# Nickel dithiolenes containing pendant thiophene units: precursors to dithiolene–polythiophene hybrid materials†

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The synthesis, electrochemical and spectroscopic properties of the new thiophene-substituted metal dithiolene complexes [Ni(b-3ted)$_2$] (**3**) and [NBu$_4$][Ni(b-3ted)$_2$] ([NBu$_4$][**3**]) are described [b-3ted = bis(3-thienyl)-1,2-ethylenedithiolene] and compared with new studies of the known compounds [Ni(b-2ted)$_2$] (**2**) and [NBu$_4$][Ni(b-2ted)$_2$] ([NBu$_4$][**2**]). X-Ray structures were determined for the neutral complexes **2** and **3** and both showed planar nickel dithiolene units with thiophene groups twisted out of the molecular plane, precluding close molecular π-stacking. Electrochemical investigations revealed two redox processes corresponding to interconversion between neutral, monoanionic and dianionic species for **3**, analogous to **2**. Oxidation of 0.1 mM [**3**]$^-$ in CH$_3$CN was shown to give a green molecular film of **3** which, in contrast to as-prepared crystals of **3**, showed significant conductivity. Electrochemical polymerisation of **3** carried out at different concentrations resulted in films; electrochemical, SNIFTIRS and UV-Vis results were consistent with incorporation of the intact metal dithiolene complex in these films. In contrast, electrochemical polymerisation of **2** gave a film charateristic of a polymerised thiophene but with no evidence of incorporation of the intact metal dithiolene complex. Copolymerisation of **3** with thiophene gave a gold-coloured electropolymerised film of significant conductivity that, upon dissolution in CH$_2$Cl$_2$, showed the characteristic low energy absorption of the Ni-dithiolene complex, confirming its incorporation. This copolymerisation approach offers a versatile route to the synthesis of metal dithiolene–polythiophene hybrid films.

## Introduction

Conducting polymers based on the electropolymerisation of heterocyclic monomers offer the possibility to prepare versatile, persuasible electronic materials, and as such have received wide attention over recent years.[1] Within this context, substituted polythiophenes exhibit attractive electronic properties, such as a low band-gap combined with good stability and ease of film formation *via* electrochemical or solution methods.[2]

Conducting molecular/organic materials based on π-stacking of planar redox active molecules have also been widely studied, involving molecular building blocks such as tetrathiafulvalene (TTF)[3] or metal-bis-1,2-dithiolene complexes.[4,5] In contrast to conducting polymers, molecular conductors typically show greater structural regularity allowing improved understanding of structure–property relationships, and this has led to a variety of materials showing properties such as metallic conductivity and superconductivity.[6] Furthermore metal-bis-1,2-dithiolene complexes also show low energy absorption bands in the NIR region of the spectrum which has led to their study as non-linear optical materials.[7]

From the viewpoint of technological applications however, processability of brittle crystalline molecular conducting materials is difficult, and conducting polymers have remained more prevalent in the development of technological devices, such as organic light emitting diodes and photovoltaics.[8] To fully utilise the attractive properties of molecular species such as metal dithiolene complexes and TTF derivatives it is important to find ways of increasing the processability of these materials. In this context, some of us developed over recent years TTF derivatives bearing thiophene moieties and showed that electrochemical polymerisation of these thiophene units could be achieved.[9–11] This demonstrated the possibility of preparing polythiophenes bearing TTF side groups with the potential to develop conducting materials combining the processability of the conducting polymer with some of the structural regularity that can be achieved in TTF-based conductors. The TTF may alter the conductivity properties

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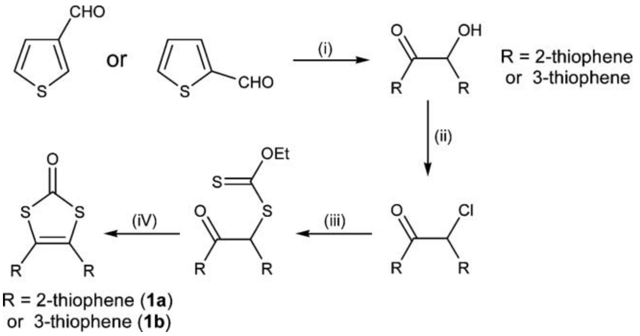
† Electronic supplementary information (ESI) available: Fig. S1: Voltammograms of the polymerisation of **3**. Fig. S2: Cyclic voltammogram (CV) of poly-**3** in monomer-free solution. Fig. S3: IR spectrum of **3** in KBr disc. Fig. S4: SNIFTIRs spectra of polymerised product from **3**. Fig. S5: CV of **2**. Fig. S6: Voltammograms of the polymerisation of **2**. Fig. S7: CV in monomer-free solution of polymerised product from **2**. Fig. S8: SNIFTIRS spectra of polymerised product from **2** and discussion of results. Fig. S9: CV of **3** in CH$_3$CN at a higher scan rate and fuller description of the formation of a molecular film of **3**. See DOI: 10.1039/b714372a

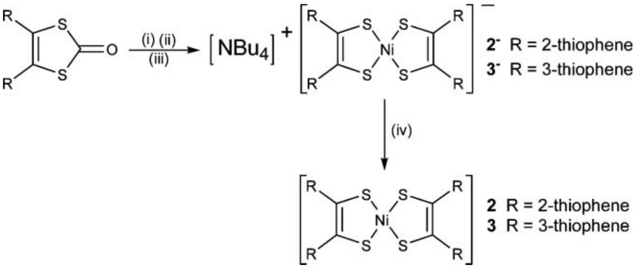


**Scheme 1** Preparation of the bis(2 or 3-thienyl)-1,3-dithiole-2-one ligand precursors (**1a**, **b**). Reagents and conditions: (i) $NEt_3$–MeOH (ii) $PPh_3$, $CCl_4$–$CH_2Cl_2$, RT (iii) KSC(S)OEt, acetone, RT (iv) HBr–AcOH, 0 °C.

of the resulting hybrid material either by providing an alternative conductivity pathway or by modifying the properties of the polymer by cooperative electronic effects.

