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Syntheses and electro(co)polymerization of novel thiophene- and 2,2′:5′,2″-terthiophene-functionalized metal–tetraazamacrocycle complexes, and electrochemical and spectroelectrochemical characterization of the resulting polythiophenes

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We have prepared novel tetraazacyclotetradecane derivatives, functionalised at nitrogen with a pendant thiophene or oligothiophene group, for electropolymerisation. Square planar Ni(II) complexes of these ligands, [Ni(L)](ClO_4)$_2$, have been prepared, and their electropolymerisation has been examined. The terthiophene-bearing complex was electrooxidised in CH_3CN–0.2 M Et_4NBF_4 to give soluble oligomers, which are likely to be the products of dimerisation (sexithiophenes). However, by employing a more positive potential limit, they are electropolymerised, to afford polythiophene films on indium-doped tin oxide (ITO)-coated glass or platinum electrodes, and the Ni(II)/Ni(III) wave is superimposed upon the polythiophene redox process. Attempts to isolate films of the dimerised terthiophene by the oxidation of neutral [$NiCl_2$(L)] complexes in less polar media were unsuccessful. A polymer film could not be generated from the thiophene-bearing complex alone, even though a 'spacer' of five carbon atoms was incorporated between the thiophene and the bulky metal centre. However, copolymerisation with 3-methylthiophene successfully gave polythiophene copolymers incorporating the nickel(II) complex. *In situ* FTIR reflectance spectroelectrochemistry shows that in the early stages of film oxidation, the film behaves as a conventional polythiophene, but at higher potentials, the electronic band attributable to the transition from the valence band to the first intergap state undergoes some very unusual changes. Possible explanations for these are suggested.

Introduction

The generation of conjugated polymer-modified electrodes containing covalently-attached functional groups of various kinds has attracted much attention, and issues in the design and syntheses of these systems have recently been reviewed.[1,2] Metal complexes and potential ligands have been particularly attractive targets, and polythiophenes and polypyrroles bearing crown ethers,[3,4] redox-active pyridine and bipy (2,2′-bipyridine) complexes,[5,6] and ferrocenes,[7,8] have all been well studied. Potential applications in electrocatalysis and in sensing drive this work. Recently, there has been a tendency to employ metal complexes with free or potentially free coordination sites,[9] including metal–phosphine complexes.[10a,10b]

For applications, polypyrroles have the potential advantage that they can be cycled in aqueous electrolytes. However, the electroactivity of polypyrrole films bearing pendant metal complexes is destroyed when, as is often the case, the redox potential of the metal complex is positive of that of the polypyrrole backbone.[1] Therefore, the study of possible interactions between a metal centre and a conjugated polymer backbone is better addressed with polythiophenes. We have been interested in the incorporation of the well-known electrocatalyst [Ni(cyclam)]$^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) into poly-3-methylthiophene,[11] and have used FTIR spectroscopy to probe, *in situ*, the effect on the polymer properties of the incorporation of the metal complex.[12] Bulky substituents have adverse effects upon important polythiophene properties such as mean conjugation length,[13] and it is preferable to separate substituents from the conjugated polymer backbone by an alkyl 'spacer' of at least four carbon atoms to minimise this.[1] We have therefore prepared a thiophene-appended cyclam with a longer alkyl 'spacer', and have examined the electropolymerisation of its square planar Ni(II) complex.

Copolymerisation has the advantage that thiophene-functionalised metal complexes are relatively straightforward to synthesise, but the disadvantage that control over the copolymer composition is not straightforward. Some control over the monomer ratio in the electrogenerated polymer can be exerted by varying the monomer ratio in the electrolyte solution. However, although an idea of monomer ratio in the resulting copolymers can be obtained by comparing charge passed for the polymer redox process with that for the redox process(es) of the metal complex,[11] there is no control over, or means of determining, whether the copolymer is random or block.

Bäuerle and co-workers previously showed that while thiophene-functionalised crown ethers often cannot be electropolymerised because of the solubility of the electrogenerated species, the corresponding 2,2′-bithiophene- and 2,2′:5′,2″-terthiophene-functionalised crowns readily afforded polythiophene films containing covalently-attached crown ether moieties.[3,4] Therefore, an alternative method of avoiding copolymerisation is to use an oligothiophene-appended metal complex as monomer. We have therefore investigated the synthesis of an oligothiophene-functionalised cyclam and its Ni(II) complexes. In this paper, we report these syntheses, the electro(co)polymerisation of the complexes to give polymer-modified electrodes, and preliminary *in situ* FTIR spectroscopic data on one of the polymer films.

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Experimental

General

Instrumentation and general methods were as previously described,[14] with the following exceptions and additions. Pet. ether refers to the petroleum ether fraction boiling between 40–60 °C. Fast atom bombardment mass spectra were recorded either in house by Mr Allan Mills, or by the EPSRC Mass Spectrometry Service at Swansea. Electrochemical experiments were conducted as previously described.[10a]

Syntheses

1-[5-(3-Thienyl)pentyl]-1,4,8,11-tetraazacyclotetradecane, 3. To a solution of 1,4,8,11-tetraazacyclotetradecane (cyclam) (1.55 g, 7.76 mmol) in refluxing benzene (50 cm^3) and pyridine (15 cm^3) was added a solution of 3-(ω-bromopentyl)thiophene[15] (0.9 g, 3.88 mmol) dropwise with stirring. After being refluxed for a further 4 h, the reaction mixture was allowed to cool and the solvent was removed under reduced pressure. The residue was dissolved in 0.2 M aqueous NaOH (60 cm^3) and extracted with diethyl ether (4 × 30 cm^3). The ether extracts were dried over $MgSO_4$. The ether was evaporated off to leave a waxy oil. Yield 0.73 g, 53%. Selected ^1H NMR ($CDCl_3$): $\delta = 7.18$ (dd, 1H, H5), 6.74 (m, 2H, H4, H2), 3.82 (t, 2H, $CH_2C_4H_3S$). MS (EI): *m*/*z* 352 ([M^+], 1), 199 ([$M-C_5H_{10}C_4H_3S^+$], 95).

{1-[5-(3-Thienyl)pentyl]-1,4,8,11-tetraazacyclotetradecane}-nickel(II) perchlorate, [Ni(3)](ClO_4)$_2$, 4. The ligand **3** (0.32 g, 0.653 mmol) in MeOH (20 cm^3) was added to a solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.32 g, 0.87 mmol) in hot methanol (30 cm^3). After 15 min, the hot solution was filtered from a little insoluble impurity, and allowed to cool. An oil separated. This was decanted off and washed with diethyl ether (10 cm^3), whereupon it crystallised. The solid was filtered off and recrystallised three times from hot MeOH–EtOH, then dried in *vacuo*. Elemental analysis, calc. for $C_{19}H_{36}Cl_2N_4NiO_8S$: C, 37.40; H, 5.95; N, 9.18. Found: C, 37.74; H, 6.12; N, 8.05%. MS (FAB positive ion): *m*/*z* 510 ([$M-ClO_4^+$], 88), 409 ([$M-HClO_4-ClO_4^+$], 100). $E_{1/2}$ [Ni(II)/Ni(III)] + 0.70 V (*vs.* Fc/Fc^+).

