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Thiophene-substituted nickel dithiolene complexes. Precursors for low band gap conjugated metallopolymers

Christopher L. Kean, David O. Miller and Peter G. Pickup*

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7. E-mail: ppickup@mun.ca

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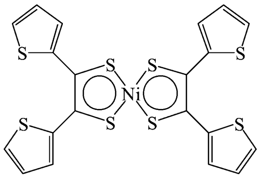
A series of electrochemically polymerizable Ni dithiolene complexes have been prepared and their electrochemical and spectroscopic properties have been characterized. Three thiophene-substituted complexes were anodically polymerized to give polymer films whose electrochemical properties correlated well with their predicted structures. Thus, a complex with two thiophene substituents in one dithiolene ligand [*cis*-1,2-di(2′-thienyl)-1,2-ethenedithiolene] gave a polymer with electrochemistry characteristic of a poly(dithienylenevinylene), while a complex with one thiophene substituent on each dithiolene ligand [*cis*-1-(2′-thienyl)-2-phenyl-1,2-ethenedithiolene] gave a polymer with electrochemistry characteristic of a coordination polymer. A polymer prepared from a complex with four thiophene substituents {bis[*cis*-1,2-di(2′-thienyl)-1,2-ethenedithiolene]nickel} also gave electrochemistry characteristic of a poly(dithienylenevinylene), indicating that it contained extended poly(dithienylenevinylene)-like chains. A cathodically polymerizable complex, bis[*cis*-1,2-di(4-bromophenyl)-1,2-ethenedithiolene]nickel, is also reported.

Introduction

The incorporation of transition metal complexes into conjugated organic polymers offers a new dimension for the development of advanced electronic, catalytic, and sensing materials.[1,2] Dithiolene complexes[3] are attractive building blocks for such systems because of their aromaticity and facile reduction (n-doping). The observation of superconductivity[4] and non-linear optical properties[5,6] in metal dithiolene salts provides great incentive for their hybridization with conjugated polymers.[2]

We have previously reported on a dithiolene-based conjugated metallopolymer prepared by the electrochemical polymerization of bis[*cis*-1,2-di(2′-thienyl)-1,2-ethenedithiolene]nickel (**1**).[7] The extensive conjugation of this complex and the electron donating effect of the peripheral thiophenes make it an attractive unit for constructing intrinsic (neutral) molecular conductors.[8] Indeed, poly-**1** has one of the lowest band gaps (*ca.* 0.4 eV) reported to date for a conjugated polymer. However, its conductivity of 10^{-4} S cm^{-1} when p-doped is disappointing, and indicates that sufficient conjugation between molecules was not achieved in the polymers prepared in the preliminary work. The presence of four peripheral thiophene rings on **1** may result in a highly cross-linked polymer without extended linear chains. It is therefore of great interest to investigate similar materials that will form linear polymers.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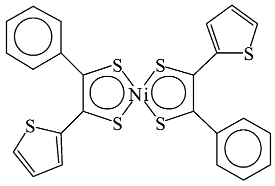
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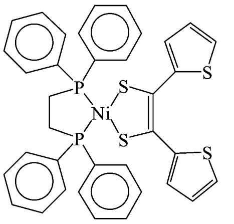
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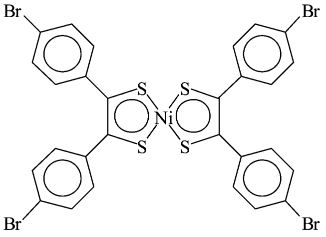
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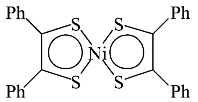
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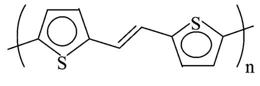
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In this paper, we report on three additional examples (structures **2**–**4**) of polymerizable Ni dithiolene complexes. These complexes have been designed to allow us to explore structure–property relationships in dithiolene-based conjugated metallopolymers. The expected, ideal structures of polymers prepared from complexes **2**–**4** are shown in Fig. 1. Thus, complex **2** will form a coordination polymer in which the Ni atoms form links in the polymer chain, while in poly-**3**, the Ni will be peripheral to the polymer chain. Comparison of the properties of these polymers with those of poly- **1** provides insight into its structure. Complex **4** reveals details of the role of the thiophene linkages in poly-**1** by enabling a comparison with a similar material containing phenyl linkages (Fig. 1).