It is also of interest to incorporate metal-bis-1,2-dithiolene complexes into such systems and the precursors we have developed for the preparation of TTF compounds (Scheme 1) can also be used as precursors for such dithiolene species. Indeed previous studies involving electropolymerisation of metal-bis-1,2-dithiolene complexes with appended thiophene units have been carried out by the groups of Pickup[12,13] and Skabara.[14] This approach offers tremendous opportunities for variation of the polymer side groups, as an enormous range of different metal centres and ancillary ligands can be employed for fine control of the redox, structural and optical properties. For example, the work of Skabara and co-workers led to the synthesis of an unusually low band-gap material with a broad absorption profile demonstrating that the incorporation of metal dithiolene complexes can prove useful in control of the optical properties of the polymer. Other advantages that may be envisaged include introducing a new pathway for conduction, exercising improved structural regularity or in introducing new functionality such as receptor groups, long-wavelength chromophores or catalytic sites.

In the work by Pickup and co-workers, the electrochemical polymerisation of **2** (Scheme 2) to achieve a conducting polymer was described, demonstrating the potential of these systems as functional materials.[12,13] In addition, our previous work on the electropolymerisation of thiophene-substituted TTF systems demonstrated that the substitution position of the thiophene greatly alters the ability of the molecules to be polymerised. Given that polythiophene consists predominantly of 2,5-linked thiophenes, copolymerisation of **2** with thiophenes should result in the incorporation of the metal-bis-1,2-dithiolene complex into the polymer backbone, whereas copolymerisation of the 3-substituted isomer **3** with thiophene should allow polythiophene to form with the metal complex attached as a side chain. Thus it is important to explore the role played by the thiophene substituent position in determining the electropolymerisation and copolymerisation capability of these molecules and the properties of the resultant films.



**Scheme 2** Preparation of the nickel-bis[bis(2 or 3-thienyl)-1,2 ethylenedithiolene] complexes (**2**, **3**). Reagents and conditions: (i) NaOMe–MeOH, RT (ii) $[NBu_4][Br]$–MeOH (iii) $NiCl_2\cdot6H_2O$–MeOH (iv) $I_2$–acetone.

This report therefore concerns a detailed study of complex **3** in comparison with the properties of the previously-studied complex **2**, which differs only in the point of attachment of the thiophene rings. The synthesis, structural properties, electrochemistry and electropolymerisation of both complexes are reported and a comparison given of their potential for use in functional materials. Following this, study of the copolymerisation of complex **3** with thiophene demonstrates the use of this precursor in hybrid materials.

## Results and discussion

The synthesis of the ligand precursors **1a** and **1b** is shown in Scheme 1. Full experimental details have been reported by us previously in the context of TTF-based compound syntheses.[10] These ligand precursors were each suspended in methanol under a dry argon atmosphere. Treatment of **1a** or **1b** with sodium methoxide in methanol afforded the soluble disodium salt of the dithiolate dianion, which was then allowed to react with $NiCl_2\cdot6H_2O$ dissolved in methanol. The monoanionic salts, $[\mathbf{2}]^-$ and $[\mathbf{3}]^-$, were precipitated from the dark brown reaction mixture using tetrabutylammonium bromide (Scheme 2). Recrystallisation of the crude complexes from $CH_2Cl_2$–ethanol, acetone–methanol or acetone–ether yielded the pure salts as dark purple crystalline solids.

The neutral complexes **2** and **3** were prepared by reacting the corresponding monoanion with iodine in acetone. A darkening of the solution colour was observed, followed by precipitation of the neutral complex. Alternatively, preparation of neutral **3** was achieved in higher purity by recrystallisation of $[NBu_4][\mathbf{3}]$ from acetone–ethanol in air. The deep red colour of the salt ($[NBu_4][\mathbf{3}]$) contrasts with the very pale green–brown colour of the final product and is consistent with an oxidation from the monoanionic to the neutral complex taking place during the recrystallisation process.

Crystals of **2** show one independent molecular unit (Fig. 1) with an approximately planar central $NiS_4C_4$ unit (rms deviation = 0.028) and a centre of inversion located on the Ni. The thiophene units however, show significant twists from this plane [12.50(18) and 81.91(12)° for the two independent rings containing S2 and S4 respectively]. Significant disorder is apparent within all of the thiophene units, due to free rotation of the thiophene rings through 180°, which results in a 15% partial occupation of the sulfur sites by carbon. The molecules stack along the *b*-axis with the $NiS_4C_4$ plane tilted at 43.15(13)° with respect to this axis. The twist within the

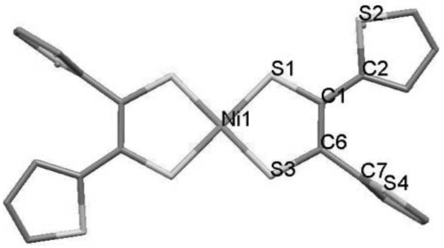


**Fig. 1** X-Ray structure of [Ni(b-2ted)$_2$] (**2**) showing the molecular unit and numbering scheme and with disorder and hydrogen atoms omitted for clarity. Selected bond lengths/Å: Ni1–S1 2.1302(7), Ni1–S3 2.1254(6), S3–C6 1.706(2), S1–C1 1.714(2), C6–C7 1.477(3), C1–C2 1.464(3), C6–C1 1.399(3).

thiophene units effectively prevents strong intermolecular contacts within the stacks and the separation between the planes within the stacks is 4.31(16) Å.