2-(2,5-Dibromo-3-thienyl)ethanol, 6. In the absence of light, and under dinitrogen, *N*-bromosuccinimide (8.00 g, 45 mmol) in dry DMF (30 cm^3) was added dropwise to a stirred solution of 2-(3-thienyl)ethanol (2.5 g, 19.5 mmol) in DMF (35 cm^3). The reaction mixture was stirred for 3 h at 40 °C before being poured onto crushed ice (100 g). The mixture was extracted with diethyl ether (3 × 40 cm^3). The ether phase was washed with water, dried ($MgSO_4$) and treated with decolourising charcoal (1 g). Removal of the solvent afforded the product as a yellow oil. Yield 4.70 g, 85%. Elemental analysis, calc. for $C_6H_6Br_2OS$: C, 25.20; H, 2.11. Found: C, 25.17; H, 2.11%. ^1H NMR ($CDCl_3$): $\delta = 6.80$ (s, 1H, C_4HBr_2RS), 3.78, 2.78 (t's, 2H each, $J = 6.5$ Hz, $-CH_2CH_2-$), 2.05 (s, 1H, -O*H*). MS (EI): *m*/*z* 286 ([M^+], 47), 255 ([$M-CH_2OH^+$], 100).

2-[2-(2,5-Dibromo-3-thienyl)ethoxy]tetrahydropyran, 7. A solution of **6** (2.00 g, 7.27 mmol) in CH_2Cl_2 (50 cm^3), containing pyridinium toluene-*p*-sulfonate (0.18 g, 0.70 mmol) and dihydropyran (0.91 g, 10.85 mmol), was stirred for 36 h under dinitrogen. The reaction mixture was diluted with diethyl ether, washed with 50 : 50 sat. brine–water, and dried over Na_2SO_4. Removal of the solvent *in vacuo* yielded the crude product as a yellow oil. Column chromatography (petroleum ether–ethyl acetate, 9 : 1) gave pure **7**. Yield 1.95 g, 73%. Elemental analysis, calc. for $C_{11}H_{16}Br_2O_2S$: C, 35.69; H, 3.81. Found: C, 35.80; H, 3.84%. Selected ^1H NMR ($CDCl_3$): $\delta = 6.88$ (s, 1H, C_4HBr_2RS), 4.59 (t, 1H, pyranyl -OC*H*O-), 3.92–3.44 (overlapping m, 4H, $-CH_2CH_2O-$ and pyranyl CH_2O), 2.82 (t, 2H, $J = 6.7$ Hz, $-CH_2CH_2O-$). MS (EI): *m*/*z* 370 ([M^+], 1), 268 ([$M-OTHP^+$], 27).

3′-[2-(Tetrahydropyranyloxy)ethyl]-2,2′:5′,2″-terthiophene, 8. A solution of 2-thienylmagnesium bromide (from 2-bromothiophene [1.96 g, 12.0 mmol] and Mg [0.36 g, 15 mmol] in diethyl ether [10 cm^3]) was added dropwise *via* cannula to a solution of **7** (1.75 g, 4.73 mmol) and $[NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)]$ (0.13 g, 2 mol. %) at 0 °C. The mixture was then refluxed for 24 h, before being cooled to 0 °C and hydrolysed with 0.5 M HCl (10 cm^3). The organic phase was extracted with CH_2Cl_2 (3 × 20 cm^3) and the extracts were washed with water (20 cm^3) before being dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by repeated column chromatography (hexanes, then pet. ether–ethyl acetate, 9 : 1). Yield 1.08 g, 61%. Elemental analysis, calc. for $C_{19}H_{20}O_2S_3$: C, 60.61; H, 5.35. Found: C, 60.80; H, 5.44%. Selected ^1H NMR ($CDCl_3$): $\delta = 7.31$ and 7.20 (dd's, 1H, H5 and H5″, $J = 5.25$, 1.05 Hz), 7.18 and 7.15 (dd's, 1H, H3 and H3″, $J = 3.60$, 1.20 Hz), 7.11 (s, 1H, H4′), 7.06 and 7.01 (dd's, 1H, H4 and H4″, $J = 5.10$, 3.60 Hz), 4.63 (t, 1H, -OC*H*). MS (EI): *m*/*z* 376 ([M^+], 16), 274 ([$M-OTHP^+$], 23).

3′-(2-Hydroxyethyl)-2,2′:5′,2″-terthiophene, 9. Compound **8** (1.0 g, 2.66 mmol) in THF (20 cm^3) and 0.5 M HCl (10 cm^3) was gently refluxed with monitoring of the reaction by TLC (pet. ether–ethyl acetate, 8 : 2). Reaction was complete in 2 h. The volume of the solution was reduced and CH_2Cl_2 (50 cm^3) was added. The layers were separated, the organic layer was washed with water and dried over $MgSO_4$, then evaporated. Flash chromatography (silica gel, pet. ether–ethyl acetate 8 : 2) gave the product as a yellow oil which crystallised on standing. Yield 0.71 g, 91%. Elemental analysis, calc. for $C_{14}H_{12}OS_3$: C, 57.50; H, 4.14. Found: C, 57.42; H, 4.14%. ^1H NMR ($CDCl_3$): $\delta = 7.29$–6.97 (m, 7H, thienyl H), 3.87 (t, 2H, $-CH_2CH_2OH$), 2.98 (t, 2H, $-CH_2CH_2OH$). MS (EI): *m*/*z* 292 ([M^+], 87), 261 ([$M-CH_2OH^+$], 100).

Toluene-*p*-sulfonic acid 2-(2,2′:5′,2″-terthiophen-3′-yl)ethyl ester, 10. Toluene-*p*-sulfonyl chloride (0.86 g, 4.5 mmol) was dissolved in anhydrous pyridine (10 cm^3), left for 10 min, then cooled to 0 °C. To this solution was added **9** (1.0 g, 3.42 mmol) in pyridine (10 cm^3) dropwise with stirring. After a further 2 h at 0 °C, ice (100 g) was added, the solution was extracted with CH_2Cl_2, the organic phase was washed with 2 M HCl, then water, dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by flash chromatography (CH_2Cl_2 eluant). Yield 1.40 g, 70%. Elemental analysis, calc. for $C_{21}H_{18}O_3S_4$: C, 56.48; H, 4.06. Found: C, 55.98; H, 3.72%. ^1H NMR ($CDCl_3$): $\delta = 7.69$ (m, 4H, Ph), 7.32–7.02 (m's, 7H, thienyl H), 4.23 (t, 2H, $-CH_2CH_2O-$, $J = 6.87$ Hz), 3.06 (t, 2H, $-CH_2CH_2O-$), 2.36 (s, 3H, $-CH_3$). MS (EI): *m*/*z* 446 ([M^+], 76), 273 ([$M-OTs^+$], 100).

