

Nickel dithiolenes containing pendant thiophene units: Precursors to dithiolenes/polythiophene hybrid materials

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Supplementary Information

Cyclic Voltammetry of **3**

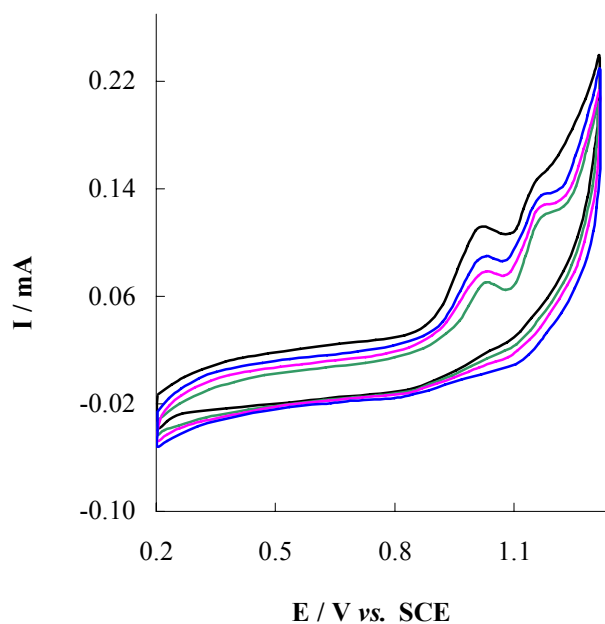


Fig. S1: Voltammograms of the polymerisation of **3** recorded at 0.1 Vs^{-1} (1st, 5th, 10th and 15th cycles), showing increasing currents due to film formation.

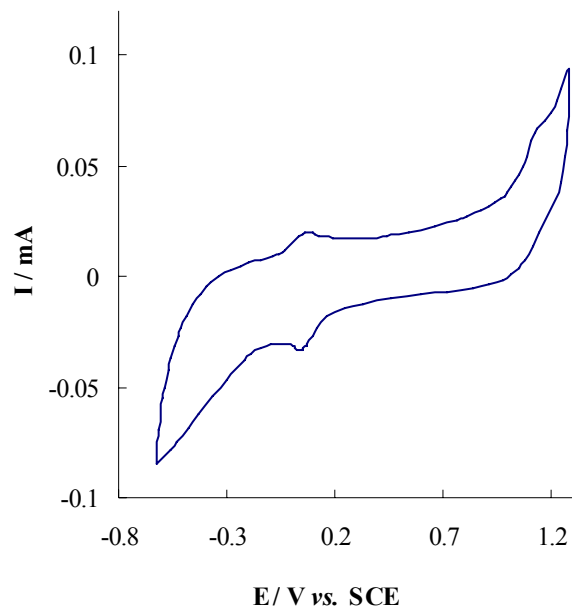


Fig. S2: Cyclic voltammogram of poly-**3** in monomer-free solution (0.1 M TBAPF₆ / MeCN) recorded at 0.1 Vs⁻¹ using a Pt disc working electrode (0.44 cm²).