The structure of **3** consists of one independent molecular unit (Fig. 2) with some rotational disorder present in three of the four thiophene units leading to partial occupation of S5/C4 (75/25 ratio), S6/C9 (85/15 ratio) and S8/C19 (55/45 ratio). The central NiS$_4$C$_4$ moiety is essentially planar (rms deviation = 0.0552). All of the thiophene units are again twisted out of this plane [S5 ring = 29.93(6)°, S6 ring = 55.72(7)°, S7 ring = 50.42(8)° and S8 ring = 41.12(8)°] preventing the close molecular stacking typical for such dithiolene complexes. Thus the interplanar separation between the NiC$_4$S$_4$ cores of adjacent molecular units is 11.773(12) Å and the molecules are slipped along the short molecular axis away from a directly overlapping stack arrangement.

Many hundreds of structures have been reported for nickel-bis-1,2-dithiolene complexes, however the large majority of these involve dianionic, monoanionic or partially-charged species.[15] This reflects both the extensive study of these molecules in the field of conducting/magnetic materials and also the greater difficulty of crystallising the neutral complexes which normally have a lower solubility. Thus, only a few tens of literature reports of the structures of neutral nickel-bis-1,2-dithiolenes are recorded.[15] Many of these represent materials prepared for the study of conducting properties and include extended, delocalised frameworks attached to the dithiolene core such as TTF units[16,17] or thioalkyl units.[18] Similar species have also been prepared and studied to explore their optical properties.[7,19] Planar or approximately planar species generally show stacked complexes; examples are [Ni(dmit)$_2$][20] or [Ni(dddt)$_2$][21] (dmit = 2-thioxo-1,3-dithiole-4,5-dithiol; dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) which have interplanar distances of 3.562 Å and 3.76 Å respectively. In contrast, the lack of close stacking shown by **2** and **3** is more comparable with species such as [Ni(S$_2$C$_2$Ph$_2$)$_2$] which has phenyl rings twisted out of the plane.[22]

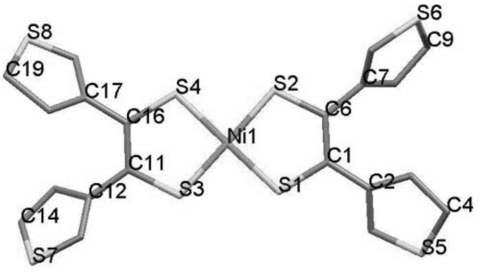


**Fig. 2** X-Ray structure of [Ni(b-3ted)$_2$] (**3**) showing the molecular unit and numbering scheme and with disorder and hydrogen atoms omitted for clarity. Selected bond lengths/Å: Ni1–S1 2.1275(8), Ni1–S2 2.1156(8), Ni1 S3 2.1242(8), Ni1–S4 2.1285(8), S1–C1 1.716(2), S2–C6 1.707(2), S3–C11 1.702(2), S4–C16 1.701(2), C1–C2 1.466(3), C6–C7 1.474(3), C11–C12 1.470(3), C16–C17 1.468(3), C11–C16 1.401(3), C1–C6 1.394(3).

Typical of nickel-bis-1,2-dithiolene species in the neutral or monoanionic form, is the intense low energy absorption around 920–970 nm that all of these new nickel dithiolenes exhibit, and this has been assigned as the $2b_{1u} \rightarrow 3b_{2g}$ transition.[23] The lack of significant bands in the visible region of the spectrum results in pale colours for the neutral complexes, and **3** in particular appears almost colourless, suggesting possible applications for this type of complex where strong NIR absorption is required without visible absorption. The presence of this intense low energy band has proven useful in the analysis of electrochemically-generated films as discussed below.

The electrical conductivity of compressed pellets of **3** was measured using the four-probe method and gave a room temperature value of $1 \times 10^{-5}$ Scm$^{-1}$. This is as expected for an undoped molecular material based on a metal-bis-1,2-dithiolene complex and the relatively low value is likely to also reflect the lack of π-stacking or strong intermolecular interactions observed in the X-ray structure.

### Electrochemical and spectroelectrochemical studies

**(a) Electrochemical studies at low concentration.** Cyclic voltammetry studies were performed on [NBu$_4$][**3**] (0.2 mmol in CH$_3$CN), with the salt chosen due to the poor solubility of the neutral complex **3** in CH$_3$CN. The results show two reversible or quasi-reversible one electron redox processes at $E^1_{1/2} = -0.79$ V, $\Delta E = 0.09$ V and $E^2_{1/2} = 0.07$ V, $\Delta E = 0.05$ V (Fig. 3). By analogy with the electrochemical behaviour reported for many dithiolene complexes these can be assigned

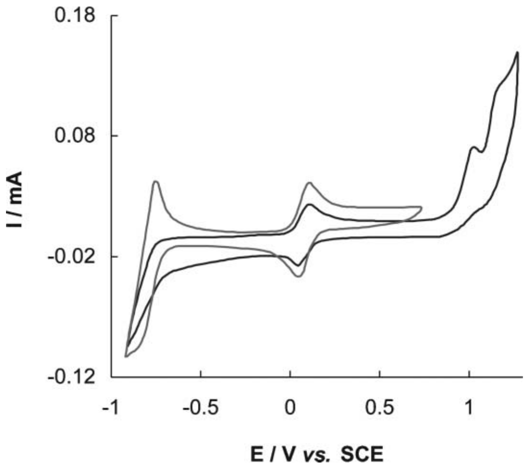


**Fig. 3** Typical voltammograms of a solution of **3** (0.2 mmol) in CH$_3$CN–0.1 M TBAPF$_6$ at $\upsilon = 0.1$ V s$^{-1}$.