1-[2-(2,2′:5′,2″-Terthiophen-3′-yl)ethyl]-1,4,8,11-tetraazacyclotetradecane, 11. Prepared as for **3**, using compound **10** (0.68 g, 1.5 mmol) and cyclam (0.74 g, 3.7 mmol). Crude yield 0.41 g, 59%, used directly to make **12**. ^1H NMR ($CDCl_3$): $\delta = 7.24$–6.94 (m's, 7H, thienyl H), 2.88–2.49 (overlapping m's, 23H, cyclam ring and ethyl CH_2's), 1.64 (m, 4H, $-CH_2CH_2CH_2-$). MS (EI): *m*/*z* 474 ([M^+], 2).

[Ni(11)](ClO_4)$_2$, 12. Prepared from **11** (1.00 g, 2.11 mmol) and $[Ni(H_2O)_6](ClO_4)_2$ (0.91 g, 2.50 mmol) using the method described for complex **4**. Yield, after three recrystallisations from hot MeOH–EtOH, 0.68 g, 44%. Elemental analysis, calc. for $C_{24}H_{34}Cl_2N_4NiO_8S_3$: C, 39.36; H, 4.68, N = 7.65. Found: C, 39.34; H, 4.76, N = 7.37%. MS (FAB): *m*/*z* 631 ([M−ClO_4^+], 76), 531 ([M−2ClO_4−H^+], 100).

[Ni(11)Cl₂], 13. The ligand **11** (0.80 g, 1.68 mmol) was dissolved in MeOH (20 cm^3) and added dropwise to a hot solution of [$Ni(H_2O)_6$]Cl_2 (0.45 g, 1.90 mmol) in MeOH (20 cm^3). The mixture was stirred and refluxed for 15 min. The solution was filtered hot, and evaporated to dryness. The residue was extracted with CH_2Cl_2. Removal of the CH_2Cl_2 in *vacuo* gave the green product, which was recrystallised once from CH_2Cl_2–diethyl ether. Yield 0.42 g, 41.5%. Elemental analysis, calc. for $C_{24}H_{34}Cl_2N_4NiS_3$: C, 47.70; H, 5.67, N, 9.27. Found: C, 47.27; H, 5.26, N, 8.83%. MS (FAB): *m*/*z* 567 ([M−Cl^+]), 531 ([M−2Cl−H^+]). MS (FAB, accurate mass): Found, 567.104224, calcd. for ([M−Cl^+]) 567.098763.

Electrochemical polymer syntheses and characterisation

Electrochemical copolymerisation of 4 with 3-methylthiophene. A Pt disc (0.3 cm^2) or ITO-coated glass (2 cm^2) working electrode was employed, in a standard 3-electrode cell with Pt gauze counter electrode and saturated calomel reference electrode separated from the working compartment by a salt bridge. The stability of the reference electrode was checked by periodically examining the ferrocene/ferrocinium redox process, which occurred at +0.45 V in this set-up. A solution of complex **4** (0.012 M) and 3-methylthiophene (0.025 M) in 0.2 M Et_4NBF_4–CH_3CN electrolyte was employed. The potential of the working electrode was cycled repeatedly, initially between −0.45 and +1.35 V (1 scan; +1.55 V in *in situ* FTIR experiments), then subsequently to +1.25 V, at 0.1 V s^{-1}.

Electrochemical polymerisation of complex 12. A 5 mM solution of complex **12** in 0.2 M Et_4NBF_4–CH_3CN electrolyte was employed for the electropolymerisation experiments. The onset of terthiophene oxidation occurred at *ca.* +0.75 V. Adherent, redox-active films were grown by repetitive cycling between −0.35 and +1.05 V. Similar experiments were also performed using 0.2 M Bu_4NBF_4–CH_2Cl_2 electrolyte.

Electrochemical polymerisation of complex 13. A 5 mM solution of complex **13** in 0.2 M Bu_4NBF_4–CH_2Cl_2 electrolyte was employed for the electropolymerisation experiments. The onset of oxidation occurred at *ca.* +0.45 V. Adherent, redox-active films were grown by repetitive cycling between −0.35 and +0.95 V.

Polymer cyclic voltammetry

Modified electrodes were removed from the growth solution with the film in the reduced form, washed with the appropriate pure solvent, and stored in dust-free conditions prior to redox cycling experiments, which were conducted in fresh background electrolyte (0.2 M Et_4NBF_4–CH_3CN) as described in the Results section.

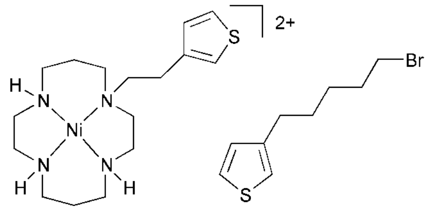
Infrared spectroscopy

The electrochemical cell and FTIR instrumentation, and general methods, were as described recently.[16] All electrolyte solutions were prepared under Schlenk conditions in flame-dried glassware, and were injected into the cell under nitrogen. The reference electrode (Ag/AgCl) was separated from the sample compartment by a salt bridge containing the same electrolyte as used in the sample compartment. To grow copolymer films of **4** with 3-methylthiophene in such a way that the highly polished bulk Pt working electrode was uniformly coated for reflectance measurements, it was found necessary to use 20 mM **4** and 50 mM 3-methylthiophene. The electrolyte employed was 0.2 M Et_4NBF_4–CH_3CN. Polymer films were grown with the working electrode pulled back from the CaF_2 window. The growth solution was then flushed from the cell with fresh electrolyte and the film was cycled between −0.25 and +0.75 V until no further changes occurred (*ca.* 3 cycles). It was then held at +0.2 V for several minutes before being secured against the CaF_2 window for FTIR experiments.

Results and discussion

Syntheses

Treatment of excess 1,4,8,11-tetraazacyclotetradecane (‘cyclam’) with a suitable electrophile, followed by selective extraction of the less-polar functionalised derivative from aqueous base with a solvent such as diethyl ether, is a reliable and rapid method for mono-functionalising cyclam.[17] The expensive excess cyclam can be recycled by subsequent extraction with dichloromethane. The required 5-(3-thienyl)-1-bromopentane, **2**, was made from 3-bromothiophene using the method developed by Bäuerle.[15] Treatment of excess cyclam with **2**, followed by extraction from aqueous base using diethyl ether, afforded crude 1-[5-(3-thienyl)pentyl]-1,4,8,11-tetraazacyclotetradecane **3** as a waxy solid. Mass spectra of the crude product suggested the presence of small amounts of unfunctionalised and difunctionalised cyclam impurities in addition to **3**. Treatment of [$Ni(H_2O)_6$]$(ClO_4)_2$ in MeOH with crude **3** gave [Ni(**3**)]$(ClO_4)_2$, **4**, which was recrystallised from hot MeOH–EtOH.† As with the ligand in complex **1**, which was similarly prepared by reacting excess cyclam with the toluene-*p*-sulfonate of commercially-available 2-(3-thienyl)ethanol,[11] we found that it was more satisfactory to use crude **3** to prepare the complex **4**, and subsequently to purify **4** by recrystallisation, than it was to purify **3**.



