# PROPIEDADES ELECTROQUÍMICAS Y ESPECTROSCÓPICAS DE LOS DITIENILETILENOS Y SUS POLÍMEROS

# THE ELECTROCHEMICAL AND SPECTROSCOPIC PROPERTIES OF DITHIENYLETHYLENES AND THEIR POLYMERS

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## Resumen

Se describen la síntesis y las propiedades electroquímicas y espectroscópicas de los ditieniletilenos (cis-DTE y trans-DTE). La polimerización de los dos isómeros se llevó a cabo con éxito y los polímeros resultantes se analizaron por métodos electroquímicos y espectroelectroquímicos. El comportamiento voltamperométrico de los cis-PDTE y trans-PDTE electropolimerizados sugirió que se producían polarones y bipolarones tras la oxidación. Sin embargo, la formación de un estado conductor no se observó en las mediciones SNIFTIRS. Tras el dopaje químico con I2, el cis-PDTE y el trans-PDTE mostraron una mayor estabilidad en el estado dopado y se observó una respuesta espectroscópica significativamente diferente para el trans-PDTE dopado químicamente, mostrando características IR similares a las de los polímeros conductores.

**Palabras clave:** ditieniletilenos, voltamperometría cíclica, SNIFTIRS, dopaje químico.

## Abstract

The synthesis, electrochemical and spectroscopic properties of dithienylethylenes (cis-DTE and trans-DTE) are reported. The polymerisation of the two isomers was successfully carried out and the resultant polymers were analysed by electrochemical and spectroelectrochemical methods. The voltammetric behaviour of the electropolymerised cis-PDTE and trans-PDTE suggested that polarons and bipolarons were produced upon oxidation. Nonetheless, the formation of a conducting state was not observed in the SNIFTIRS measurements. Upon chemical doping with I2, cis-PDTE and trans-PDTE showed increased stability in the doped state and a significantly different spectroscopic response was observed for the chemically doped trans-PDTE, exhibiting IR characteristics similar to those of conducting polymers.

**Key words:** dithienylethylenes, cyclic voltammetry, SNIFTIRS, chemical doping.

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## Introduction

Conjugated polymers obtained from the polymerisation of dithienylethylenes have attracted increasing interest due to their electrical and optical properties.[1-3] This class of compounds can be viewed as a combination of the structures of thiophene and polyacetylene[4,5]. In such systems, the presence of double bonds produces both, a decrease in the overall aromatic character of the molecules allowing a better delocalisation of π-electrons over the polymeric chain, and a attracted increasing interest due to their electrical and optical properties. Limitation of the rotational disorder[6-8]. The combination of these two effects has been confirmed in polymers like poly-thienylenevinylene (PVT)[5,9] and poly-dithienylethylene (PDTE)[6,10], shown in figure 1, which exhibit lower bandgaps by around 0.3 eV compared to that of polythiophene.

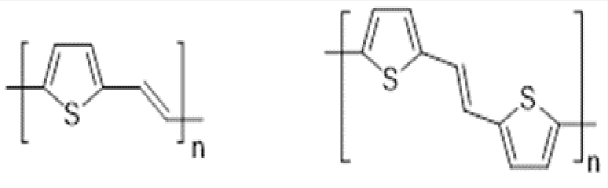


Figure 1 - Structures of poly(thienylenevinylene) (left) and poly-dithienylethylene (right).

A major drawback in the study of ethylene linked thiophene derivatives lies in the enhanced stability of the corresponding radicals which exerts detrimental consequences for the efficiency of the electropolymerisation process.[4] The existence of a poorly soluble precursor leads to a limited number of couplings, thus preventing the formation of extensively conjugated polymer chains.[10]
In this paper we report the investigations carried out on the two thienylethylenes isomers shown in Figure 2.

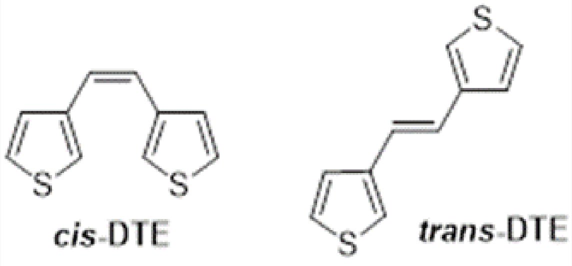
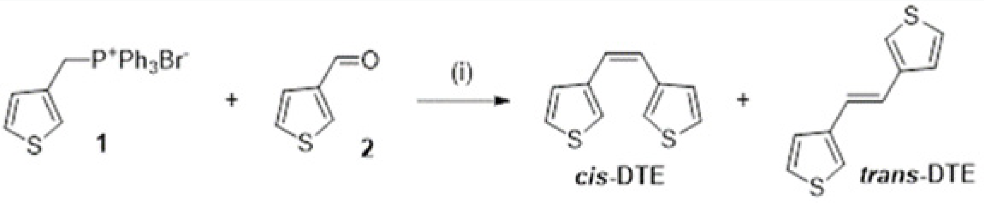


Figure 2 - Structures of cis-1,2-di(3-thienyl)ethylene cis-DTE and trans-1,2-di(3-thienyl) ethylene trans-DTE (right).

The interest in investigating the polymerisation of dithienylethylenes with the ethylenic double bond bridging two thiophene rings in the β-position arises from the possibility that the charge movement in the resultant polymers could occur either via the polythiophene backbone, through the ethylene bond or using both routes.

In addition, the presence of the ethylene linkage, acting as a "conjugated spacer" and reducing steric interactions on successive aromatic rings, could lead to an enhancement of the degree of coplanarity and therefore, increased polymer conjugation.[9]

Dithienylethylenes can be synthesised in three steps starting with the bromination of 3-methyl-thiophene.[11] The obtained product is then reacted with triphenylphosphine in toluene forming a phosphonium salt. The final step of the synthesis, the formation of cis-DTE and trans-DTE, is accomplished by a Wittig reaction as seen in equation 1.



(1)

(Reagents and conditions: (i) n-BuLi, 2 h, -78 °C).