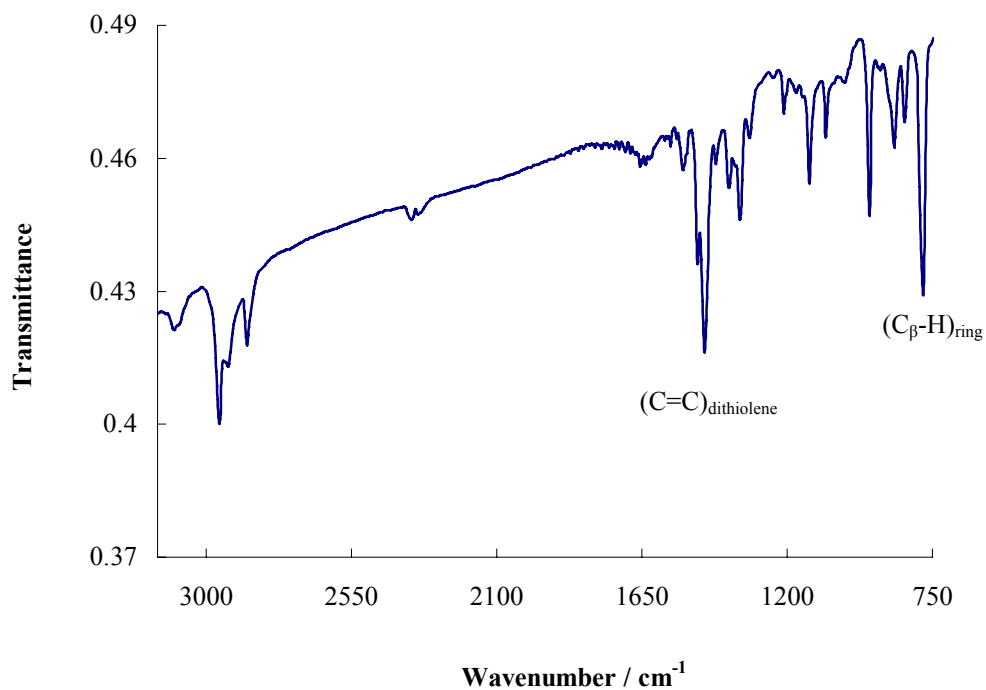


Fig. S3: Infrared spectrum of **3** in KBr disc pellet

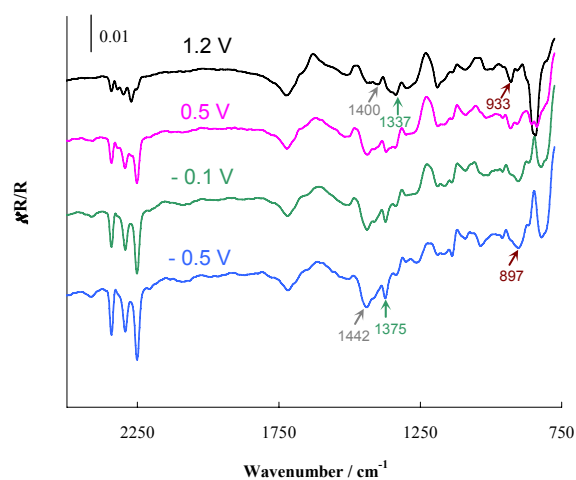


Fig. S4 SNIFTIRS spectra of poly-3 between 2300 and 750 cm^{-1} . Reference spectra collected at 0.3 V. Spectra are shifted for clarity.

Cyclic Voltammetry of 2

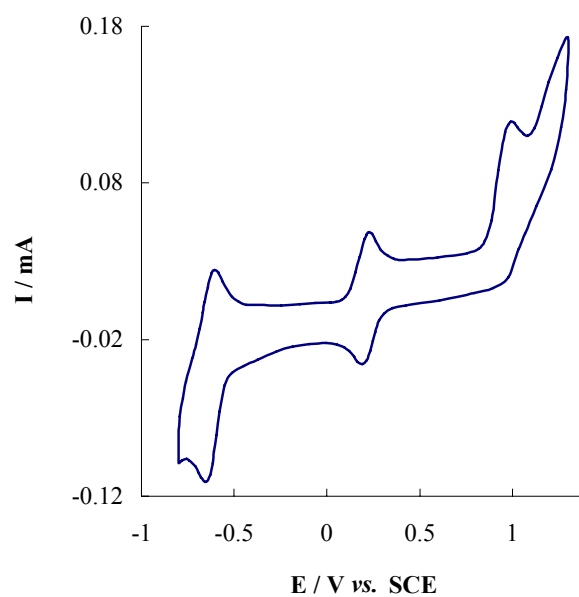


Fig. S5 Voltammogram of a solution of 2 ($0.0002 \text{ mol dm}^{-3}$) in electrolyte recorded at $\nu = 0.1 \text{ V s}^{-1}$.