Experimental

Reagents

CH_3CN (spectroscopic grade) was distilled over CaH_2 under Ar before use. $[Et_4N]ClO_4$ (prepared from $[Et_4N]Br$ and $HClO_4$) was recrystallized three times from water and dried under vacuum at 110 °C for 12 h. $[Bu_4N]PF_6$ (electrochemical grade, Fluka), CH_2Cl_2 (spectroscopic grade), and all other chemicals were used as received.

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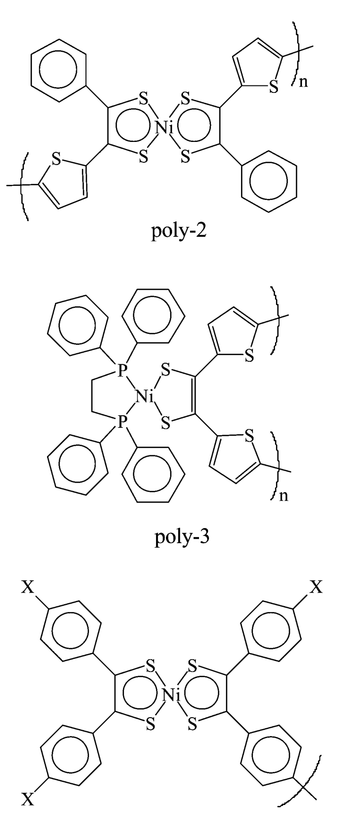


poly-2

poly-3

poly-4: X = -PhC $_2$S$_2$PhXNi(XPhC $_2$S$_2$PhX) or Br or H

Fig. 1 Expected ideal structures for polymers prepared electrochemically from complexes **2**–**4**.

Instrumentation

GE-300NB 300 MHz and Bruker Avance 500 MHz NMR spectrometers, Hewlett Packard Series 1100 and V.G. Micromass 7070HS mass spectrometers, a Cary 5E UV-vis-NIR spectrometer, and a Pine Instruments RDE4 potentiostat were used. Atomospheric pressure ionization electrospray (API-ES) mass spectra were recorded for complexes in methanol at a fragmentation voltage of 100 V. Elemental analyses were performed by Canadian Microanalytical Service Ltd (Delta, BC).

Synthesis

4,5-Dithienyl-1,3-dithiol-2-one (6a)[9] A mixture of 2,2′-(ethyne-1,2-diyl)bis(thiophene)[10] (1.00 g, 5.30 mmol), *O*,*O*-diisopropyldithiobis(thioformate) (3.62 g, 13.4 mmol) and 2,2′-azobis(2-methylpropionitrile) (AIBN; 0.88 g, 5.30 mmol) was dissolved in 6 mL of dry benzene and heated at reflux under a flow of nitrogen for 32 h. The solvent was then removed under reduced pressure to give a brown residue which was purified by column chromatography on silica gel using a 2 : 1 mixture of hexanes and chloroform. The residue was then crystalized from hexanes to give a yellow solid (0.83 g, 3.0 mmol, 56%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm *vs.* TMS): δ 7.37 (1H, dd J = 5.4 and 1.2 Hz), 7.09 (1H, dd, J = 3.8 and 1.2 Hz), 7.01 (1H, dd).

Tetraethylammonium bis[*cis*-1,2-di(2′-thienyl)-1,2-ethenedithiolato]nickel ([Et$_4$N]1). **6a** (0.60 g, 2.1 mmol) was mixed with 30 mL of anhydrous ethanol and placed under an atmosphere of argon. Addition of Na(s) (0.10 g, 4.5 mmol) caused the yellow mixture to become an orange solution. This solution was stirred for 10 min and transferred dropwise *via* cannula into an ethanol solution of nickel(II) dichloride hexahydrate (NiCl$_2$·6H$_2$O; 0.26 g, 1.1 mmol, 60 mL). The solution immediately turned a deep red and was stirred at room temperature for 20 h. The reaction mixture was then filtered and a solution of tetraethylammonium bromide ([Et$_4$N]Br; 0.83 g, 4.0 mmol) in ethanol (10 mL) was added to induce precipitation of the product as a red solid. The solid was isolated by vacuum filtration and washed three times with ethanol and a further three times with diethyl ether. After drying, a red solid was obtained (0.66 g, 0.95 mmol, 90%).