## Results and Discussion

The isomers were separated by column chromatography and characterised by $^{1}$H, $^{13}$C and IR spectroscopy in addition to mass spectrometry (for detailed information

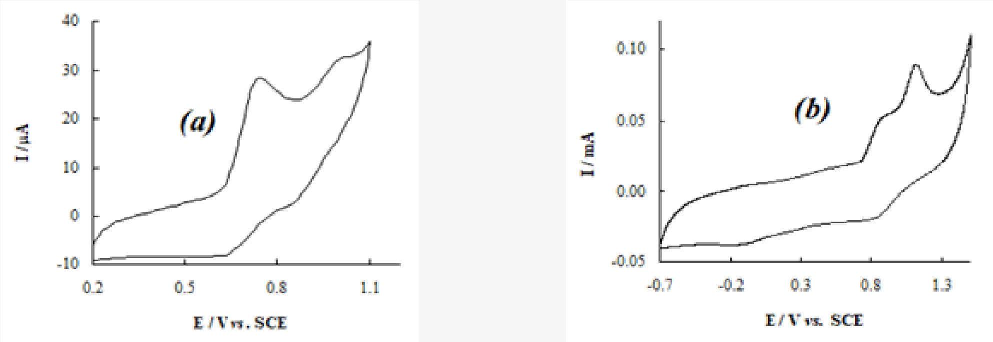


Figure 3 - (a) Voltammogram of a **trans-DTE** solution (0.003 mol dm$^{-3}$) in electrolyte recorded at $\upsilon = 0.1$ V s$^{-1}$. (b) Cyclic voltammogram of **trans-PDTE** in monomer free solution (0.1 M $TBAPF_6$ / MeCN) recorded at $\upsilon = 0.1$ V s$^{-1}$ using a Pt disc working electrode (0.44 cm$^2$).

please see the supporting information).

## Electrochemical and Spectroelectro chemical Studies on trans-DTE

The redox properties and electro polymerization ability of **trans-DTE**, shown in Figure 3a, have been studied by cyclic voltammetry. Two oxidation and two reduction peaks can be seen at $E^1_{ox} = 0.74$ V, $E^2_{ox} = 1.01$ V, $E^1_{red} = 0.63$ V, and $E^2_{red} = 0.86$ V.

These redox couples correspond to the formation of a radical cation ($E^1_{ox}$ / $E^1_{red}$), as previously observed[3], and a dication ($E^2_{ox}$ / $E^2_{red}$). The reversible one electron oxidation of oligothiophenes to radical cations and dications has been very well documented.[12-16] However, electrochemical reversibility is very unusual in monomers with three or fewer thiophene rings.[17]

This fact can explain the large peak separation and therefore low reversibility observed in the voltammetric behaviour of **trans-DTE**. Polymerisation occurs at $E^3_{ox} = 1.34$ V (not shown) where an increase in the peak current with every potential cycle is due to the continuous growth of material on the electrode and consequent increase in the effective surface area of the electrode.[18,19]

The cyclic voltammogram of electrochemically polymerised light-yellow **trans-PDTE** (Figure 3(b)) shows a one electron redox process at $E^1_{ox} = 0.89$ V / $E^1_{red} = 0.83$ V and a second oxidation at $E^2_{ox} = 1.12$ V. These peaks can be assigned to the sequential oxidation of the conjugated polymer chain to form polarons and bipolarons.[20-23]

Even though previous studies on the electroactivity of polythiophene films indicate that the formation of polarons and bipolarons usually occurs at essentially the same potential, variations in the electrolyte medium or temperature may facilitate the separation of the two processes by cyclic voltammetry.[21] For example, using a Pt ultramicroelectrode at low temperature, Chen et al.[22] were able to distinguish the reversible formation of the polaron, bipolaron and even a metallic state in (3,4-ethylenedioxythiophene) (PEDOT) and poly(3-methylthiophene).

Taking the potential towards more negative values reveals further reduction of the polymeric chain at $E^2_{red} = -0.11$ V. This peak might be attributed to the removal of trapped positive charges remaining in the polymer after being cycled through the p-doped state[24-26]. The film was found to be stable from -1.0 to 2.0 V. Potential cycling outside this potential interval leads to polymer degradation.

The oxidation of **trans-PDTE** (Figure 3 (b)) takes place at a lower potential than that of polythiophene (1.1 V vs. SCE)[27]. It can then be concluded that, as already seen for PVT[28] and PDTE[29], the introduction of the ethylene linkage between the thiophene rings induces a negative shift of the anodic peak potential.

The spectroelectrochemical investigation of **trans-PDTE** was performed in a monomer-free electrolyte solution and using the same range of potentials as those applied during the voltammetric characterisation of the film. The aim of this study was to achieve

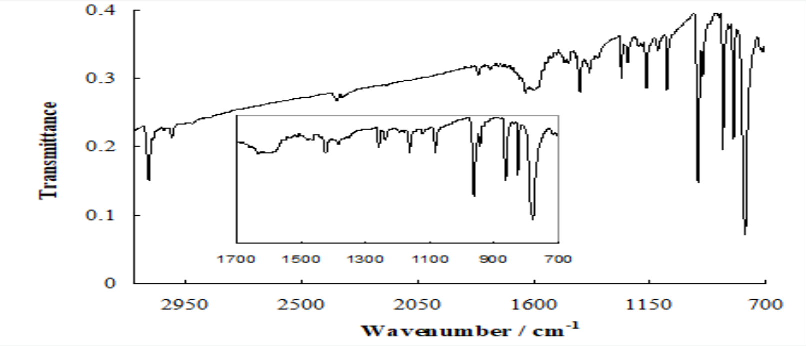


Figure 4 - Infrared spectrum of trans-DTE in KBr disc pellet and expansion of the IR spectrum between 1700 and 700 cm$^{-1}$.

a better understanding of the structural changes occurring during the oxidation of the polymer. In order to assign the peaks observed in the SNIFTIR spectra of **trans-PDTE**, the FTIR spectrum of the monomer **trans-DTE** was initially recorded (Figure 4). The FTIR spectrum of trans-DTE displays its strongest bands at 780 and 965 cm$^{-1}$. These signals are due to the out-of-plane $C_\beta$-H deformation in the thiophene ring and C-H out-of-plane bending of the trans-vinylene linkage, respectively.[15,28,30,31]

The C=C ethylene vibration is seen at of the 945 and 1630 cm$^{-1}$.[28,32] Vibrations between 1000-1400 cm$^{-1}$ are in the range of the stretching frequencies of C-C, C=C and C-S bonds and of bending frequencies of C-H bonds in thiophene. The C-H stretching vibration and out-of-plane deformation due to α-hydrogen in the thiophene rings are found at 3095 and 703 cm$^{-1}$, respectively.[34-36]

Figure 5 shows the SNIFTIRS spectra of trans-PDTE collected at successively increasing positive potentials and normalised to the reference spectrum taken at 0 V.