to the sequential interchange between the neutral, anionic and dianionic states of the nickel dithiolene complex.[13,24–28] The separation of the two redox potentials is comparable to[29] $[Ni(S_2C_2H_2)_2]^{x-}$ and analogous systems where the metal-bis-1,2-dithiolene core is extended with –SR groups.[30] It is however significantly larger than in $[Ni(dmit)_2]^{x-}$ which indicates a poorer ability of **3** to delocalise the added charges. This implies that little conjugation onto the thiophene rings occurs and suggests that the twisted geometry evidenced in the X-ray structure is also found in solution. This is in keeping with the typical behaviour of 3-linked thiophene species.[31]

Cycling towards positive potential values reveals two oxidation peaks at $E^3_{ox}$ = 1.04 V and $E^4_{ox}$ = 1.17 V. The irreversible peak at $E^3_{ox}$ is probably due to the formation of the cationic state in the dithiolene unit.[13,32] The increase in the electrochemical potential up to $E^4_{ox}$ leads to the deposition of a polymer on the electrode surface, and therefore this peak can be assigned to the oxidation of the thiophene units to form radical cations, which link to form a polymer. Polymerisation of **3** was achieved by continued potential cycling between 0.3 V and 1.25 V (Fig. S1, ESI†).

The increase in peak currents with potential cycling is characteristic of electropolymerisation and continuous growth of a redox active film on the electrode.[2,33,34] The electroactivity of this yellow poly-**3** film was investigated using CV in monomer-free electrolyte solution. This voltammetric response (Fig. S2, ESI†) reveals a redox couple at $E_{1/2}$ = 0.06 V, $\Delta E$ = 0.03 V. The small peak separation, 30 mV, and the variation of current in direct proportion to scan rate are characteristic of a surface bound species.[35,36]

This confirms the immobilisation of an active redox couple at the electrode surface. By comparison with the electrochemical behaviour of **3** in solution, this can be attributed to the redox reaction involving the −1/0 states of the nickel dithiolene centre, which indicates that the incorporation of the intact metal complex into the polymer has occurred. The cyclic voltammogram of poly-**3** also shows a second peak at $E_{ox}$ = 1.17 V that is likely to arise from unlinked thiophenes in the film.

The spectroelectrochemical investigation of poly-**3** was carried out in a monomer-free electrolyte solution using the same range of potentials as those applied during the characterisation of the film by CV. In order to assign the IR peaks present in the SNIFTIRS spectra of poly-**3**, the FTIR spectrum of the neutral dithiolene **3** was initially measured (Fig. S3, ESI†). The FTIR spectrum of **3** displays several IR absorption bands related to the thiophene and dithiolene units. Peaks at 836 and 869 cm$^{-1}$ are assigned to C–S symmetric and asymmetric stretching vibrations of the thiophene rings.[11,37] The $C_\alpha$–H vibration and $C_\beta$–H out-of-plane deformation are observed at 3101 and 779 cm$^{-1}$, respectively.[38–40] The C=C stretching vibrations of the dithiolene group can be found at 1456 and 1346 cm$^{-1}$.[41–44] The C–C ring vibration is seen at 1378 cm$^{-1}$.[45,46] Smaller peaks at 1132 and 945 cm$^{-1}$ are due to the C=S and C–S vibrations of the dithiolene unit.[47,48]

The SNIFTIRS spectra of poly-**3** between 4000 and 750 cm$^{-1}$ were collected at successively higher potentials and normalised to the reference spectrum taken at 0.3 V. The spectra (Fig. 4) show an increase in the intensity of the IR absorbance peaks as the polymer is oxidised from 0.9 to 1.2 V. Solvent bands are seen centred at 3200 and 2300 cm$^{-1}$.[34,49] The sharp peak at 847 cm$^{-1}$, is due to the incorporation of hexafluorophosphate ions[50] balancing the charge formed on the poly-**3** film by the oxidation process.

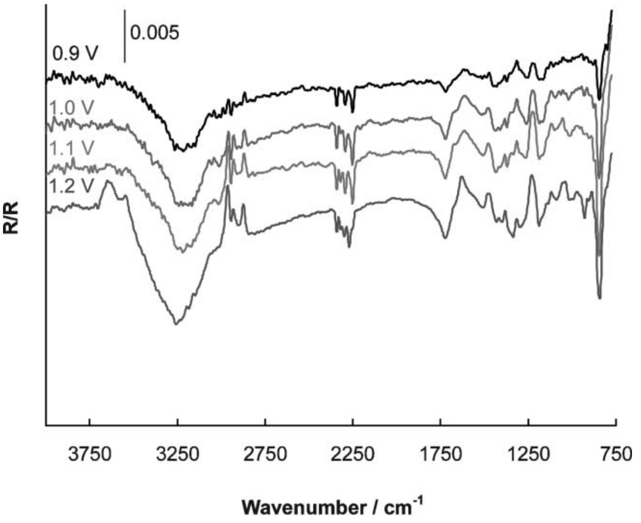


**Fig. 4** SNIFTIRS spectra of poly-**3** taken from 0.9 to 1.2 V. Reference spectra collected at 0.3 V. Spectra are shifted for clarity.

The presence of the $C_\beta$–H out-of-plane deformation at 795 cm$^{-1}$ suggests that, as previously concluded for the other polythiophene derivatives investigated, the coupling of thiophene units occurs primarily through the α- (2,5) positions. In keeping with this, IR peaks assigned to the $C_\alpha$–H bond are not observed although the presence of the solvent band makes assignment in this region less reliable. The spectroelectrochemical response of poly-**3** upon oxidation does not display the characteristic features usually found in the IR spectra of oxidised polythiophenes [*i.e.*, IRAVs (Infra-Red Active Vibrations) and a broad absorbance band in the near infrared] which further indicates that the degree of conjugation in poly-**3** is rather limited. Polymerisation through the four peripheral thiophene rings in **3** is possible, each one with two α-positions available for bonding, which would potentially produce a highly crosslinked polymer. However, the presence of the sterically bulky nickel dithiolene side groups and the significant twist of the thiophene centres would be expected to reduce the thiophene polymer chain length and the overall conjugation length in the polymer. This would also explain the lack of redox peaks attributable to polythiophene.