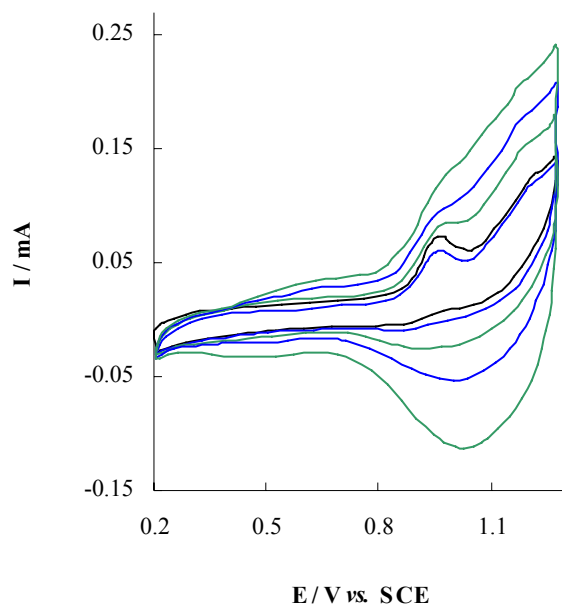


Fig. S6: Voltammograms of the polymerisation of **2** recorded at 0.1 Vs^{-1} (1^{st} , 2^{nd} , 8^{th} , 15^{th} and 25^{th} cycles), showing increasing currents with cycling.