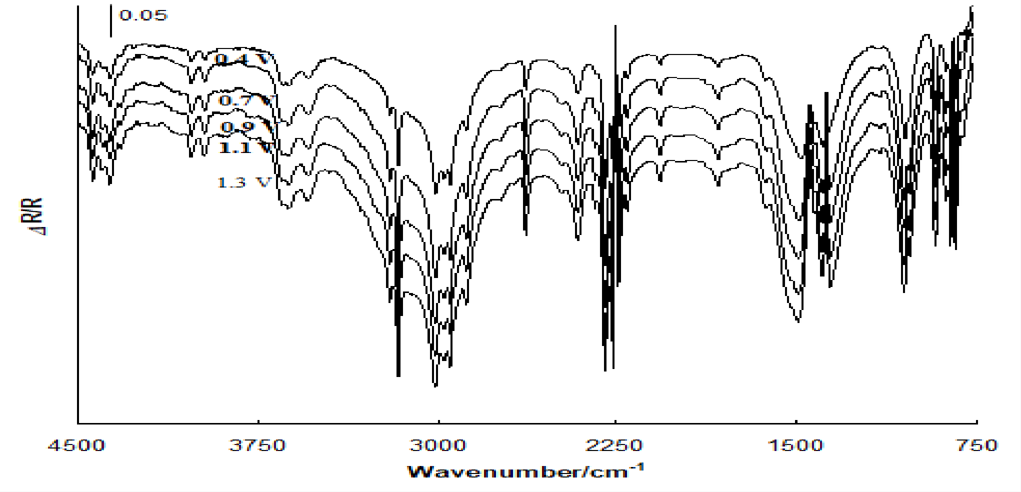


Figure 5 - SNIFTIRS spectra of trans-PDTE taken from 0.4 to 1.3 V. Reference spectra collected at 0 V. Spectra were shifted for clarity.

The spectra obtained between 4500 and 750 cm$^{-1}$ show an increase in the intensity of the IR absorbance peaks as the polymer is oxidised from 0.4 to 1.3 V. Solvent bands are seen at 2250 cm$^{-1}$ (acetonitrile C≡N stretch) and centred at 3000 cm$^{-1}$ (symmetric and asymmetric stretching modes of $CH_2$ and $CH_3$ due to the electrolyte salt - tetrabutyl ammonium salt).[18, 37]

The absence of the peaks at 3095 and 1082 cm$^{-1}$ related with the $C_\alpha$-H stretching vibration and in-plane deformation, respectively, indicates that the coupling of thiophene units occurs mainly through the α-α positions. However, a decrease in the intensity of the $C_\beta$-H vibration at 780 cm$^{-1}$, better observed in Figure 6, is also seen in the spectra of **trans-PDTE** when compared

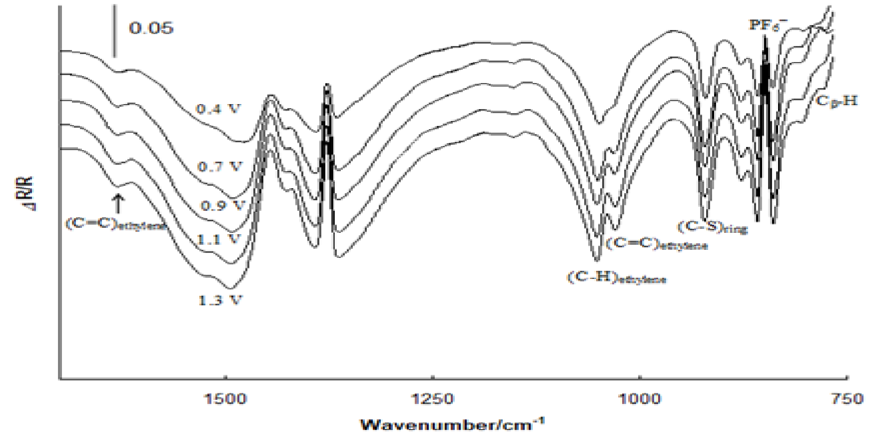


Figure 6 - SNIFTIRS spectra of trans-PDTE between 1750 and 750 cm$^{-1}$. Reference spectra collected at 0 V. Spectra were shifted for clarity.

with the IR of the monomer. This is attributed to the presence of cross-linked thiophene units or the occurrence of "mislinkages" through the β- positions.[38]

SNIFTIRS peaks at 1631, 923/ 858 and 839 cm$^{-1}$ are in good agreement with the υ(C=C)$_{ethylene}$, υ(C-S)$_{ring}$ and γ(C-H) vibrations found in the FTIR spectrum of **trans-DTE**. Peaks at 1049 and 1032 cm$^{-1}$ can be related with the out-of plane deformation (C-H)$_{ethylene}$ and stretching vibration (C=C)$_{ethylene}$ seen in the IR spectrum of the monomer at 965 and 945 cm$^{-1}$.

New absorption peaks are observed at 1365, 1390 and 1476 cm$^{-1}$ (shifts to 1493 cm$^{-1}$ as the polymer oxidised). The emergence of these bands upon p-doping is due to the displacement of the position of the double bonds forming quinoid structures.[39,40]The incorporation of electrolyte anions ($PF_6^-$) into the film during oxidation of trans-PDTE is seen 848 cm$^{-1}$ as an increasing positive band.[18,41]

The SNIFTIR spectra of **trans-PDTE** seems to lack some of the characteristic features usually found in IR spectra of p-doped polythiophenes , i.e. the presence of the Infra Red Active Vibrations - IRAV (created from the coupling of the quinoid-type vibrations of the polymer backbone), or a broad absorbance band in the near infrared due to the existence of free charge carriers.[42]

Their absence indicates that, even though polarons and bipolarons could be formed as **trans-PDTE** is oxidised, their mobility throughout the chain must be considerably limited. This can be explained by the presence of mislinkages through the β-positions that would result in "defects" in the polymer backbone, reducing the conjugation length and interfering with the formation of bipolarons in the oxidised polymer.[38, 43]

Another possible justification for the low conductivity exhibited by **trans-PDTE**-is that a branched polymer is formed upon polymerisation (Figure 7). In such case, the occurrence of head-to-head couplings during the electropolymerisation can induce a considerable deviation from coplanarity between adjacent rings leading to poor π-orbital overlap and consequently, a reduction in the electrical conductivity.[38]

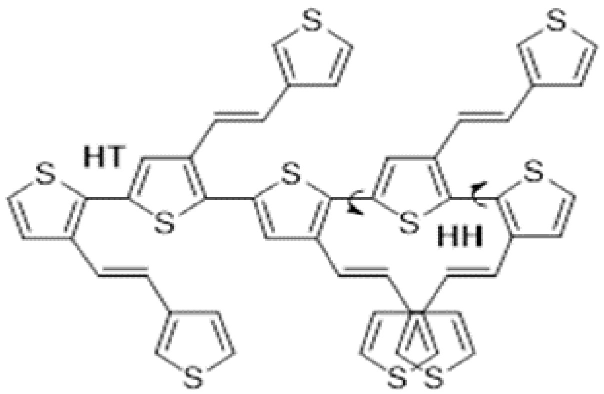


Figure 7 - Possible structure of **trans-PDTE** with head-to-tail (HT) and head-to-head (HH) coupling between thiophene units.