The symmetric C=C stretching vibration of the thiophene ring can be seen at 1511 cm$^{-1}$.[34,51] SNIFTIRS peaks at 1400, 1337, 1193 and 933 cm$^{-1}$ can be assigned to the stretching vibration of the C=C, C–S and C–S bonds present in the dithiolene unit, respectively.[44,47,48] The vibrations of the Ni–C bond occur below the spectral range (at 465 and 435 cm$^{-1}$), and therefore cannot be seen in the SNIFTIRS spectra.

Analysis of the SNIFTIRS spectra of poly-**3** upon reduction (Fig. S4, ESI†) revealed a shift of the C=C dithiolene vibrations to higher frequencies (from 1400 and 1337 cm$^{-1}$ to 1442 and 1375 cm$^{-1}$, respectively). At the same time, a decrease in the C–S stretching frequency of the dithiolene centre from 933 to 897 $cm^{-1}$ was also observed. In addition, the C–S vibration at 1193 $cm^{-1}$ becomes less intense as the polymer is reduced. Similar shifts have been reported for a vast number of metal dithiolenes, and are an indication that the dithiolene ligands assume a dithiolate character upon reduction.[26,32,43,52] As expected, upon reduction, there is a progressive increase in the intensity of the positive band at 847 $cm^{-1}$, representing the expulsion of $PF_6^-$ anions from the poly-**3** as the polymer is electrochemically reduced.

For comparison with **3**, we investigated the electrochemistry of **2** under the same conditions. The CV response (Fig. S5, ESI†) was found to be generally consistent with that previously reported,[12] with similar voltammetry to **3**, giving peaks at $E^1_{1/2} = -0.62$ V, $\Delta E = 0.05$ V, $E_{1/2} = 0.21$ V, $\Delta E = 0.04$ V, $E^3_{ox} = 0.99$ V, $E^4_{ox} = 1.23$ V. As expected, the separation $E^2_{1/2} - E^1_{1/2} \sim 0.8$ V is similar to **3**. Electropolymerisation of **2** was achieved by potential scanning between 0.3 and 1.3 V (Fig. S6, ESI†) and a gradual increase in the current intensity upon consecutive cycles indicated a continuous growth of a redox active film on the electrode surface. The response of this red film, investigated by CV in a monomer-free solution (Fig. S7, ESI†) and by SNIFTIRS (Fig. S8, ESI†), resembles that of many polythiophenes; in particular the CV is quite different to that described by Kean and Pickup.[12] In our work, neither electrochemical nor spectroscopic evidence for significant incorporation of the intact metal complex into the film was found (Fig. S7, S8, ESI†). These results are consistent with decomposition of the metal complex during coupling and formation of a polythiophene-like film. The difference between our results and those of Kean and Pickup may be due to the difference in solvent as the prior literature work was carried out in $CH_2Cl_2$.

Overall, we have shown distinctly different characteristics in the polymerisation of **3** and **2** under the same experimental conditions, which reflects the differing linkage postions of the thiophene. In the case of **3**, electropolymerisation can occur without the need to incorporate the dithiolene units into the polymer backbone since the thiophenes are unsubstituted in both the 2 and 5 positions. In contrast, **2** has the 2-position substituted which would require incorporation of the metal dithiolene centre into the polymer backbone. Our observation that electropolymerisation of **3** results in a film incorporating the intact complex **3** under conditions where we were unable to obtain a comparable film incorporating **2** is consistent with results for the analogous 2-thienyl substituted TTF compounds,[10] where the suggestion was made that 3-thienyl substitution in these systems would be more suitable for polymerisation. These results suggest greater potential for **3** to be used in electropolymerised films and this is explored further in the section below.

**(b) Electrochemical studies of 3 at higher concentration: towards the formation of hybrid films for devices.** CV studies of **3** have been carried out at higher concentrations (1–10 mM in $CH_3CN$) giving further insight into the film-forming capability of this complex. Three types of film were electrochemically formed and characterised. (i) An electrodeposited conducting molecular film comprising the neutral complex **3**. (ii) An electropolymerised film containing **3** with covalently linked thiophene units. (iii) A copolymer of **3** with thiophene.

*(i) Molecular film of 3.* In keeping with the study at lower concentration, the electrochemistry of $[NBu_4]$[**3**] (1 mM in $CH_3CN$) showed redox processes for the −2/−1 couple ($E^1_{1/2} = -0.78$ V) and the −1/0 couple ($E^2_{ox} = +0.12$ V) (Fig. 5). At fast sweep rates (Fig. S9, ESI†) an associated reduction peak for the latter (at $E^2_{red} = 0.05$ V) was observed attributable to solution-based reduction. At slower sweep rates (Fig. 5), a relatively small associated reduction wave was seen near $E^2_{red} = -0.04$ V, which is due to the aggregation and deposition of electrogenerated **3** on the electrode surface, consistent with the low solubility of **3** in $CH_3CN$ and the higher concentration conditions. Holding the potential at or above +0.29 V (above $E^2_{ox}$) resulted in the deposition of a green film. The oxidation current was independent of film thickness and, on stirring, the reaction was mass transport controlled, suggesting significant electrical conductivity in the deposited film. This is surprising given the low conductivity observed in a compressed pellet of **3** and the X-ray structure, which indicated little intermolecular contact between the molecules of **3**. This suggests that the electrochemical deposition method may result in a different, more conducting structure within the molecular layer to that seen in crystals of the material. This is further supported by the green colour of the film which may suggest enhanced delocalisation compared with the paler sample from the chemical synthesis. Greater electronic delocalisation is also suggested by the smaller separation of $E^1$ and $E^2$ compared with the solvated molecule.