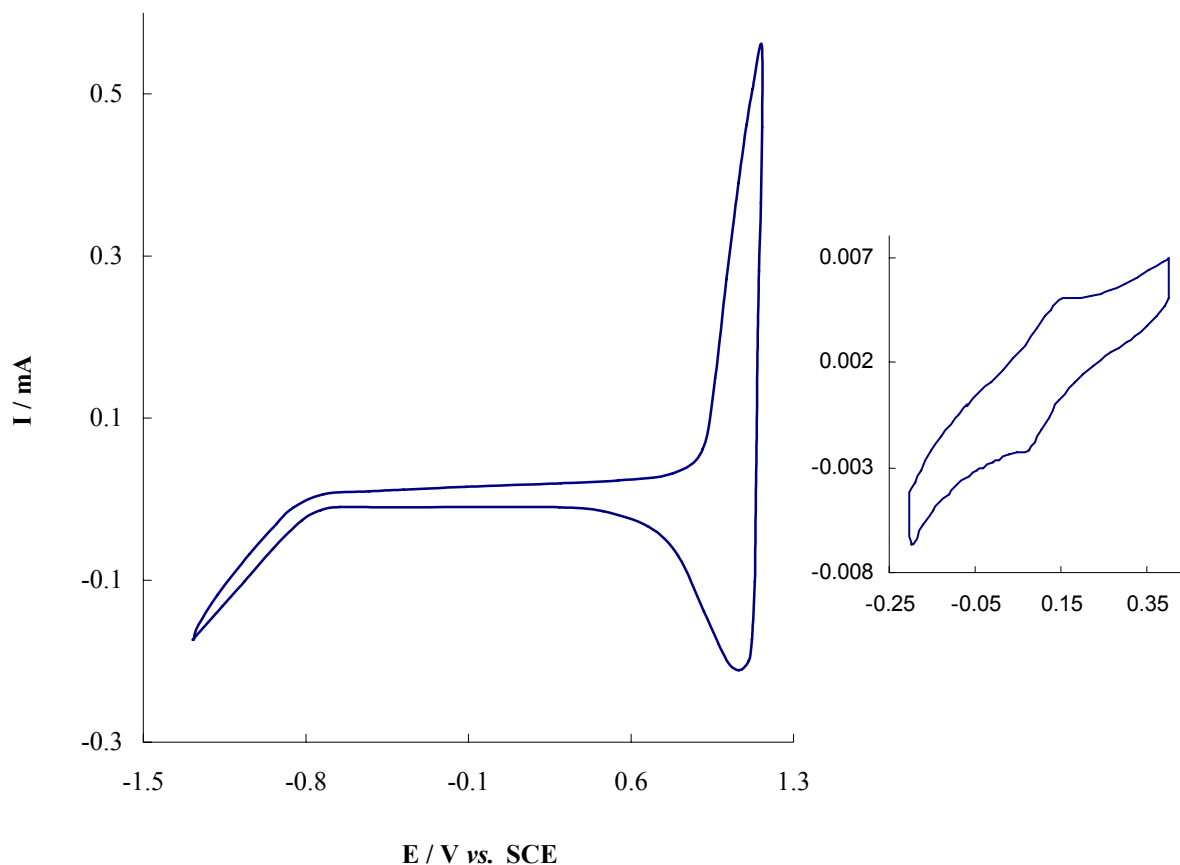


Fig. S7: Cyclic voltammogram of polymerised **2** in monomer-free solution at 0.1 Vs^{-1} . Expansion of the -0.25 to 0.35 V region to the right shows only extremely small peaks corresponding to the metal dithiolene complex $2^{-1}/1$ - redox couple .

The film formed from polymerisation of **2** shows an oxidation peak at around 1.05 V and a reduction peak around 0.94 V . The film was cycled repeatedly between the -1.4 and 1.3 V without any significant loss of electroactivity. The switching between the reduced and oxidised state was accompanied by a reversible colour change from red (reduced) to black (oxidised), a feature not observed in the yellow films of poly-**3**. The amplification of the voltammogram in Fig. S6 between -0.2 and 0.4 V reveals a reversible couple at $E_{\text{ox}} = 0.14 \text{ V}$ and $E_{\text{red}} = 0.08 \text{ V}$. These values are similar to the ones seen for the $-1/0$ redox process of the **2** monomer solution and therefore can be attributed to the electroactivity of the dithiolene unit, although the very low value of current observed suggests little incorporation of intact dithiolene complex and/or the presence of monomer trapped in the film. Overall, the electroactivity of poly-**2** seems to be very similar to a simple polythiophene and rather different from the one observed for poly-**3** which shows that the mode of attachment of the thiophene units considerably affects the outcome of the polymerisation. To shed light on the properties and the structure of polymerised **2**, *in*

situ SNIFTIRS measurements were performed on an electropolymerised film. The spectroelectrochemical investigation of the film was carried out employing a monomer-free electrolyte solution and using the same range of potentials as those applied during the characterisation of the film by cyclic voltammetry. The SNIFTIRS spectra (Fig. S7) were collected at successively higher potentials and normalised to the reference spectrum taken at 0.3 V. Analysis of the spectra between 800 cm^{-1} and 1600 cm^{-1} shows the Infra Red Active Bands characteristic of conducting polymers such as polythiophenes.^{S1, S2} These bands arise from the coupling of the quinonoid-type vibrations of the polymer backbone and become increasingly dominant as the film is oxidised.^{S3, S4} A very broad absorbance, attributed to the electronic transition between the valence band and the lowest polaron or bipolaron state,^{S5} is observed extending from about 2500 cm^{-1} out into the near-IR. Small peaks at 867 and 833 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of the C-S bonds of the thiophene rings.^{S6, S9} The absence of the spectroelectrochemical response characteristic of the electroactivity of the dithiolene unit (which was previously observed for poly-3) suggests that the dithiolene centre has not been incorporated. The voltammetric data appear to confirm this given that the charge involved on the redox process assigned to the dithiolene unit is significantly smaller than the one related with the oxidation of the polythiophene chain.