Bis[*cis*-1,2-di(2′-thienyl)-1,2-ethenedithiolene]nickel(1). [Et$_4$N]**1** (0.66 g, 0.95 mmol) was dissolved in 80 mL of dry acetonitrile and placed under a flow of argon. An acetonitrile solution of I$_2$ (1.62 g, 6.4 mmol, 60 mL) was added dropwise over a 20 min period, during which time the crude product formed as a black precipitate. Once the reaction mixture had been stirred for 2 h the crude product was isolated by vacuum filtration and purified by a mixed solvent recrystallization using dichloromethane and methanol, to yield the desired product as a black powder (0.15 g, 0.27 mmol, 28%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm *vs.* TMS): δ 7.59 (1H, dd, J = 5.7 and 1.4 Hz), 7.29 (1H, dd, J = 4.6 and 1.4 Hz), 7.07 (1H, dd). MS (API-ES) *m*/*z* (%): 566 (M$^+$, 0.3), 245 (36), 190 (100). Elemental analysis calculated for $C_{20}H_{12}S_8Ni$: C 42.33, H 2.13, S 45.20; found: C 42.09, H 2.16, S 44.49%.

2-(2′-Thienyl)-1-phenylethyne (5b). A solution of 2-iodothiophene (2.26 g, 10.7 mmol) in 80 mL of freshly distilled benzene was degassed using the freeze–pump–thaw method and placed under a flow of nitrogen. Tetrakis(triphenylphosphine)palladium (0.60 g, 0.52 mmol) was added, followed by CuI (0.10 g, 0.52 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (2.63 g, 17.3 mmol). Then, phenylacetylene (1.12 g, 11.0 mmol) in 20 mL of distilled degassed benzene was added dropwise over an hour. This mixture was allowed to stir at room temperature in the absence of light for 18 h. The reaction mixture was then poured into two times its volume of petroleum ether, filtered, and concentrated, to leave a brown residue. The residue was dissolved in 50 mL of petroleum ether and washed successively with NaHCO$_3$, H$_2$O, and brine, followed by drying over MgSO$_4$, filtration, and concentration, to give a brown liquid. Further purification was achieved *via* column chromatography on silica gel with petroleum ether as eluent. Upon concentration, the desired product was obtained as a white powder (1.36 g, 7.39 mmol, 70%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm *vs.* TMS): δ 7.01 (1H, dd, J = 4.6 and 4.5 Hz), 7.52 (2H, m), 7.34 (3H, m) 7.29 (2H, m). MS (API-ES) *m*/*z* (%): 184 (M$^+$, 100).

4-(2′-Thienyl)-5-phenyl-1,3-dithiol-2-one (6b). A mixture of **5b** (0.76 g, 4.10 mmol), *O*,*O*-diisopropyldithiobis(thioformate) (2.80 g, 10.4 mmol) and AIBN (0.70 g, 4.3 mmol) were dissolved in 6 mL of dry benzene and heated at reflux under a flow of nitrogen for 18 h. A second portion of AIBN (0.30 g, 1.8 mmol) was added and the reaction mixture refluxed for an additional 14 h. The solvent was then removed under reduced pressure to give a brown residue, which was purified by column chromatography on silica gel using a 2 : 1 mixture of hexanes and chloroform. The residue was then crystallized from hexanes and vacuum filtered to give a yellow–orange solid (0.52 g, 1.9 mmol, 46%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm *vs.* TMS): δ 7.38 (5H, m), 7.20 (1H, dd, J = 4.6 and 2.1 Hz), 6.91 (2H, m). ^{13}C NMR (125 MHz, CDCl$_3$, ppm *vs.* TMS): δ 189.9, 133.0, 131.6, 130.1, 129.7, 129.3, 129.1, 128.9, 127.6, 127.2, 122.3. MS (API-ES) *m*/*z* (%): 276 (M$^+$, 91), 248 (25), 184 (100), 121 (65). Elemental analysis calculated for $C_{13}H_8S_3O$: C 56.49, H 2.92, S 34.80; found: C 56.29, H 2.95, S 35.17%.

Tetraethylammonium bis[*cis*-1-(2′-thienyl)-2-phenyl-1,2-ethenedithiolato]nickel ([Et$_4$N]2). **6b** (0.20 g, 0.72 mmol) was mixed with 30 mL of anhydrous ethanol and placed under an atmosphere of argon. Addition of Na(s) (0.033 g, 1.4 mmol) caused the yellow mixture to become an orange solution. This solution was stirred for 10 min and transferred *via* cannula dropwise into an ethanol solution of $NiCl_2 \cdot 6H_2O$ (0.09 g, 0.4 mmol, 20 mL). It immediately turned a deep red and was allowed to stir at room temperature for $\sim$20 h. The reaction mixture was then filtered and $[Et_4N]Br$ (0.30 g, 1.4 mmol) was added, which caused the formation of a red precipitate which was isolated through vacuum filtration and washed three times with ethanol and an additional three times with diethyl ether, then dried *in vacuo* for 6 h, giving a red complex (0.20 g, 0.29 mmol, 82%).