## Electrochemical and Spectroelectro chemical Studies on Iodine-doped trans-PDTE

In order to improve the electrical properties of the neutral and doped state of **trans-PDTE**, iodine (an electron acceptor) was used as a chemical p-doping agent. Iodine has been frequently employed as an oxidant for the doping of conducting polymers due to the ease of the doping procedure.[44-46]

Upon exposure to iodine vapour, an ionic complex consisting of positively charged polymer chains and counter anions ($I_3^-$) is formed. , The reaction between **trans-PDTE** and iodine can be summarised in equation 2.[49,50]

$$[trans - PDTE] + 1.5\, I_2 \rightleftarrows [trans - PDTE]^{+} + I_3^{-} \qquad (2)$$

The presence of charge transfer (CT) complexes in the form of $I_3^-$, or even $I_5^-$, next to the absorbed $I_2$ has been confirmed by several techniques such as Raman spectroscopy, and UV-Vis spectroscopy.[51, 52]

It is now widely accepted that the conductivity of conjugated polymers upon doping is governed by charge carriers generated by these charge transfer complexes.[30]

The electrochemically prepared **trans-PDTE**, light-yellow in colour, was exposed to iodine vapour. Upon doping with $I_2$, a colour change took place to dark-orange due to extra $I_2$ on the film surface. The doped polymer was carefully washed with acetonitrile to remove any excess iodine and analysed by cyclic voltammetry (Figure 8).

The voltammogram of iodine doped **trans-PDTE** is considerably similar to the one of the undoped polymer with the sequential oxidation to polarons and bipolarons taking place at $E^1_{ox}$ = 0.80 and $E^2_{ox}$ = 1.09 V, respectively. An extra oxidation peak is seen at $E^3_{ox}$ = 0.36 V attributed to the oxidation of iodine[50] The comparison of the voltammetric response of **trans-PDTE** (Figure 12) before and after exposure to iodine vapour reveals a decrease in the oxidation potential values. This is most likely caused by the presence of $I_3$- ions incorporated into the film, which can induce the existence of partially oxidised areas in **trans-PDTE** facilitating the formation of polarons and bipolarons. The reduction of $I_2$ doped **trans-PDTE** occurs at $E^1_{red}$ = 0.57 V, a considerably lower potential value than the one observed for **trans-PDTE** before chemical doping ($E^1_{red}$ = 0.83 V). This shift in the reduction peak potential indicates an increased stability of the p-doped state upon exposure to iodine vapour.[53] A second reduction peak, attributed to the removal of trapped positive charges remaining on the polymer can be seen at $E^2_{red}$ = - 0.11 V.[24,26]

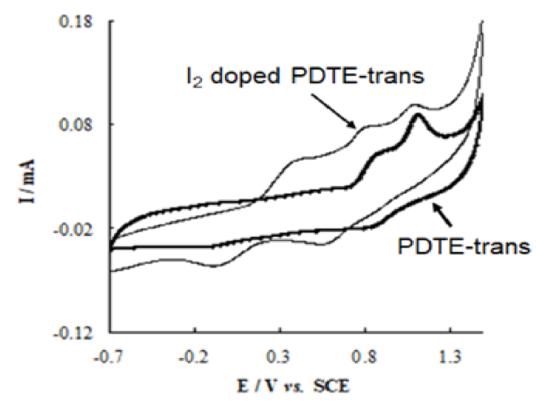


Figure 8 - Cyclic voltammogram of **trans-PDTE** in monomer free solution (0.1 M $TBAPF_6$ / MeCN), before and after $I_2$ doping recorded at υ = 0.1 V $s^{-1}$ using a Pt disc working electrode (0.44 $cm^2$).

The redox response of $I_2$ doped **trans-PDTE** was investigated by SNIFTIRS. Using as reference the spectrum taken at 0 V, the stepwise oxidation is shown in Figure 9.

**Trans-PDTE** exhibits significantly different spectroelectrochemical behaviour after chemical doping displaying similar IR characteristics to those of polythiophenes. As the polymer is oxidised, a very large broad band, extending into the near IR region is seen. This band is caused by the transition of electrons from the valence band to new electronic states in the bandgap.[23,35] In addition, new infrared vibrations bands (IRAV) at 1072, 1116, 1193 and 1373 $cm^{-1}$, not seen in the spectra of **trans-PDTE**, are observed. Previous studies have shown that these peaks are due to the selective enhancement of four thiophene ring modes associated with the formation of polaronic or bipolaronic structures in the polymer chain.[54]

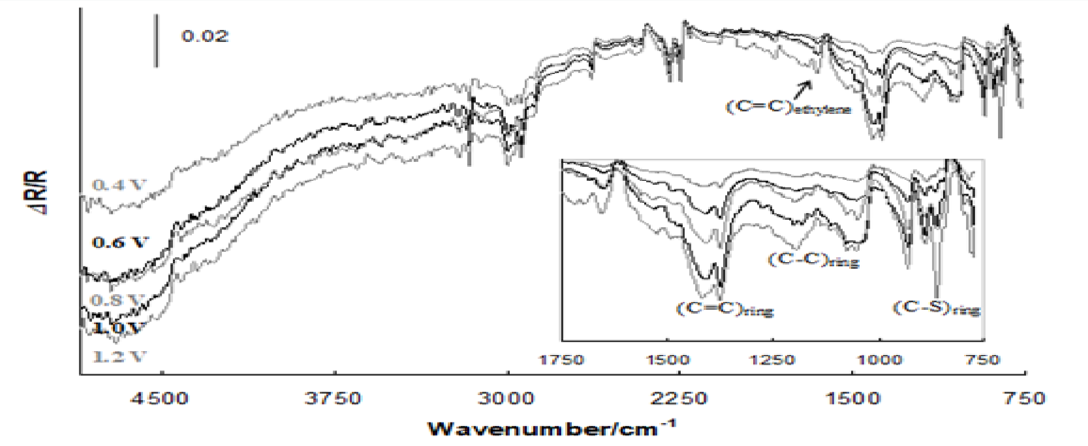


Figure 9 - SNIFTIRS spectra of iodine doped **trans-PDTE** taken from 0.4 to 1.2 V and expansion of the SNIFTIRS spectra between 1750 and 750 cm-1. Reference spectra collected at 0 V. Spectra were shifted for clarity.