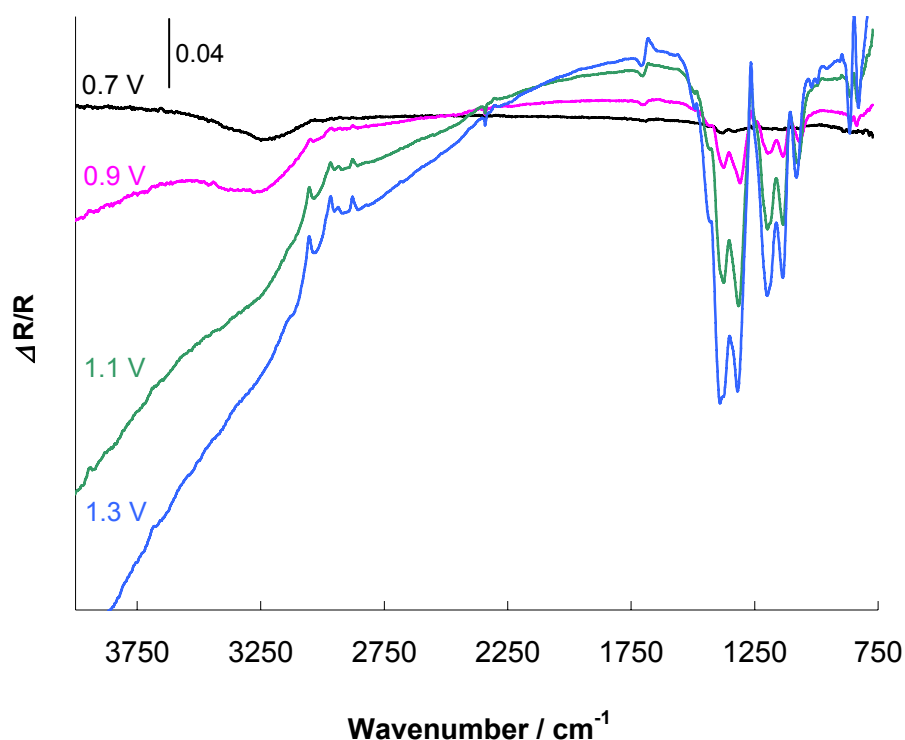


Fig. S8 SNIFTIRS spectra of polymerised 2 taken from 0.8 to 1.4 V. Reference spectra collected at 0.3 V.

(i) Fuller description of the formation of a molecular film of 3

Due to the unusual formation of a conducting molecular film of **3**, the electrochemical characteristics of this are described in more detail below.

A reversible redox process was observed at a half-wave potential of -0.78 V assigned as the 2-/1- process for the complex. Upon cycling towards more positive potential, an oxidation process was observed at a peak potential of $+0.12$ V, which can be assigned to the 1-/0 process. This peak is sharper than is generally observed for a simple electrochemical oxidation, and on reversing the direction of the scan the oxidation current was greater than that observed in the forward scan. This indicates that this oxidation results in film deposition, with subsequent oxidation being slightly more thermodynamically favoured on the film surface than on bare platinum. In addition, holding the potential at or above $+0.29$ V resulted in the deposition of a green film. The deposition of a film as a result of this oxidation is not surprising as it was previously observed that the neutral complex **3** is not soluble in CH_3CN . Oxidation at $+0.29$ V at a rotating disk electrode gave a constant current, i , with time at a fixed rotation speed, W , whilst i varied linearly with $W^{1/2}$ between 1 and 4 Hz. This indicates that the oxidation current is independent of film thickness and that the reaction is mass transport controlled. Both of these observations suggest significant electrical conductivity in the deposited film. The electrochemical reversibility of the oxidation at $+0.12$ V was found to be sensitive to both scan rate and concentration. The process became more reversible at increased scan rate (fig. S9), indicating that under these conditions the rate of the deposition process is comparable with the rate of CV cycling. The redox process was also more reversible at reduced concentration of $[\text{NBu}_4][\mathbf{3}]$ (see earlier results). This concentration dependence suggests that following oxidation, the chemical step involves the aggregation of electrochemically-generated neutral complexes to form the film.