1 **2**

Treatment of 2-(3-thienyl)ethanol, **5**, with two equiv. of NBS gave 2-(2,5-dibromo-3-thienyl)ethanol **6**. This was converted to the tetrahydropyranyl (THP) derivative **7**. Although protection as the THP derivative followed by bromination was unsatisfactory, and other protection strategies failed, conversion of **5** to **7** was straightforward. Nickel-catalysed cross-coupling of **7** with two equiv. of 2-thienylmagnesium bromide ([$NiCl_2$(dppp)], Et_2O) afforded **8**, in only moderate yield following the extensive column chromatography necessary for its purification. Although we did not attempt to identify byproducts, related coupling reactions between 3-alkyl-2,5-dibromothiophene and 2-thienylmagnesium bromide give significant amounts of 2,2′-bithiophene, 2,2′:3′,2″-terthiophene and 5′-(2-thienyl)-2,2′:3′,2″-terthiophene,[18] and similar side-reactions may occur during the preparation of **8**. Compound **8** was deprotected by treatment with acid in aqueous THF to give the free alcohol **9**, and this was converted to the toluene-*p*-sulfonate **10**. Reaction of **10** with excess cyclam gave **11**. Once again, crude **11** contained trace amounts of unfunctionalised

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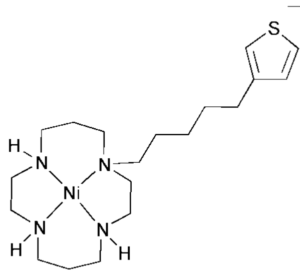
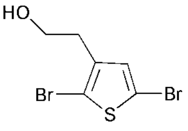
†WARNING! Perchlorate salts are highly oxidising and potentially explosive. No accidents were encountered with the compounds in this study, but perchlorate salts should be isolated in small quantities, and should never be scratched or subjected to shock.

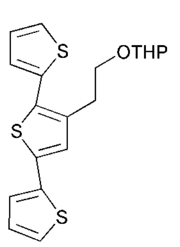


4 (perchlorate salt)



6

and difunctionalised cyclams, and was used directly to prepare the complex [Ni(**11**)]$(ClO_4)_2$, **12**, which was purified by recrystallisation from hot MeOH. Crude **11** was also used to prepare the neutral complex [Ni(**11**)Cl_2] (**13**) by treatment with $[Ni(H_2O)_6]Cl_2$ in MeOH, followed by removal of the solvent and extraction into hot CH_2Cl_2. The electronic spectrum of a CH_2Cl_2 solution of **13** was consistent with six-coordinate Ni(II).



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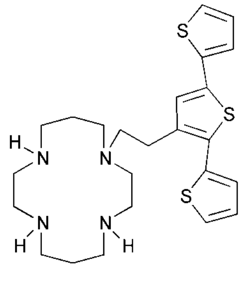


11

12 = [Ni(**11**)]$(ClO_4)_2$
13 = *trans*–[Ni(**11**)Cl_2]

Electropolymerisation of complex 4

A solution of complex **4** (5 mM) in 0.2 M Et_4NBF_4–CH_3CN showed a chemically reversible one-electron oxidation wave at +0.70 V (*vs.* internal ferrocene/ferrocinium) due to the Ni(III)/Ni(II) couple. As observed for other square planar nickel(II) complexes of monofunctionalised cyclams,[11] this is slightly more positive than the redox potential for $[Ni(cyclam)]^{2+}$ itself, as tertiary amines are significantly weaker donors than secondary amines, destabilising the higher oxidation state. The positive potential limit of consecutive scans was then increased in 0.1 V steps until the onset of a further, irreversible, oxidation was seen commencing at +1.4 V. On repeated cycling between 0.00 and +1.45 V, there was no evidence for the formation of a conducting polymer film. Varying the concentration (1–20 mM), electrolyte concentration (0.05–0.4 M), working electrode (Pt disk, Au disk, ITO-coated glass) or positive limit (up to +1.6 V) also failed to yield a polymer film. As with the electro-oxidation of **1** (perchlorate salt),[11] dark blue material was seen in solution around the working electrode at > +1.45 V, indicating that oxidised oligothiophenes were being generated, but that these were soluble. Clearly, the effect of the longer 'spacer' on the electropolymerisation of **4** compared with **1** is negligible.

We therefore studied co-polymerisation with 3-methylthiophene. Fig. 1 shows a typical cyclic voltammogram for the initial stage of the growth of a copolymer of 3-methylthiophene (25 mM) and complex **4** (12 mM) on a Pt disk working electrode. The peak currents for both the polythiophene and Ni(III)/Ni(II) redox waves increase with cycle number, suggesting the growth of a copolymer film. Copolymer films were grown on both Pt disk and ITO electrodes. After film growth, the electrodes were removed from the solution with the polythiophene film in its insulating form, washed with acetonitrile, and transferred to a monomer-free electrolyte solution. Fig. 2 shows a typical cyclic voltammogram for such a film, on Pt. As expected for a surface-localised redox process, peak current varies linearly with scan rate.[19] Peak-to-peak separation for the Ni(III)/Ni(II) redox wave (Pt) are small, but non-zero, and increase with scan rate (0.02 V at 25 mV s^{-1}; 0.09 V at 150 mV s^{-1}), presumably because of kinetic limitations to the movement of charge-balancing anions and associated solvent.[20] As expected for a polythiophene, the films were electrochromic, being red in the reduced state and dark blue when oxidised.

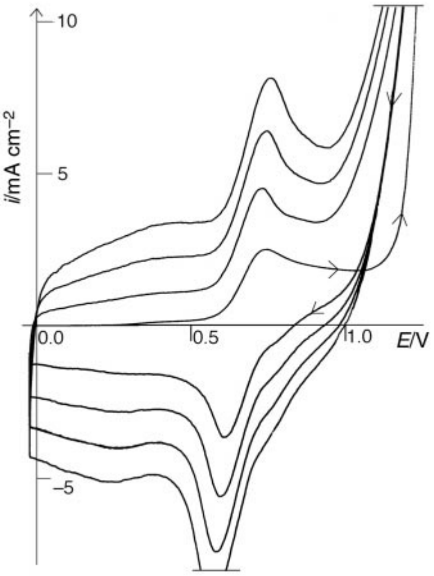


Fig. 1 Growth of a **4**–3-methylthiophene copolymer by repetitive cyclic voltammetry at a Pt disk working electrode. The arrows on the first scan illustrate the nucleation loop seen on the first scan, indicative of the formation of a conducting phase. Solution composition: 0.2 M Et_4NBF_4–CH_3CN, 12 mM **4**, 25 mM 3-methylthiophene. Scan rate 0.1 V s^{-1}. Potentials *vs.* internal ferrocene/ferrocinium.