Peaks at 1521/1413 cm-1 and 1373/1193 cm-1 are assigned to C=C and C-C ring stretching vibrations.[18,23] Strong C-S ring vibrations appear at 923, 888, and 860 cm-1.[55]The C=C ethylenic stretching vibration can be seen at 1650 cm-1.[32]

From the cyclic voltammetry and SNIFTIRS data it is clear that, on exposure to $I_2$ vapour, changes occur in the electrical properties of **trans-PDTE**. Not only an increased stability in the doped state was achieved, but also, the previously not seen transition of electrons from the valence band to intermediate energy levels could be observed in the near infrared. Studies on polythiophenes have suggested that this can be explained by the occurrence of changes in the polymer morphology caused by charged species introduced through the oxidation by $I_2$.[56] As the polymer is chemically oxidised, a certain amount of **trans-PDTE** salt is formed and therefore, the doped **trans-PDTE** becomes an ionomer. An ionomer refers to polymers containing ionic groups that have the capability to form intermolecular ionic bonds.[56, 57] Association between ionic groups would lead to the formation of multiplets that can aggregate and form clusters.[57, 58] This could prompt an enhancement in conductivity as the conducting entity would no longer be a single polymer chain, but rather, many chains. Increased spatial arrangement of the polymeric chains could also lead to a more stabilised doped state which is responsible for higher conductivity levels.[56]

## Electrochemical and Spectroelectrochemical Studies on cis-DTE

Dithienylethylene **cis-DTE** was also investigated by cyclic voltammetry and SNIFTIRS. The voltammogram of **cis-DTE** exhibits two redox couples corresponding to the formation of radical cations ($E^1_{ox} = 0.75$ V / $E^1_{red} = 0.61$ V) and dications ($E^2_{ox} = 1.04$ V / $E^2_{red} = 0.88$ V).

These peaks occur at potentials similar to those seen in the voltammogram of **trans-DTE**, which leads to the conclusion that the different structures of the two isomers do not influence their electroactivity. However, attempts to potentiodynamically grow a **cis-PDTE** film failed. Instead, it was possible to potentiostatically grow a film at 1.6 V over 4-5 minutes. The resultant light-yellow polymeric film was characterised in a monomer-free electrolyte solution. Figure 10 shows the voltammetric response obtained between different potential limits.

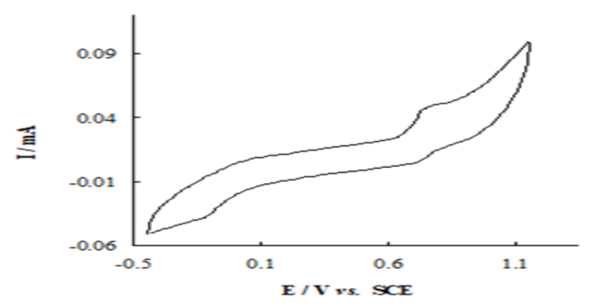


Figure 10 - Cyclic voltammogram of cis-PDTE in monomer free solution (0.1 M $TBAPF_6$ / MeCN) recorded at $\upsilon = 0.1$ V s-1 using a Pt disc working

electrode (0.44 cm²).

The cyclic voltammogram of **cis-PDTE** shows a redox process at $E^1_{ox}$= 0.71 V / $E^1_{red}$= 0.65 V. In contrast with the electrochemical behaviour observed for **trans-PDTE**, the formation of a bipolaronic state at more positive potential values cannot be identified by voltammetry. The reduction of **cis-PDTE** occurs at $E^2_{red}$= -0.17 V (Figure 10).

Reproducible voltammograms could only be obtained when cycling in the potential range between -0.6 and 1.3 V. **cis-PDTE** loses its electroactivity when cycled beyond this potential range. This is a significantly smaller window of potential stability when compared with **trans-PDTE** (from -1.0 to 2.0 V). In addition, the oxidation of **cis-PDTE** ($E^1_{ox}$= 0.71 V) occurs at a lower potential than that of the **trans-PDTE** isomer ($E^1_{ox}$= 0.89 V) These observations suggest that the electropolymerised **cis-PDTE** is "less stable" than the **trans-PDTE** isomer. The diminished stability of the cis isomer is consistent with reported data for both polyacetylene and poly-dithienylethylene.[59, 60]

For polyacetylene, the cis form was found to be thermodynamically less stable than the trans one, undergoing isomerisation upon doping.[61, 62] In the case of dithienylethylene, the polymerisation of the trans and cis isomers has produced the same trans polymer.[60]

SNIFTIRS studies were carried out to examine the changes in the spectral properties of **cis-PDTE** upon oxidation. The obtained difference spectra recorded from 0.5 to 1.1 V and referenced to the spectrum collected at 0 V are shown in Figure 11.

A significant increase of infrared vibrations is observed from 0.8 V, coinciding with the polymer oxidation at $E_{ox}$ = 0.71 V seen in the cyclic voltammogram of **cis-PDTE** (Figure 10). Electrolyte absorption peaks appear around 2250 and 3000 cm-¹.[18] Large peaks centred at 1420 and 1056 cm-¹ are assigned to $\upsilon(C=C)_{ring}$ and $\upsilon(C=C)_{ethylene}$, respectively.[5, 63] The broadness of these peaks is probably obscuring $(C-C)_{ring}$ and $(C-H)_{ethylene}$ vibrations expected in this frequency region. Vibration of the C-S bonds in the thiophene rings can be seen at 923 cm-¹. However, the notable absence of a large baseline shift extending into the near IR is indicative of a lack of electronic conductivity.