Holding the potential in the region −0.12 to −0.52 V leads to the quantitative reduction of neutral **3** to [**3**]$^-$ and dissolution of the green film. This reduction wave in Fig. 5 is relatively small and the reduction current is insensitive to potential, indicating a kinetically controlled dissolution process; this is sufficiently slow to enable the film-based −1 to −2 reduction to be seen in the second cycle in Fig. 5 (the relatively sharp peak labelled b) for the deposited film at −0.75 V, superimposed upon the reduction of solution-based [**3**]$^-$ near −0.8 V. A film was generated on the working electrode by holding the potential at +0.29 V and reduction of this film at −1.01 V in background electrolyte resulted in a total reduction charge 2.1 times greater than the oxidation

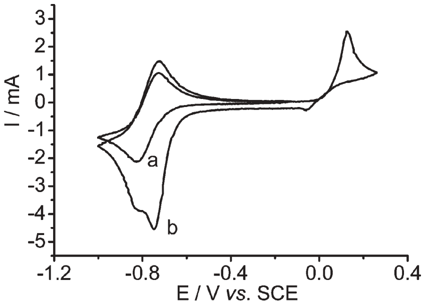


**Fig. 5** Cyclic voltammogram of [NBu4][**3**] in $CH_3CN$–0.1 M $[TBA][PF_6]$ at 50 $mVs^{-1}$. The first cycle (a) is between −0.11 and −1.01 V and shows the reversible couple at −0.78 V. The second cycle (b) is from −0.11 V to +0.29 V, then −1.01 V and back to −0.11 V.

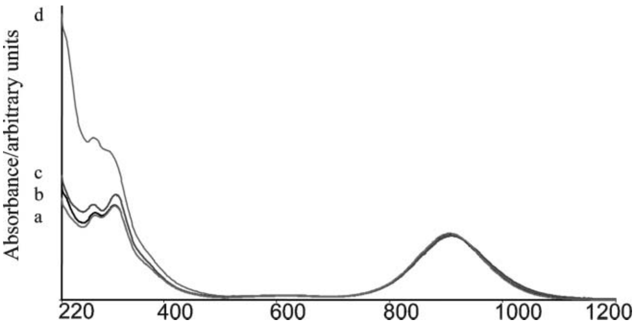


**Fig. 6** UV-Vis spectrum in $CH_2Cl_2$ of films deposited in electrochemical experiments compared with **3**. All spectra have been normalised to show the same intensity of absorbance at around 920 nm. Films generated by electrochemical oxidation in $CH_3CN$ were washed from the electrode using $CH_2Cl_2$ after being rinsed in electrolyte solution. (a) (Red line) film formed by holding potential at +1.39 V for electrolyte solution containing $[\mathbf{3}]^-$. (b) (Black line) complex **3** prepared by chemical synthesis. (c) (Blue line) film formed by holding potential at +0.29 V for electrolyte solution containing $[\mathbf{3}]^-$. (d) (Green line) copolymer film formed by holding potential at +1.79 V for electrolyte solution containing $[\mathbf{3}]^-$ and thiophene.

charge. This is consistent with reduction of [**3**] from 0 to −2 and confirms the assignment of the 2nd CV reduction peak at −0.75 V to the reduction of the −1 state to the −2 state. The green film was then dissolved in $CH_2Cl_2$ and comparison of the UV-Vis spectrum with that for the neutral complex **3**, Fig. 6 shows identical spectroscopic features. Thus, a neutral molecular film, showing significant conductivity and with kinetically controlled rather than potential dependent re-reduction, has been formed by oxidation of this nickel dithiolene complex. To the best of our knowledge the electrochemical formation and characterisation of such a film has not previously been reported. Conducting materials composed of neutral dithiolene molecules are currently of significant interest[16–18] and future work will explore the formation, possible electrocrystallisation and crystal structure of this film.

*(ii) Electropolymerisation of **3**.* Scanning the above solution to a more positive potential revealed an irreversible oxidation peak at +1.39 V. After this process, cycling back to negative potentials revealed no significant electroactivity at any of the potentials where features were previously observed (Fig. 7). This indicates that the film obtained at +1.39 V is insulating and prevents further redox processes occurring at the electrode. A rotating disc electrode (RDE) experiment was performed with the potential held at +1.39 V and a steadily declining current was observed, confirming that this oxidation process leads to a film. The film was dissolved in $CH_2Cl_2$ and the UV-Vis spectrum recorded (Fig. 6), however this shows no significant differences compared with **3**. Evidently, some large chemical change has taken place within the film upon oxidation at +1.39 V as evidenced by both the passage of current and the loss of conductivity of the layer.

As the electrochemical process does not involve alteration of the Ni-bis-dithiolene core, it seems likely that covalent linkage of the thiophene units is occurring at this potential. The low conductivity however and the lack of alteration of the electronic spectrum suggest that the linked thiophenes cannot readily adopt a conjugated arrangement and that the geometric constraints of the system require a twisted configuration of these units. The complete solubility in $CH_2Cl_2$ also suggests limited chain length. The low conductivity and the limited polythiophene chain length observed are consistent with the previous results for electropolymerised **3** at lower concentration (see above).

