure 5 and Table 4).

### Table 4. Voltammetric data in CH\textsubscript{3}CN/TEAPF\textsubscript{6} 0.1 M and UV-Vis data of the polymer films.

| Polymer     | \(E_{\text{ox}}\) (V) | \(E_{\text{red}}\) (V) | HOMO (eV) | LUMO (eV) | \(E^{\text{g,ec}}\) (eV) | \(E^{\text{g,opt}}\) (eV) |
|-------------|-----------------------|------------------------|-----------|-----------|---------------------|---------------------|
| Poly-2      | 1.24                  | -1.44                  | -5.68     | -3.34     | 2.34                | 2.08                |
| Poly-3      | 1.28                  | -1.48                  | -5.81     | -3.35     | 2.46                | 2.21                |
| Poly-5-ET   | 0.93                  | -1.68                  | -5.37     | -3.63     | 1.74                | 1.89                |
| Poly-3'-ET  | 1.05                  | -1.73                  | -5.47     | -3.40     | 2.07                | 2.06                |

The voltammetric response of poly-2 shows a doping/de-doping process at +1.26/+0.57 V. The sharp shape of the anodic peak, quite unusual for a conducting polymer, is commonly ascribed to a narrow distribution of molecular weights along the polymer chains, leading to a harder oxidation process and to less conductive polymers [25]. On the following scans, the doping peak shifts to +1.1 V and becomes broader, suggesting a rearrangement of the polymer chains with different internal interactions.

The voltammetric behavior of poly-3 is similar to poly-2, showing a sharp doping at 1.24 V, with a double-step de-doping at +1.03 V and +0.80 V. In the case of the polymer form of Br-terthiophene, besides the narrow molecular weight distribution (attributed to the high conjugation of terthiophene monomer), the C-5 position is not available to the growth of the polymer chain due to the presence of -Br, hence reasonably only dimer species are formed. Both poly-2 and poly-3 show a cathodic process at −1.44 and −1.48 V, respectively, associated to the n-doping process on the polymer chain.

The voltammetric response of poly-5-ET evidences a significative lowering in the potential value of the doping/de-doping process, that appears at +1.05/+0.87 V. Furthermore, a pre-peak at +0.5 V is visible, maybe due to charge trapping phenomena [22]. The cathodic scan shows a sharp peak at −1.39 V and a second, broad at −1.68 V, suggesting the presence of charge trapping processes also in the negative section of the potential window.

UV-Vis characterization of neutral polymers (Table 4 and Figure 6) was performed on films grown on ITO as a working electrode. The spectra of poly-2 and poly-3 show three broad absorption bands between 600 and 450 nm ascribed to short-chain oligomers, and a transition around 360 nm due to the unreacted monomer. Hence, UV-Vis spectra of the polymer species deriving from unsubstituted and Br-substituted terthiophene confirm the hypothesis from the electrochemical data about the low efficiency of the polymerization process giving only low-molecular-weight species.
On the other side, the spectra of poly-5-ET and poly-3′-ET [22] do not evidence the presence of unpolymerized monomer, showing a broad absorption band over 400 nm. 

\[ \text{Eg, opt values were calculated from the onset wavelength. They are in good qualitative agreement with the corresponding values from the electrochemical investigation (Table 4). For all polymers, both electrochemical and spectroscopic Eg values are lower than the relevant monomers. Furthermore, the lowering of the Eg value from poly-2 (unsubstituted poly-terthiophene) to poly-3′-ET (ethynyl substituent on the central ring) looks smaller than to poly-5-ET (ethynyl on a peripheral ring). Such a difference suggests some comments on the effect of the ethynyl fragment depending on the position (central or external ring, respectively) where it is anchored on the relevant terthiophene monomer. A plausible reason for this behavior can be found according to the proposed coupling route for poly-3′-ET and for poly-5-ET in Figure 7. In particular, an unsaturated function on the central heterocycle ring (3′-ET) seems to be scarcely influencing the growing mechanism of the polymer chain. This feature can be reasonably attributed to α-α couplings between external thiophene rings of two different terthiophene units, not directly involving the ethynyl substituent on C-3′, which appears outside of the main chain. On the other hand, the growth of a poly-5-ET chain can also involve homo-couplings between terminal ethynyl-functions, as well as hetero-couplings between a free α position on a terminal ring and the ethynyl fragment on a second one. The presence of the unsaturated portion inside the polymer chain facilitates a more extended electron density delocalization along the polymer chain, causing the observed higher lowering of Eg values in poly-5-ET.}

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\[ \text{Figure 6. UV-Vis spectra of poly-2, poly-3, poly-5-ET and poly-3′-ET on ITO.} \]

\[ \]

\[ \text{Figure 7. Plausible coupling of terthiophene fragments in poly-3′-ET (top) and in poly-5-ET (bottom).} \]

4. Conclusions

The effect of the nature of the substituent on a terthiophene skeleton has been investigated based on electrochemical, UV-Vis and theoretical data. In particular, 2,2′:5′,2″-terthiophene (2), 5-Br-terthiophene (3) and 5-ethynyl-terthiophene (5-ET), as well as the
resulting electrogenerated conducting polymers were considered. Experimental and theoretical data indicate a more extended electron density delocalization in 5-ethynyl-terthiophene, compared to both 5-Br-terthiophene and unsubstituted terthiophene. On these bases, the use of 5-ET as the building block for highly delocalized conducting polymers can be expected to be more efficient than 2 and 3. Such a prediction was confirmed by characterization of films obtained by electrochemical polymerization of the investigated thiophene-species. Voltammetric and UV-Vis responses evidenced a higher extended charge delocalization (expressed as Eg values) for poly-5-ET compared to poly-2 and poly-3. Voltammetric data suggest that the lowering in Eg is mainly ascribable to a lowering in the LUMO and, in minor extension, to an increasing in the HOMO.

Finally, a comparison of 5-ethynyl-terthiophene and the resulting polymer film with the analogues reported previously, 3’-ethynyl-terthiophene (3’-ET) and its polymer, respectively, was performed to take into account the effect of the position of the substituent. Experimental and theoretical results again indicate a higher electron delocalization when the unsaturated fragment is located on a terminal heterocyclic ring (5-ET) rather than on the central one (3’-ET), both in the monomer and in the polymer species.

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