Bis[*cis*-1-(2′-thienyl)-2-phenyl-1,2-ethenedithiolene]nickel (2). $[Et_4N]$**2** (0.15 g, 0.22 mmol) was dissolved in 20 mL of acetonitrile and placed under a flow of argon. An acetonitrile solution of I_2 (0.34 g, 1.3 mmol, 20 mL) was added dropwise over a 20 min period, which caused the formation of a black precipitate. Once the reaction mixture had been stirred for 2 h, the crude product was purified through a mixed solvent recrystallization from methanol and dichloromethane, yielding a black solid (0.033 g, 0.060 mmol, 30%). ^{1}H NMR (500 MHz, CD_2Cl_2, ppm *vs.* TMS): δ 7.38 (6H, m), 7.03 (1H, d, J = 4.3 Hz), 6.88 (1H, dd, J = 4.3 and 5.0 Hz). MS (API-ES) m/z (%): 554 (M^+, 10), 248 (46), 184 (100).

[1,2-Bis(diphenylphosphino)ethane][4-(1',2'-ethylenedithiolate)-1,3-dithienyl]nickel (3). Anhydrous ethanol (4 mL) was placed under a flow of argon, then Na(s) (0.032 g, 1.4 mmol) was added and allowed to stir until the Na(s) had completely reacted ($\sim$10 min). This solution was then transferred *via* cannula dropwise into a THF solution of **6a** (0.20 g, 0.70 mmol, 40 mL). Stirring for 10 min was accompanied by a color change from clear yellow to orange. Then, $Ni(dppe)Cl_2$ (0.38 g, 0.72 mmol) was added, which resulted in an immediate color change to blue. After additional stirring for 18 h under an atmosphere of Ar, the solvent was removed under reduced pressure to give a dark green residue. This residue was purified by column chromatography on silica using dichloromethane. The blue band was collected to give a forest green solid (0.29 g, 0.42 mmol, 57%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm *vs.* TMS): δ 7.80 (6H, m) 7.44 (4H, m), 7.02 (1H, d, J = 5.1 Hz) 6.87 (1H, d, J = 3.4 Hz), 6.76 (1H, dd, J = 3.4 and 5.1 Hz), 2.35 (2H d, J = 17.1 Hz). MS (API-ES) m/z (%): 398 (8), 262 (68), 245 (100), 190 (97). Elemental analysis calculated for $C_{36}H_{30}S_4P_2Ni$: C 60.77, H 4.25, S 18.03; found: C 60.51, H 4.40, S 18.11%.

Bis[*cis*-1,2-(4-bromobenzene)-1,2-ethenedithiolene]nickel (4). 4,4′-Dibromobenzil (1.02 g, 2.8 mmol) and P_2S_5 (0.86 g, 1.9 mmol) were mixed with 4.5 mL of 1,4-dioxane. Upon refluxing for 2 h, a brown solution was formed. The solution was then cooled to room temperature and gravity filtered to remove excess P_2S_5. An aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.30 g, 1.3 mmol, 1.2 mL) was added to the filtrate. The reaction mixture was refluxed for an additional 2 h, cooled, and poured into 25 mL of acetone. This resulting green precipitate was purified by a mixed solvent recrystallization from dichloromethane and methanol. A black solid was isolated (0.14 g, 0.16 mmol, 14%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm *vs.* TMS): δ 7.46 (2H, m), 7.24 (2H, m). MS (API-ES) m/z (%): 400 (39), 336 (100), 240 (73), 201 (82), 176 (65). Elemental analysis calculated for $C_{28}H_{16}S_4Br_4Ni$: C 39.15, H 1.88, S 14.63; found: C 38.71, H 1.98, S 14.49%.

Crystal structures

Crystals of tetraethylammonium bis[*cis*-1,2-di(2′-thienyl)-1,2-ethenedithiolato]nickel and tetraethylammonium bis[*cis*-1-(2′-thienyl)-2-phenyl-1,2-ethenedithiolato]nickel were grown by a diffusion process, whereby these salts were dissolved in a minimal amount of acetonitrile. These solutions were placed in a 50 mL Erlynmeyer flask and these flasks were enclosed within a larger vessel containing benzene. After approximately 1.5 weeks, crystals formed that were suitable for X-ray analysis. All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation. Calculations were performed using the teXsan crystallographic software package (Molecular Structure Corporation, The Woodlands, TX, USA) and graphics were created using Ortep-3 for Windows (L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565).

Each structure was found to contain a "loose" or disordered tetraethylammonium cation on a special position. The carbon atoms (and nitrogen for compound **1**) associated with this were refined isotropically.