Reduction of this deposited film results in a small associated reduction wave at around -0.04 V. The reduction wave is located significantly more negative in potential than would be expected for the simple reduction associated with oxidation of the 1-/0 couple if the process were occurring in solution. This is consistent with film formation on oxidation, as the thermodynamic stabilisation of **3** due to aggregation in a film would be expected to stabilise the neutral complex with respect to its reduction. Holding the potential anywhere in the region -0.12 to -0.52 V leads to the reduction and dissolution of the green layer. Thus, the reduction wave is attributed to the reduction of the neutral complex **3** to $[\mathbf{3}]^-$, which would be expected to lead to enhanced solubility and film dissolution. The relatively small height of the reduction wave indicates that reduction of this film is kinetically slow and the insensitivity of the reduction current to changes in potential (the constancy of the current, resulting in a wave, rather than a peak being seen) indicates that a chemical rather than an electrochemical step is the rate determining process for this reduction. Examples of possible chemical steps during dissolution are changes in molecular orientation and resolution. The formation of such a neutral, conducting film where re-reduction is kinetically controlled rather than potential dependent, from a nickel dithiolene complex has, to the best of our knowledge, not been previously observed.

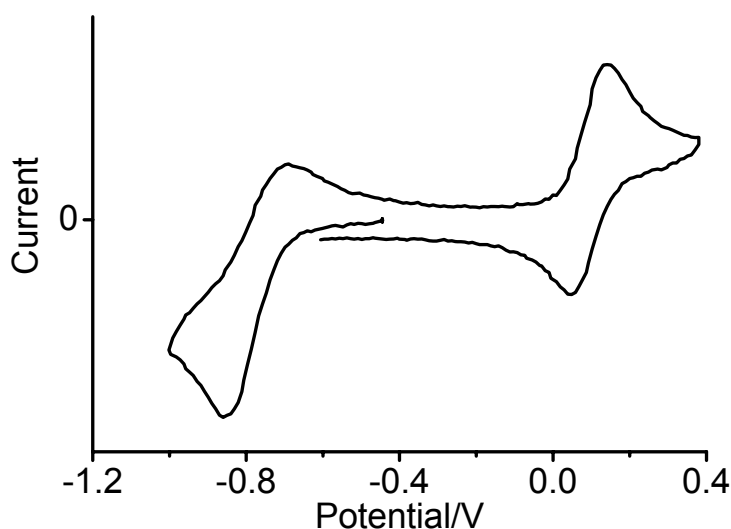


Fig. S9: Cyclic voltammogram of $[\text{NBu}_4][\mathbf{3}]$ in $\text{CH}_3\text{CN}/0.1\text{M} [\text{TBA}][\text{PF}_6]$ at 500mVs^{-1} showing increased chemical reversibility of the process at $+0.12\text{ V}$ when compared with slower scan rates.

Continuation of the scan shows the second reduction due to the deposited film at -0.75 V . This is superimposed upon the second reduction of the solution-based $[\mathbf{3}]$. It is interesting that the kinetic limitation of the first reduction is sufficiently slow to enable the second reduction due to the film to be seen. Furthermore, this second reduction is seen to be at a more positive potential than that observed for the solution species, indicating that the film species are less stable to reduction than the solution species at this potential. To fully account for the electrons involved in these processes, a film was generated on the working electrode by holding the potential at $+0.29\text{ V}$. Following this, the electrode was rinsed, then immersed in fresh electrolyte solution. In the first experiment, the cell was connected with the potential held at -0.31 V and the reduction current recorded with time. The total reduction charge was found to be 0.95 of the oxidation charge, confirming a stable, insoluble film for which, within experimental error, both the oxidation peak and the reduction wave correspond to a one-electron process attributable to the 1-/0 redox couple. In contrast, connecting the cell after oxidation at -1.01 V resulted in a total reduction charge 2.1 times greater than the oxidation charge. This indicates within experimental error that connecting the film at -1.01 V results in the reduction and dissolution of the neutral film in the -2 oxidation state, which confirms the assignment of the 2nd CV reduction peak at -0.75 V to the reduction of the 1- state to the 2- state.

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