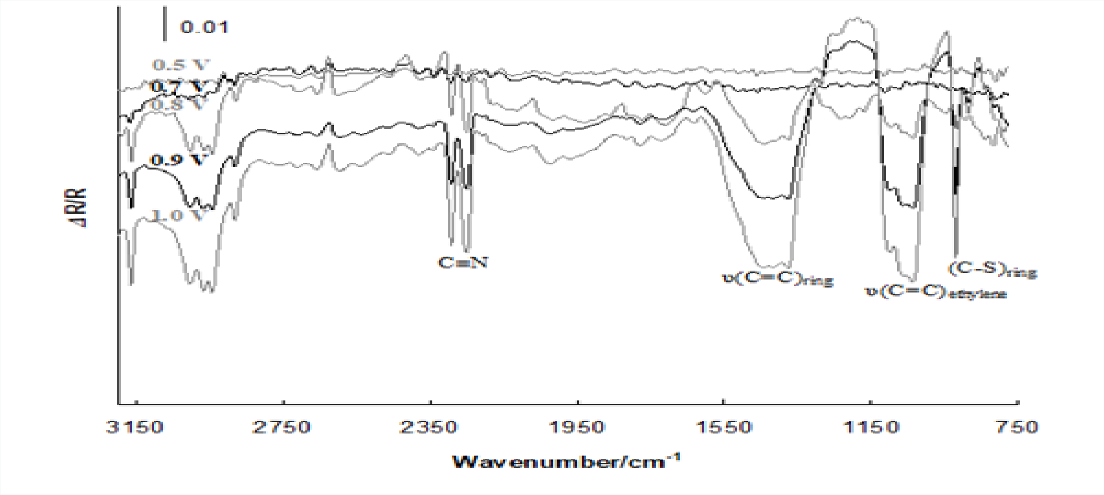


Figure 11 - SNIFTIRS spectra of **cis-PDTE** taken from 0.5 to 1.0 V. Reference spectra collected at 0 V. Spectra were shifted for clarity.

## Electrochemical and Spectroelectrochemical Studies on Iodine-doped cis-PDTE

Figure 12 illustrates the voltammetric response obtained between different potential limits for the $I_2$-doped and undoped **cis-PDTE**.

The presence of iodine incorporated into the polymeric film is confirmed by the appearance of an oxidation peak at $E_{ox}$= 0.33 V. The oxidation of **cis-PDTE** does not appear to be affected by the exposure to I2 vapour, taking place at $E^1_{ox}$= 0.70 V. Two clear reduction peaks ($E^1_{red}$= 0.55 V, $E^2_{red}$= -0.25 V) can be observed at lower potential values in comparison with the ones seen prior to chemical doping. This can imply an increased stability of the p-doped state upon exposure to iodine vapour as already

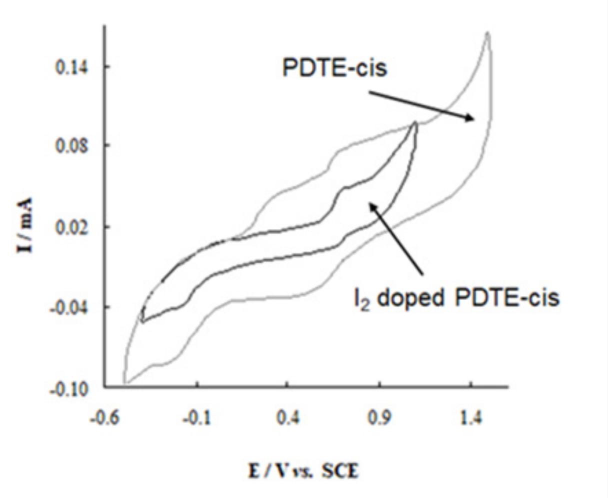


Figure 12 - Cyclic voltammogram of cis-PDTE in monomer free solution (0.1 M $TBAPF_6$ / MeCN) before and after $I_2$ doping recorded at υ = 0.1 V s⁻¹ using a Pt disc working electrode (0.44 cm²).

The redox behaviour of $I_2$ doped **cis-PDTE** film was investigated by SNIFTIRS. The obtained IR spectra taken during the stepwise oxidation are shown in Figure 13 alongside with the SNIFTIR spectrum of **cis-PDTE** at 0.9 V.

From Figure 13 it can be seen that the $I_2$-doped and the undoped **cis-PDTE** polymers exhibit similar IR responses upon oxidation. However, the peaks observed with the iodine doped film are much sharper. It is apparent that the chemical doping with iodine led to an enhancement of the IR characteristics of the polymer. This can be explained by the occurrence of morphology changes caused by the charged species resulting from $I_2$ doping, as previously suggested for $I_2$-doped **trans-PDTE**. However, in contrast with the spectroelectrochemical response of $I_2$-doped **trans-PDTE**, the chemical doping of **cis-PDTE** does not lead to the appearance of a baseline drop in the near infrared which is a typical feature of conjugated polymers as they become conductive.

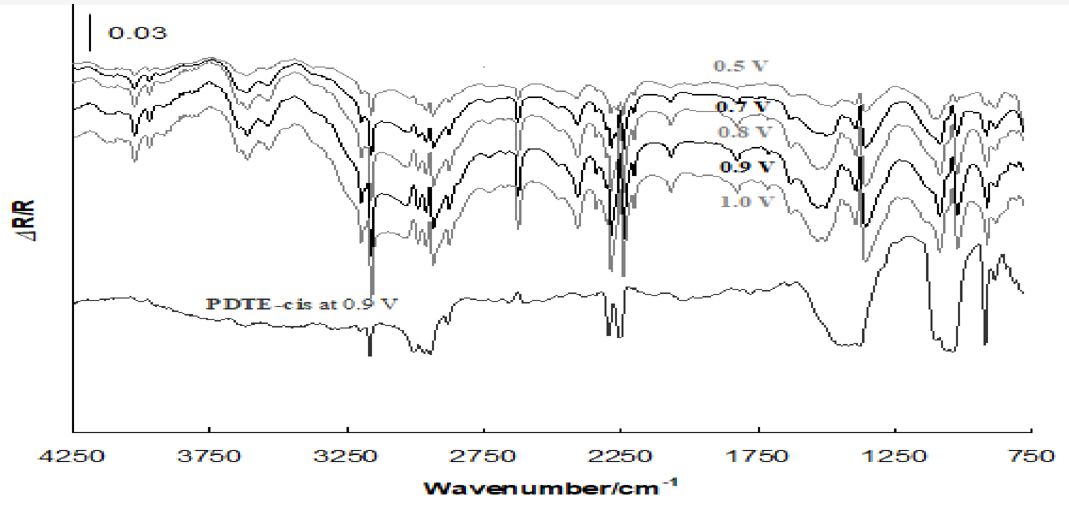


Figure 13 - SNIFTIRS spectra of iodine doped **cis-PDTE** taken from 0.5 to 1.0 V. Reference spectra collected at 0 V. Spectra were shifted for clarity.