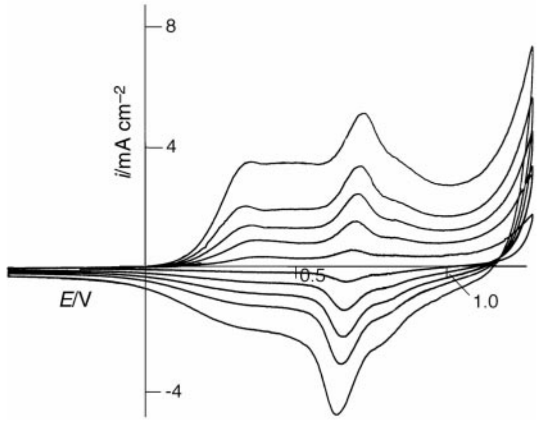
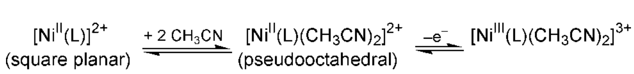


Fig. 2 Cyclic voltammograms of the **4**–3-methylthiophene copolymer, the early stages of whose growth is shown in Fig. 1, recorded in 0.2 M Et_4NBF_4–CH_3CN. In order of increasing peak currents, scan rates were 0.025, 0.05, 0.075, 0.10, 0.15 V s^{-1}.

We conducted an experiment to check that the nickel complex is not simply physically trapped within the growing polymer film. A film of poly-3-methylthiophene was grown by potential cycling on Pt under the same conditions as used for the copolymer, using 35 mM 3-methylthiophene, but in the presence of the complex {Ni[1-(*n*-octyl)cyclam]}$(BF_4)_2$[21] (5 mM). This complex was chosen to have similar charge and solubility properties to **4**, but without a polymerisable 3-thienyl group. No Ni(III)/Ni(II) wave could be detected in the cyclic



$$\underset{\text{(square planar)}}{[\mathrm{Ni^{II}(L)}]^{2+}} \xrightleftharpoons{+2\,\mathrm{CH_3CN}} \underset{\text{(pseudooctahedral)}}{[\mathrm{Ni^{II}(L)(CH_3CN)_2}]^{2+}} \xrightleftharpoons{-e^-} [\mathrm{Ni^{III}(L)(CH_3CN)_2}]^{3+}$$

Scheme 1

voltammogram of the resulting polymer film in background electrolyte.

As noted earlier for copolymers of $[\mathrm{Ni}(\mathbf{1})]^{2+}$ and 3-methylthiophene, the significance of the fact that the Ni(III)/Ni(II) wave occurs at almost the same potential in the polymer film as for the monomer in solution is that there must therefore be sufficient acetonitrile in the polymer film to allow the chemistry in Scheme 1 to occur unchanged.

The unusually symmetrical and highly reversible polythiophene redox chemistry seen is a consequence of the presence of the high ionic strength in the film, even for the undoped form of the polythiophene, owing to the presence of the anchored $[\mathrm{Ni(cyclam)}]^{2+}$ moieties. This effect has been noted before, for polypyrrole bearing covalently-tethered pyridinium ions.[22]

Infrared spectroscopy of 4–3-methylthiophene copolymers *in situ*

An intense π–π* transition dominates the visible region of the electronic spectrum for the neutral form of polythiophenes (Fig. 3). On removal of an electron from the HOMO of a polythiophene chain, the new π SOMO moves up in energy, and the corresponding π^* orbital moves down in energy, into the gap.[23] There has been much controversy over whether the removal of further electrons results in the generation of further SOMO's (polaron carriers), or whether spinless dicationic charge carriers (bipolarons) are formed, in which case the intragap levels are both empty.[24–28] More recently, compelling evidence from oligomer studies has shown that it is also possible for polarons on neighboring chains to form π-dimers, which are also spinless.[29] This may be more likely to occur in regioregular polyalkylthiophene films, in which the polymer chains can self-assemble into ordered layers.[30] Thus, the situation is complicated. Theoretical results indicate that the energy difference between polaron and bipolaron carriers is quite small.[31] Therefore, the preferred carrier for a given polythiophene (polaron, bipolaron, polaron π-dimer) may depend upon criteria such as the origin of the polymer (*e.g.* whether it was generated chemically or electrochemically by oxidative coupling, or by organometallic aryl–aryl coupling), how the carrier is generated (*e.g.* electrochemical or chemical oxidation; photoexcitation), the phase (solid or solution), the degree of doping, the nature of the substituents (if any), *etc.*

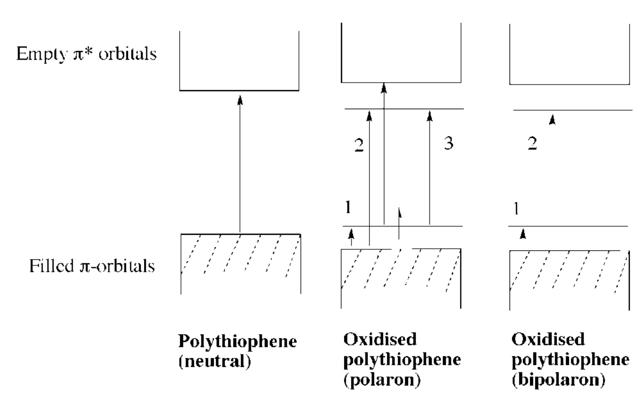


Fig. 3 Band diagram for polythiophene, showing the π–π^* transition for the neutral polymer (left), the effect of removing an electron to form a polaron (centre) together with the resulting additional electronic transitions (1–3), and the formation of a bipolaron with its resulting additional electronic transitions (right). Note that in the polaron, transitions labelled 2 are expected at equal energy by electron-hole symmetry, and that for the bipolaron, transition 3 is absent.

In the spectral region accessible in our experiments (1000–6000 cm^{-1}), a strong electronic band is generally observed on oxidation of a conducting polymer film, owing to the lowest-energy transition (from the valence band to the lowest inter-gap level; transition 1 in Fig. 3) regardless of whether the charge carrier is a polaron or bipolaron. In addition, the movement of charge carriers along polymer chains gives rise to large dipole changes in those vibrations that can couple to the carrier motion. The corresponding infrared bands are selectively enhanced, such that difference spectra such as those in Fig. 4 show only the gain of these very intense infrared activated vibrations (IRAV's).

Earlier, we studied the copolymer of **1** with 3-methylthiophene, and compared it with poly-3-methylthiophene.[12] The evolution of the spectra as a function of potential for poly-3-methylthiophene could be interpreted in terms of polaron formation early in the oxidation, then co-existence of polarons and bipolarons, and finally, bipolaron formation at the most positive potentials. In contrast, for the copolymer, while spectra early in the oxidation were little different from those of poly-3-methylthiophene, at higher potentials, different behaviour was observed. In particular, the successive increases in the electronic band intensity, which occurred at constant energy (*ca.* 5000 cm^{-1}) in the early stages of oxidation, appeared to shift to progressively lower energy thereafter. However, this was hard to quantify owing to the very low throughput at *ca.* 4500 cm^{-1} of the BioRad FTS-40 spectrometer employed. There also appeared to be a slight loss in intensity of the electronic band at high energy at the most positive potentials.