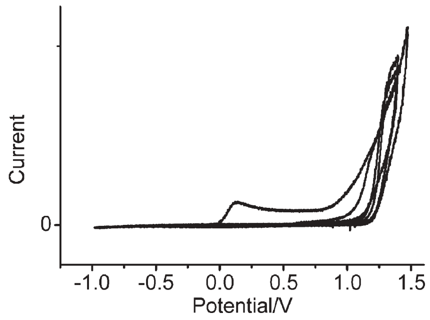


**Fig. 7** Cyclic voltammogram of $[NBu_4][\mathbf{3}]$ in $CH_3CN$–0.1 M $[TBA][PF_6]$ at 50 $mVs^{-1}$. The first scan from −0.22 V to +1.39 V shows oxidation at +0.12 V then oxidation at +1.39 V. Subsequent cycles between +1.39 V and −1.02 V showed none of the previously observed redox processes except further oxidation at around +1.28 V.

*(iii) Copolymerisation of **3** and thiophene.* In order to enhance the possibility of hybrid polythiophene–metal dithiolene complex films with significant polythiophene chain lengths and enhanced conductivities over poly-**3**, copolymerisation was carried out using 10 mM $[NBu_4][\mathbf{3}]$ and 160 mM thiophene in $CH_3CN$ electrolyte solution. Using an RDE (at 2 Hz), the potential was held at +1.79 V, sufficient to oxidise both thiophene and **3** under mass transport control. As expected, this produced a much-enhanced oxidation current compared with the oxidation of either 160 mM thiophene or 10 mM $[NBu_4][\mathbf{3}]$ alone. In contrast to control experiments with thiophene the current fell gradually with time although less steeply than for polymerisation of **3** alone. This indicates a significant, although lower, conductivity for the copolymer than for polythiophene. A gold-coloured film was formed contrasting with the black colour observed at these concentrations for a film of electrogenerated polythiophene. The film was similar in appearance to that observed previously for electropolymerisation of $[\mathbf{3}]^-$ at +1.39 V but with a markedly reduced solubility in $CH_2Cl_2$. The soluble portion was analysed by UV-Vis spectroscopy (Fig. 6) and this again confirmed the presence of the metal dithiolene species as the characteristic low energy transition could be observed. A significant difference however, was observed in the higher energy region with peaks around 220 to 400 nm. Long chain polythiophene is expected to show absorbance around 500 nm, but shorter chains show absorption considerably shifted to the blue,[2] these bands may therefore be attributed to short oligomers of polymerised thiophenes, covalently attached through the pendant thiophenes to **3**. Longer oligomers may also occur in this film but would be expected to be much less soluble in $CH_2Cl_2$. It is interesting that the portion of the film

insoluble in $CH_2Cl_2$ was also insoluble in DMF and DMSO and retained the characteristic golden colour.

These results demonstrate the capability for covalent incorporation of complex **3** into electropolymerised thiophene films, which could lead to materials that combine the high conductivity of polythiophene with the optical characteristics of a metal bis-1,2-dithiolene complex.

## Conclusions

We have prepared a novel nickel-bis-1,2-dithiolene complex bearing thiophene groups attached at the 3-position and structurally characterised it alongside the previously reported 2-substituted analogue. It was shown that complex **3**, with 3-substituted thiophenes can be electrooxidised to form a conducting molecular film (without covalent linking) which seems to be structurally different from the chemically-synthesised sample and is kinetically stabilised towards re-reduction. Furthermore, **3** can also be electrochemically linked at different concentrations to give an insulating film and can be copolymerised with thiophene to give a film with properties modified from those of either polythiophene alone or **3** alone. Comparison of these results with electropolymerisation studies on **2**[12] under the same experimental conditions has shown that the position of linkage of the dithiolene to the thiophene units is a crucial factor in determining the electropolymerisation behaviour and the properties of the resultant films.

The observed X-ray structures of **2** and **3** showed twisting of the thiophene units away from the plane of the dithiolene core, suggesting that the incorporation of **2** and **3** into conducting polymer chains may be unlikely to play a role in enhancing conductivity, consistent with our observation of a non-conducting film of poly-**3**. In this light, it seems that our strategy of copolymerisation with thiophene may be the most promising approach. We have demonstrated the incorporation of the dithiolene complex **3** into a conducting polymer while retaining significant conductivity. This has established the capability of these dithiolene complexes to lead to new hybrid materials. The synthesis developed for these species should prove suitable for the preparation of a wide variety of related bis-dithiolene or mixed-ligand complexes and the capability to copolymerise with known conducting polymers in a flexible ratio offers the prospect of varying and tuning the properties of a wide range of new hybrid materials.

## Experimental

All solvents used were dried using standard techniques. Chemicals used were purchased from Aldrich and used without further purification. Compounds **1a** and **1b** were prepared as described previously.[9–11]

Electrochemical and spectroelectrochemical experiments were performed in dry $CH_3CN$ using 0.1 M $TBAPF_6$ supporting electrolyte in a three-electrode cell using a platinum disc working electrode, a large surface-area platinum counter electrode, and a $Ag/Ag^+$ reference electrode. All potential values are quoted against SCE.

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 $cm^{-1}$, a 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 normalised difference spectra were obtained by subtracting two reflectance spectra (S2−S1) collected at different potentials ($E_2$ and $E_1$, respectively) and dividing by the reflectance spectrum obtained at $E_1$ (S1). The positive and negative bands in these difference spectra indicate decreased and increased absorbances, respectively at $E_2$ with respect to $E_1$. Throughout these studies 100 interferograms were averaged for each spectrum.