Peaks due to the C=C, C-C and C-S ring vibrations can be seen at 1506, 1355 and 916 cm⁻¹, respectively. A closer look into the SNIFTIR spectra (Figure 14) reveals the presence of the C-H out-of-plane deformation and C=C stretching vibration (C=C) of the ethylene unit at 1089 and 1022 cm⁻¹, respectively.

As the polymer is oxidised, the intensity of the $\upsilon(C{=}C)_{ethylene}$ vibration is considerably increased. This spectral behaviour was not observed for **trans-PDTE** either before or after iodine doping implying that in the trans isomer the ethylene bond is not particularly affected by doping. Also, as previously mentioned, upon doping with $I_2$, **trans-**

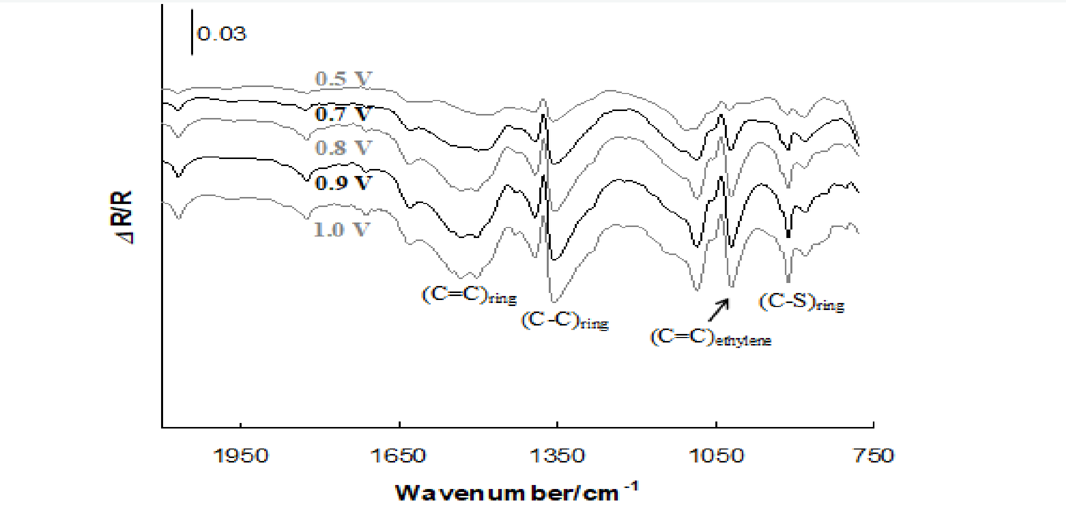
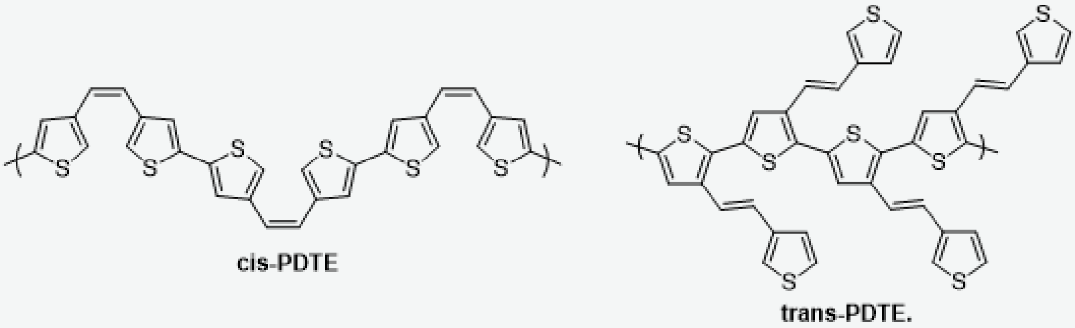


Figure 14 - SNIFTIRS spectra of iodine doped **cis-PDTE** from 2100 to 750 $cm^{-1}$. Reference spectra collected at 0 V. Spectra were shifted for clarity.

**PDTE** exhibits an IR response characteristic of polythiophenes. This suggests that the ethylene linkages are not part of the polymer backbone structure whereas the polymer backbone in **cis-PDTE** involves the ethylenic groups. Taking this into account, and bearing in mind that the coupling between the thiophene units occurs mostly through the α,α- positions, the most likely representations of the polymer structures of **cis-PDTE** and **trans-PDTE** are shown in Figure 15.

Considering the polymer structures suggested in Figure 15, charge movement in trans-PDTE occurs all the way through the polythiophene backbone, whereas **cis-PDTE** localized charged species that do not extend into the chain.



cis-PDTE

trans-PDTE.

Figure 15 - Proposed structures for **cis-PDTE** and **trans-PDTE**.

## Conclusion

Electrochemical and spectroelectrochemical investigations were carried out on two thienylethylenes isomers, **trans-DTE** and **cis-DTE**. The latter was more difficult to polymerise and a polymer film could only be obtained under potentiostatic control. SNIFTIRS data showed the emergence of new IR bands upon oxidation of the polymer films due to the formation of quinoid structures. However, the spectra of both isomeric films did not exhibit the IR features characteristic of conductive polymers.

Upon doping with $I_2$, the SNIFTIR spectra of **trans-PDTE** displayed a spectral feature similar to those of other conducting polymers manifested by a large baseline shift extending into the near IR. On the other hand, the spectra of **cis-PDTE** did not show this behaviour. The comparison between the electrochemical responses of **trans-PDTE** before and after exposure to iodine vapour showed a decrease in the oxidation and reduction potential values upon $I_2$ doping. These shifts are associated with the presence of $I_3^-$ ions (incorporated into the polymer film) that can induce the existence of partially oxidised areas in **trans-PDTE**. With $I_2$ doping, a certain amount of **trans-PDTE** salt was formed and therefore the doped **trans-PDTE** would become an ionomer - a polymer containing ionic groups that have the capability to form intermolecular ionic bonds. Association between these ionic groups would lead to the formation of multiplets with the capability to aggregate and form clusters. This could result in an increase in the conductivity levels since the conducting entity would no longer be a single polymer chain, but rather, many chains. Increased spatial arrangement of the polymeric chains could also lead to a more stabilised doped state which would be responsible for higher conductivity levels.