In the current study, we employed an FTS-60 spectrometer, which does not have the throughput limitations of the FTS-40. Moreover, we carefully excluded moisture from the working compartment by using Schlenk techniques and employing a salt bridge to separate the reference electrode from the working compartment, and this has enabled us to access somewhat more positive potentials without degrading the polymer.

A copolymer of **4** (perchlorate salt) and 3-methylthiophene was grown on a polished bulk Pt electrode (area 0.64 cm^2) for the FTIR experiments. We found that it was necessary to use a solution of 20 mM **4** and 50 mM 3-methylthiophene to promote the required even coverage of this electrode with the copolymer. However, cyclic voltammograms in background electrolyte established that the copolymer composition was similar to that observed in the earlier experiments described above. The polymer-coated working electrode was then held at -0.4 V, and a reference spectrum was collected at this potential. The potential was then increased in 0.1 V intervals up to $+0.8$ V, and then at 0.1 V intervals down to -0.4 V once more, and spectra were collected at each potential.

The spectral changes seen on progressively oxidising the **4**–3-methylthiophene copolymer film are shown in Fig. 4 (a–d). Fig. 4a shows all these spectra collected up to $+0.8$ V over the full spectral range. It is clear from Fig. 4a that these changes are not uniform as a function of potential. Fig. 4b shows the spectra taken from -0.3 to 0.1 V with respect to the spectrum taken at -0.4 V, Fig. 4c shows the spectra taken at 0.2 and 0.3 V with respect to the spectrum taken at 0.1 V, and Fig. 4d shows the spectra taken from 0.4 to 0.8 V with respect to the spectrum taken at 0.3 V.

During the first stage of oxidation distinguishable in the IR spectra, from -0.4 to $+0.1$ V, *ca.* 15% of the total oxidative charge is passed, calculated from the charge passed in the course of FTIR data collection. This region is associated with the pre-peak in the cyclic voltammogram seen in Fig. 2. It is generally accepted, even by workers who hold that bipolarons are the main charge carrier in polythiophenes, that polarons can form at low doping levels,[13] and we therefore propose that early in film oxidation, polarons are forming. The IRAV bands

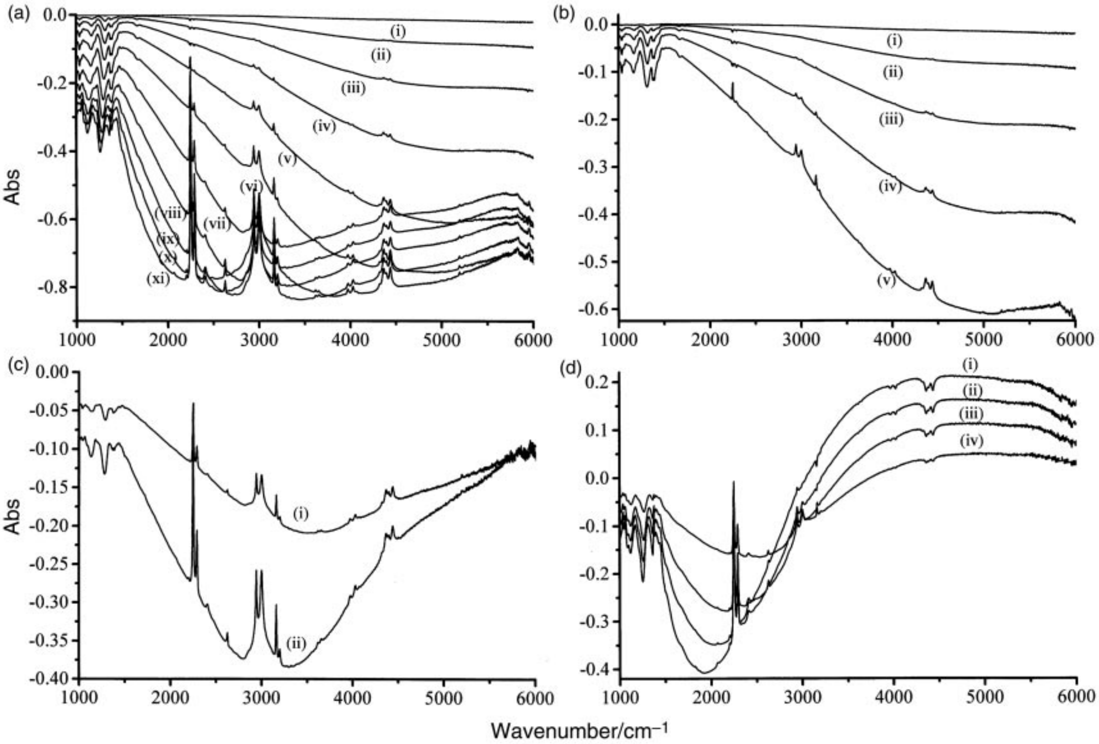


Fig. 4 (a) *In situ* FTIR spectra (8 cm^{-1} resolution, 100 co-added and averaged scans per spectrum), collected from a 0.64 cm^2 Pt electrode coated with the **4**–3-methylthiophene copolymer (see text for details), and immersed in 0.2 M Et_4NBF_4–CH_3CN. The spectra were collected in an experiment in which the potential of the coated electrode was increased in 100 mV steps from (i) −0.3 V to (xi) +0.8 V with a spectrum taken at each step and normalised to the reference taken at −0.4 V. The spectra are displayed as 'Abs' *vs.* cm^{-1}, where $Abs = \log_{10}(S[n]/S[-0.4\ V])$. (b) The spectra collected at (i) −0.3 V to (v) +0.1 V in the experiment depicted in (a). (c) The spectra collected at (i) +0.2 V and (ii) +0.3 V in (a) normalised to that taken at +0.1 V. (d) The spectra taken at (i) +0.4 V to (iv) +0.8 V in (a) normalised to that taken at +0.3 V; the spectrum collected at +0.7 V is not shown, for clarity.

seen for the copolymer (Fig. 4b; 1167, 1203 sh, 1308, 1375–1392 and 1440 sh cm^{-1}) are very similar in position and relative intensities to those seen earlier for polythiophene[32] and poly-3-methylthiophene itself in this potential region,[12,33] and a gain is seen at 1050 cm^{-1} which is assigned to tetrafluoroborate anions. The electronic band at ⩾5000 cm^{-1} is attributed to the transition from the valence band to the lowest intergap level (transition 1 in Fig. 3).

In the spectra taken at +0.2 and +0.3 V, referenced to that taken at +0.1 V, there is clearly a transition in behaviour (Fig. 4c). Further intensity increases across the electronic band occur, but the peak of these increases moves to lower energy. There are also significant changes in the IRAV bands seen in this region, which suggest the evolution of a different type of carrier. However, the absence of significant loss features in the IRAV region suggests that the carriers generated during the first stage of oxidation are not lost here.