### $[NBu_4][Ni(b\text{-}2ted)_2]$ ($[NBu_4][2]$)

The 1,3-dithiole-2-one **1a** (0.40 g, 1.4 mmol) was added under $N_2$ to a solution of Na (0.07 g, 3 mmol) in dry methanol (20 ml). An immediate colour change to dark yellow occurred and stirring was continued for 1 h to ensure complete reaction. [TBA][Br] (0.91 g, 2.82 mmol) was added and allowed to dissolve. $NiCl_2\cdot 6H_2O$ (0.16 g, 0.7 mmol) dissolved in 15 ml of dry methanol was added dropwise over 45 min to the stirred solution giving a colour change to dark red–brown and a dark brown precipitate. The flask was allowed to stand in a freezer for one hour then the precipitate filtered off and washed with ethanol and dried in air to give 460 mg of crude solid. The solid was recrystallised from $CH_2Cl_2$–EtOH to give 345 mg, 47%. Calc. for $C_{36}H_{48}NS_8Ni$, C 53.4, H 1.7, N 5.9, S 31.7; found C 53.4, H 1.5, N 5.9, S 31.9 FABMS $m/z$ = 1050 ($MNBu_4^+$), 809 ($MH^+$). UV-Vis/NIR $\lambda_{max}$ = 950 nm ($\varepsilon = 9 \times 10^3$ $M^{-1}$ $cm^{-1}$)

### $[NBu_4][Ni(b\text{-}3ted)_2]$ ($[NBu_4][3]$)

An analogous procedure was used to that of $[NBu_4]$[**2**] starting with the 1,3-dithiole-2-one **1b**. Recrystallisation was from acetone–methanol. Yield = 62%

Calc. for $C_{36}H_{48}NS_8Ni$, C 53.4, H 1.7, N 5.9, S 31.7; found C 53.5, H 2.2, N 6.2, S 31.2. FABMS $m/z$ = 1050 ($MNBu_4^+$), 809 ($MH^+$). UV-Vis/NIR $\lambda_{max}$ = 950 nm ($\varepsilon = 7.5 \times 10^3$ $M^{-1}$ $cm^{-1}$)

### $[Ni(b\text{-}2ted)_2]$ (2)

Complex $[NBu_4]$[**2**] (100 mg, 0.09 mmol) was dissolved in dichloromethane (10 ml) and to this was added $I_2$ (0.05 g, 0.19 mmol) in dichloromethane (5 ml). The colour changed immediately to dark green and a precipitate formed. Ethanol was added and the solution was placed in the freezer. The dark solid was filtered off, washed with ethanol and dried in air to yield 50 mg, 80%. Calc. for $C_{20}H_{12}S_8Ni$ C 42.3, H 2.1, N 0.0, S 45.2; found C 43.1, H 2.0, N 0.0, S 43.5. FABMS, *m*/*z* = 566. UV-Vis/NIR $\lambda_{max}$ = 970 nm.

### [Ni(b-3ted)$_2$] (3)

The 1,3-dithiole-2-one **1b** (0.16 g, 0.567 mmol) was stirred in THF (10 ml, distilled) under $N_2$ and [TMA][OH]·$5H_2O$ (0.210 g, 1.16 mmol, TMA = tetramethylammonium) added in 0.5 ml of distilled methanol. After 5 min stirring, $NiCl_2 \cdot 6H_2O$ (0.072 g, 3.0 mmol) in 0.5 ml distilled MeOH was added resulting in an immediate intense red colour. Stirring was continued overnight with the container left open to air. The dark precipitate was filtered off and washed with methanol (5 ml) giving 0.098 g of dark red solid. This was dissolved in acetone (5 ml) and reprecipitated by allowing ethanol (25 ml) to mix slowly overnight. The resultant green–brown solid was filtered off and gave 0.047 g (29% yield) of **3**. Calc. for $C_{20}H_{12}S_8Ni$, C 42.3; H 2.1; N 0.0; found C 42.5, H 2.3, N 0.0. FABMS, *m*/*z* = 566. UV-Vis/NIR $\lambda_{max}$ = 920 nm ($\varepsilon = 3 \times 10^4\ M^{-1}\ cm^{-1}$).

### X-Ray crystallography

CCDC reference numbers 170534 and 171198. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714372a

**[Ni(b-2-ted)$_2$] 2.** $C_{20}H_{12}NiS_8$, $M$ = 567.49, $\lambda$ = 0.71073 Å, monoclinic, space group = $P2_1/n$, $a$ = 12.112(2) Å, $b$ = 5.4414(11) Å, $c$ = 17.026(3) Å, $\beta$ = 110.51(3)°, $V$ = 1050.9(4) Å$^3$, $Z$ = 2, $\mu$ = 1.725 mm$^{-1}$, $T$ = 120(2) K, 7607 data were collected of which 2391 were independent. The structure was refined on $F^2$ to give $R1 = 0.0293$ ($F^2 > 2\sigma F^2$) and $wR2$ (all data) = 0.0708. Rotational disorder in thiophene rings gives partial site occupancy of S2/C5 and S4/C10 in an 85/15 ratio.

**[Ni(b-3-ted)$_2$] 3.** $C_{20}H_{12}NiS_8$, $M$ = 567.49, $\lambda$ = 0.71073 Å, triclinic, space group = $P$-1, $a$ = 9.5217(19) Å, $b$ = 9.810(2) Å, $c$ = 11.985(2) Å, $\alpha$ = 90.14(3)°, $\beta$ = 100.37(3)°, $\gamma$ = 93.73(3)°, $V$ = 1098.8(4) Å$^3$, $Z$ = 2, $\mu$ = 1.649 mm$^{-1}$, $T$ = 150(2) K, 13 623 data were collected of which 5027 were independent. The structure was refined on $F^2$ to give $R1 = 0.0356$ ($F^2 > 2\sigma F^2$) and $wR2$ (all data) = 0.0977. Rotational disorder in thiophene rings gives partial site occupancy of S5/C4 (75/25 ratio), S6/C9 (85/15 ratio) and S8/C19 (55/45 ratio).

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