The iodine doping of **cis-PDTE** brought about a negative shift of the reduction peak potential which indicates an increased stability of the p-doped state, as previously described for $I_2$ doped **trans-PDTE**. The SNIFTIRS data have shown an enhancement of the IR characteristics of the polymer upon iodine doping but, in contrast with the spectroelectrochemical behaviour of $I_2$ doped **trans-PDTE**, the chemical doping of **cis-PDTE** did not trigger the appearance of a baseline drop in the near infrared. The oxidation of $I_2$ doped **cis-PDTE** caused an increase in the intensity of the (C=C)ethylene vibration that could be monitored by SNIFTIRS. This IR behaviour has not been observed in **trans-PDTE** either before or after iodine doping indicating that in the trans isomer the ethylene bond is not particularly affected by doping. This leads to the suggestion that the ethylene linkages are involved in the charge transport mechanism across the polymer chains in the **cis-PDTE** film but not in **trans-PDTE**. Therefore, we conclude that the charge movement in trans-PDTE occurs through the polythiophene backbone whereas **cis-PDTE** exhibits a charge-transfer mechanism resembling that of polyacetylene.

## Experimental Section

### Synthesis of **cis-DTE** and **trans-DTE**

To a cooled (0 °C) stirred suspension of 1 (3.02 g, 6.82 mmol) in dry THF (30 ml), n-butyllithium (2.2 M, 3.5 ml, 7.5 mmol) was added and the reaction mixture stirred for 30 minutes. The reaction was then cooled to -78 °C and 2 (0.97 g, 8.65 mmol) was added dropwise. This solution was stirred for 2 hours at -78 °C and allowed to warm to room temperature slowly.

The reaction was quenched by the addition of water (50 ml), and was extracted with diethyl ether (3 x 50 ml). Solvents were removed in vacuo, and the crude product purified by column chromatography (0-3 % diethyl ether in hexane). Sample vials containing spots at $R_f$ 0.42 (diethyl ether/hexane 10:90) were combined to give **cis-DTE** (0.18 g, 0.93 mmol), whilst spots at $R_f$ 0.23 (diethyl ether/hexane 10:90) were combined to give **trans-DTE** (0.55 g, 2.86 mmol). The cis:trans ratio of the reaction was 1:3, with an overall yield of 56%.

**cis-DTE** 14%; oil; δH ($CD_3CN$, 400 MHz) 7.30 (2H, dd, J 5.0. 3.0 Hz, 2 x CH), 7.24 (2H, d, J 3.0 Hz, 2 x CH), 6.96 (2H, d, J 5.0 Hz, 2 x CH) 6.53 (2H, s, 2 x CH); δC ($CD_3CN$, 100 MHz) 139.5, 128.9, 126.5, 124.9, 124.9; vmax 3097, 3008, 1772, 1694, 1630, 1573, 1427, 1348, 1262, 1213, 1155, 1123, 1079, 992, 943, 922, 839, 813, 787, 754, 738, 687, 654, 637, 585; **HRMS** (CI) Found 193.0143, $C_{10}H_9S_2$ ($[M+H]^+$) requires 193.0140.

**trans-DTE** 42%; mp 163-5 °C (lit. 166-7 °C); δH (CD3CN, 400 MHz) 7.41 (2H, dd, J 4.9, 2.7 Hz, 2 x CH), 7.37 (2H, d, J 4.9 Hz, 2 x CH), 7.34 (2H, d, J 2.7 Hz, 2 x CH), 7.08 (2H, s, 2 x CH); δC ($CD_3CN$) 141.2, 127.5, 125.8, 123.8, 123.2; vmax 3092, 3003, 1816, 1767, 1578, 1467, 1420, 1269, 1235, 1163, 1082, 962, 943, 863, 823, 775, 713, 665, 640; **HRMS** (CI) Found 193.0146, $C_{10}H_9S_2$ ($[M+H]^+$) requires 193.0140.

## Cyclic Voltammetry

The voltammetric behaviour of **cis-DTE** and **trans-DTE** were investigated using monomer solutions of 0.003 mol $dm^{-3}$ in supporting electrolyte which was made of tetra-n-butyl ammonium hexafluoro phosphate (TBAPF6 purity › 98%, AVOCADO Research Chemicals Ltd; 0.1 mol $dm^{-3}$) in acetonitrile (MeCN - purity › 99.9%, Riedel-de Häen; stored over molecular sieves). All solutions were degassed with $N_2$ prior to any measurements. Experiments were performed in a three-electrode glass cell using a platinum disc as the working electrode (electrode area = 0.44 $cm^2$), a platinum foil as the counter electrode, and $Ag/Ag^+$ as the reference electrode. The reference electrode was an Ag wire dipped into a degassed solution of the supporting electrolyte containing $AgNO_3$ (0.01 mol $dm^{-3}$). Throughout this paper, all potentials have been converted and quoted against the SCE.

Attempts to grow the polymeric films were carried out potentiostatically or potentiodynamically by cycling the electrode potential in an electrolyte solution containing the monomer units. Prior to each experiment, the electrochemical cell was de-gased with $N_2$ for 30 minutes. All subsequent voltammetric measurements were carried out using a home-made potentiostat, and a waveform generator (HI-TEK instruments PP R1). The output was plotted using an X-Y recorder (LLOYD instruments PL3).

## SNIFTIRS

Subtractively normalised interfacial Fourier transform infrared spectroscopy (SNIFTIRS) measurements were performed using a completely evacuated Bruker IFS 113v computer-controlled FTIR spectrometer. The optics bench was evacuated prior to any experiment to eliminate interference from atmospheric $CO_2$ and $H_2O$. The spectrometer operates with a silicon carbide source, which has a range of 6000 -100 $cm^{-1}$, an MCT (mercury-cadmium-telluride) liquid nitrogen cooled detector and a Ge/KBr beam splitter. A silicon disc was used as the infrared transparent window, separating the electrochemical cell from the evacuated spectrometer. The instrument was set-up to allow external reflection by focusing the IR beam onto the working electrode. The potential was applied to the working electrode using a potentiostat, HI TEK type DT2101, connected to a waveform generator (HI-TEK instruments PP R1). The electrode potential was then allowed to stabilise before collecting the IR data. The difference spectra were obtained by subtracting two spectra (S2-S1) collected at different potentials ($E_2$ and E1, respectively) and dividing by the spectrum obtained at $E_1$ (S1). The positive and negative bands in the normalised difference spectra indicate decreased and increased absorbances, respectively at $E_2$. Throughout these studies 100 interferograms were collected at each potential. Since no logarithm was applied, the difference spectra are shown as reflectance units ($\Delta R/R$). Further details of the SNIFTIRS set-up and of the cell used have been described elsewhere.[65]

## Chemical doping

Chemical doping was performed by exposing the electropolymerised films to iodine vapour for a period of 24 hours at 40 °C. Subsequently, the doped polymers were carefully washed with acetonitrile to remove any excess of I2 and analysed by CV and SNIFTIRS.

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