Examining the spectra taken at > +0.4 V, referenced to that taken at +0.3 V, the gains in the electronic band continue to move to lower energy, while there is now significant loss of intensity at higher energy. Furthermore, there is now definite evidence for loss of the carriers generated in the early stage of oxidation; clear loss features are seen at 1395–1375 cm^{-1}, and in addition at 1310 cm^{-1} and 1172 cm^{-1}, although the latter two features are less certain because of the proximity of other gain peaks. These loss features coincide with the onset of the Ni(II)/Ni(III) process within the film, and they are seen much more clearly here than in our experiments with copolymers of **1** and 3-methylthiophene.[12] Although the potential limit used in these experiments is somewhat more positive than that commonly used for polythiophene films,[2,13] it is important to emphasise that the losses are not due to some irreversible degradation process, since on stepping down progressively from +0.8 V, the low-energy electronic band is lost and the high energy band intensity is re-gained. The IRAV band changes are also reversible. This process could be repeated several times with no significant irreversible spectroscopic changes.

It is difficult to be certain of the origin of the behaviour of the electronic bands, which is unlike anything observed previously. It is clear that the balance between charge carriers on polyalkylthiophenes in solution can be substantially altered by a small change of relative permittivity of the solvent,[31] and therefore it may be that relative permittivity change in the copolymer film, as a result of accessing the Ni(II)/Ni(III) redox process, may likewise alter this balance. Given that the copolymer films are less conjugated than poly-3-methylthiophene itself, leading to more extensive early polaron formation, it is possible that the loss feature seen at higher energy later in oxidation might be due to bleaching of the polaron transition involving both intergap levels (transition 3 in Fig. 3), which could tail into the near-IR. The observed IRAV changes support this possibility.

The new electronic band at low energy may be due to a photoassisted electron transfer from Ni(II) to the lowest interband state of the *oxidised* polythiophene. There is much interest in photoinduced charge separation in *neutral* polythiophenes containing electron acceptors, such as C_{60}.[2,34–36] The potential at which the new electronic band is first apparent, +0.2 V, is some 0.45 V negative of the Ni(II)/Ni(III) half-wave potential. This translates to 3640 cm^{-1}, close to the maximum of the new band. The movement of the band to lower energy as a function of increasing potential can then be understood as due to the decreasing energy needed to promote the electron from the Ni(II) to the increasingly oxidised polythiophene. To test these ideas further, we plan to examine related polymers using similar Ni(II) complexes with less positive redox potentials.

Electrochemistry of terthiophene-functionalised complexes 12 and 13

Before outlining the electrochemistry of **12** and **13**, it is worth mentioning briefly the electropolymerisation of terthiophenes which do not have a cationic substituent, for example 2,2′:5′,2″-terthiophene itself, **14**,[37] 3′-*n*-hexyl-2,2′:5′,2″-terthiophene, **15**,[14] and 3,3″-di-*n*-octyl-2,2′:5′,2″-terthiophene **16**.[38] In 0.2 M tetraethylammonium tetrafluoroborate (TEAT)–acetonitrile, the onset of oxidation of **15** occurs at *ca.* +0.35 V, and on cycling between −0.45 V and +0.55 V, a well-defined, quite sharp, chemically reversible redox system grows with cycle number, at +0.26 V. This was assigned to the reversible oxidation of a film consisting mainly of the electrodeposited sexithiophene formed by α,α′-dimerisation of **15** on formation of its radical cation, by analogy with the work of Henderson and Collard on **16** which behaves similarly.[38] To electrodeposit a redox-active, adherent polythiophene using **15** as monomer, it was necessary to employ a more positive potential limit (+0.85 V), probably because at this potential, formation of the terthiophene dication begins, which undergoes a much more rapid irreversible polymerisation reaction.[14,38]

Turning now to the oxidation of the terthiophene-bearing complex **12**, on the first oxidative sweep, the onset of oxidation was at +0.55 V (Pt electrode), some 0.2 V more positive than for **15**.[14] When the positive limit was set just beyond this potential, intensely blue material was seen in solution around the electrode surface, and a chemically reversible redox wave developed at +0.41 V, but after 12 cycles the peak currents for this process reached constant values, and no polymer layer formed. The evolving redox process at +0.41 V suggests that dimerisation of the electrogenerated terthiophene cation radical is occurring, and that a sexithiophene product (two possible regioisomers) analogous to that generated in similar experiments with **15**[14,38] is formed. However, in this case the sexithiophenes are soluble in the electrolyte, giving the intense blue colour in their oxidised form. The redox process at +0.41 V is therefore due to oxidation of sexithiophenes to the radical cation, made more positive than for **15** by the close proximity of the cationic Ni(II) centres. Although the oxidation process at > +0.55 V in these experiments is expected to overlap the Ni(II)/Ni(III) wave, this does not affect the outcome. This is supported by the observation that when the non-coordinating electrolyte CH_2Cl_2–0.2 M Bu_4NBF_4 was employed, almost identical results were obtained, although in this medium, the Ni(II)/Ni(III) redox wave would not be expected until > +1.0 V.[17]

When the positive limit was increased to +1.05 V, we were able to obtain an adherent and electrochromic polymer layer, and new broad redox waves due to polythiophene redox chemistry developed, a minor wave centred at +0.35 V and a major wave, which overlapped the Ni(III)/Ni(II) system, at +0.70 V. Films of varying thickness could be deposited by repetitive redox cycling, on either ITO or Pt working electrodes.

After growth experiments, the films were held at the negative potential limit, then removed from the cell at open circuit, washed with acetonitrile and transferred to fresh background electrolyte. The voltammogram of a typical film, grown by 20 potential cycles between −0.25 and +1.05 V on an ITO-coated glass electrode, is shown in Fig. 5. It was noticeable that some material dissolved when the films were washed. A greater proportion of the material appeared to dissolve for nominally thicker films: when a film (grown using 20 redox cycles) was cycled in background electrolyte after washing (Fig. 5), the charge passed was only 2.9 times that for a nominally much thinner film, grown using 5 cycles.

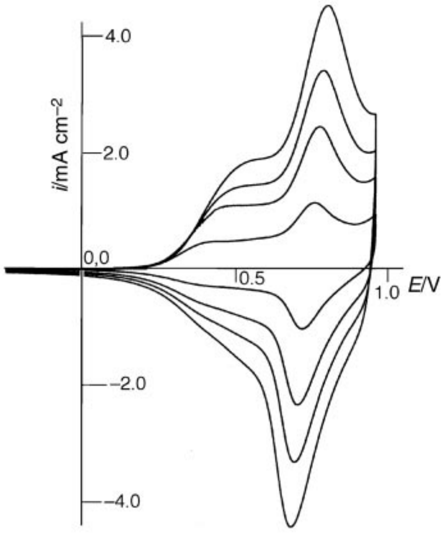


Fig. 5 Cyclic voltammograms of a film of poly-**12** (grown from a solution of 5 mM **12** in 0.2 M Et_4NBF_4–CH_3CN) on an ITO-coated glass electrode, in 0.2 M Et_4NBF_4–CH_3CN. Scan rates, in order of increasing peak currents, were 0.01, 0.02, 0.03 and 0.04 V s^{-1}.

Interestingly, the voltammograms of these polyterthiophene films are remarkably symmetrical, and are very different from the usual polyterthiophene voltammograms (see Fig. 4 of ref. 36).[14,37,38] They are notably similar in profile to the CV's of the poly-**4**–poly-3-methylthiophene copolymer, except that the onset of the polyterthiophene oxidation, +0.30 V, is more positive than that for the copolymer oxidation (+0.15 V on Pt), suggesting that the copolymer film contains at least some polymer chains with more extensive conjugation. It is well-established that polythiophene films grown using thiophene oligomers often have shorter conjugation lengths than films grown using thiophenes as monomers.[38] The Ni(III)/Ni(II) redox potential, at + 0.75 V, is *ca.* 0.1 V more positive than that observed in solution and in the copolymer. We suggest that the high ionic strength in poly-**12** films regardless of the polythiophene redox state, due to the presence of the cationic metal complex, makes the redox processes more reversible than those of the hydrophobic poly-**14**, **-15** or **-16**, owing to easier ion ingress and egress.

Because the thiophene : nickel stoichiometry is fixed at 3 : 1 by polymerising **12**, we can use the voltammograms in Fig. 3 to estimate the ratio of Ni(II) to thiophene rings in **4**–3-methylthiophene copolymers. Earlier, we estimated the composition of **1**–3-methylthiophene copolymers by integrating the charge under the Ni(II)/Ni(III) wave,[11,12] and under the 'polythiophene' redox wave, and assuming that fully-oxidised polythiophene chains have one positive charge per four thiophene rings.[13] This consistently gave a composition of approximately one Ni(II) site per ten thiophene rings. If we apply the same procedure to our poly-**4**–3-methylthiophene films (Fig. 2), we find that Ni(II) : thiophene is slightly smaller, 1 : 12. However, for poly-**12** the same procedure gives a composition of Ni(II) : thiophene 1 : 6, which is clearly a serious underestimate. This suggests that we have also previously underestimated the Ni(II) content of our copolymers.[11,12]

The 'polythiophene' redox wave of the copolymers is clearly different from that of poly-3-methylthiophene itself, and this may invalidate simple extrapolation to estimate the charge under the 'polythiophene' redox wave; the current due to polythiophene oxidation may, in fact, fall as the Ni(II)/Ni(III) wave is accessed. Moreover, the assumption that one charge is removed per four thiophene rings for fully oxidised polythiophene films[13] may be an underestimate at our positive potential limit, which must be significantly more positive than those normally employed for polythiophenes[13] to allow us to access the Ni(II)/Ni(III) redox wave. Wrighton *et al.* examined the electrochemistry of some polythiophenes up to +1.8 V *vs.* Ag wire quasi-reference in liquid SO_2–Bu_4NPF_6 electrolyte under anhydrous conditions, and found that they could be oxidised to the extent of approximately 0.5–1.0 electrons per thiophene ring at the most positive potential.[39] Using these results, we estimate that our polythiophene may, in fact, be oxidised to the extent of up to 0.35 electrons per thiophene ring at the positive limit.

Given the observations of Henderson *et al.* that it is possible to deposit electrochemically dimerised terthiophene films,[38] we were interested in the possibility of electrodepositing the soluble oligomers generated at low potentials in the above experiments, by using a less polar electrolyte in which the charged oligomer solubility might be smaller. Electropolymerisation of **12** in CH_2Cl_2–0.2 M tetrabutylammonium tetrafluoroborate (TBAT) resulted in essentially the same voltammetric behaviour as in acetonitrile.

We also prepared the neutral, pseudo-octahedral *trans*-[Ni(**11**)Cl_2] (**13**), with the idea that it might be possible to 'tune' the Ni(II)/Ni(III) potential by controlling the coordination chemistry at Ni(II); a related complex (CH_2Cl_2–0.2 M Bu_4NCl) shows the Ni(II)/Ni(III) process at +0.175 V.[17] Moreover, we hoped that by using a neutral complex, we could move to a less polar solvent, and so isolate the terthiophene dimers in film form.[38]

However, the fact that we wished to electro-oxidise the terthiophene unit meant that we were unable to use Bu_4NCl as the electrolyte salt.[40] When we investigated the electrochemistry of **13** in CH_2Cl_2–0.2 M TBAT, we found that the *onset* of oxidation did not occur until +0.30 V. Moreover, when the dark green solid **13** was dissolved in CH_2Cl_2–0.2 M TBAT, it gave an orange–yellow solution, the electronic spectrum of which was consistent with the square planar form, $[Ni(\mathbf{12})]^{2+}$. In cases where the anion is moderately coordinating, such as for chloride, there is an equilibrium between octahedral, paramagnetic $[Ni(L)X_2]$ and square planar, diamagnetic $[Ni(L)]X_2$, and high ionic strength drives this to the square planar form.[17] Assuming that the large excess of tetrafluoroborate anions leads to metathesis from $[Ni(\mathbf{12})]Cl_2$ to $[Ni(\mathbf{12})](BF_4)_2$, this irreversible oxidation must be due to the generation of the terthiophene radical cation, since the Ni(III)/Ni(II) redox potential for $[Ni(\mathbf{12})](BF_4)_2$ would not be expected until > +1 V in CH_2Cl_2.[17] Thus, our efforts were defeated by solution equilibria involving the coordination geometry of the Ni(II) site. Once more, dark blue material was seen streaming away from the working electrode surface positive of +0.3 V, and no polymer film was deposited.

When a higher potential limit (+0.9 V) was employed, an electrochromic, redox-active polymer film was deposited. The electrochemistry of these films, cycled in 0.2 M TEAT–CH_3CN as background electrolyte, was essentially indistinguishable from that of films grown using complex **12** in 0.2 M TEAT–CH_3CN. Interestingly, the presence of chloride ions in the electrodeposition solution does not appear adversely to affect the polymer formation.

In summary, we have shown that the short alkyl 'spacer' between the thiophene and the bulky metal complex substituent in **1** is not a significant factor in preventing its electrochemical homopolymerisation, since electropolymerisation of **4** did not afford homopolymer films, whereas electropolymerisation of **12** and **13** was successful. Copolymerisation of **4** with 3-methylthiophene gave polythiophene films bearing covalently-attached $[Ni(cyclam)]^{2+}$ units. *In situ* infrared spectroscopy reveals unusual evolution of the lowest energy electronic transition as a function of potential in the copolymer, possibly owing to charge transfer from the nickel(II) centre to the oxidised polymer backbone.

Acknowledgements

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