Crystal data for [Et$_4$N]1. $C_{42}H_{48}S_{12}Ni_{1.50}N_{1.50}$, M = 1046.62, triclinic, a = 14.522(2), b = 19.507(2), c = 8.667(1) Å, α = 101.18(1), β = 98.39(1), γ = 79.837(9)°, V = 2354.9(5) Å^3, T = 299(1) K, space group $P\bar{1}$ (#2), Z = 2, μ(Mo-K$_\alpha$) = 11.70 cm^{-1}, 11329 reflections measured, 10898 unique (R_{int} = 0.040), which were used in all calculations. The final R and R_w were 0.063 and 0.050, respectively [$I > 2.00\sigma(I)$].

Crystal data for [Et$_4$N]2. $C_{32}H_{36}NS_6Ni$, M = 685.70, monoclinic, a = 28.856(4), b = 7.518(3), c = 16.377(5) Å, α = 106.73(2)°, V = 3402(2) Å^3, T = 299(1) K, space group $C2/c$ (#15), Z = 4, μ(Mo-K$_\alpha$) = 9.61 cm^{-1}, 4316 reflections measured, 4233 unique (R_{int} = 0.040), which were used in all calculations. The final R and R_w were 0.098 and 0.094, respectively [$I > 2.00\sigma(I)$].

CCDC reference numbers 184723 and 184724.

See http://www.rsc.org/suppdata/jm/b2/b204090e/ for crystallographic data in CIF or other electronic format.

Electrochemistry

All cyclic voltammetry was carried out in a conventional three-compartment glass cell at room temperature under a flow of argon. For the monomeric complexes, de-oxygenated dichloromethane was the solvent of choice in most cases, since it provided the greatest solubility. Monomer concentrations were typically *ca.* 2 mM. The working electrode was a 0.0052 cm^2 Pt disk sealed in glass, unless otherwise specified. The reference electrode was either a saturated sodium chloride calomel electrode (SSCE) or Ag/AgCl, as specified, while the counter electrode was a Pt wire.

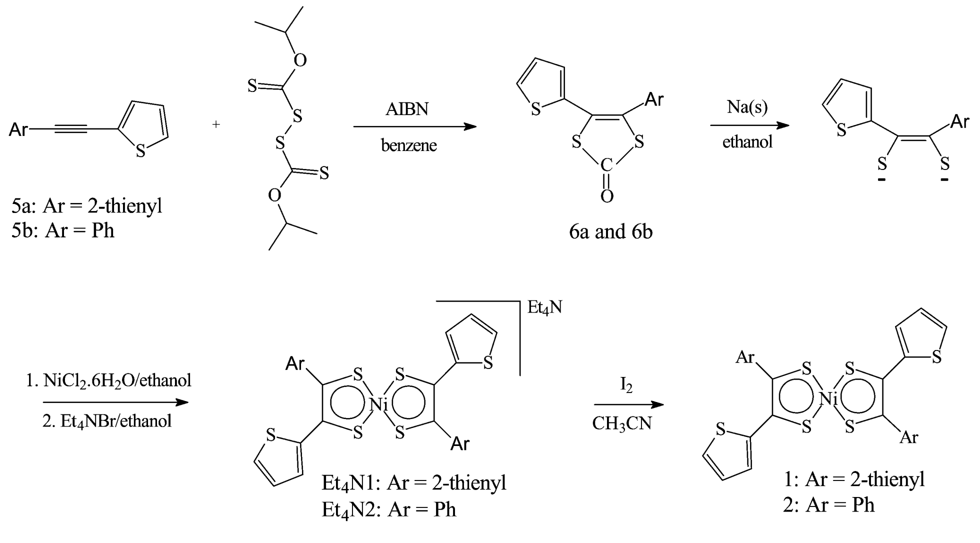
Cathodic polymerization of 4

A procedure similar to that described by Schiavon *et al.*[11] for the cathodic polymerization of 2,5-dibromopyridine was followed. Complex **4** (0.025 mM), $[Ni(2,2'\text{-bipyridine})_3](ClO_4)_2$ (0.025 mM), and $[Bu_4N]PF_6$ (0.1 M) were dissolved in CH_2Cl_2 and the solution was deoxygenated in an electrochemical cell. The potential of the Pt working electrode was scanned repeatedly between 0 and −2.0 V at 50 mV s^{-1}. After 8 potential cycles, the electrode was removed from the cell and rinsed well with acetone. Electron microprobe analysis indicated that less the 5% of the Br from the monomer was retained in the polymer film on the electrode.

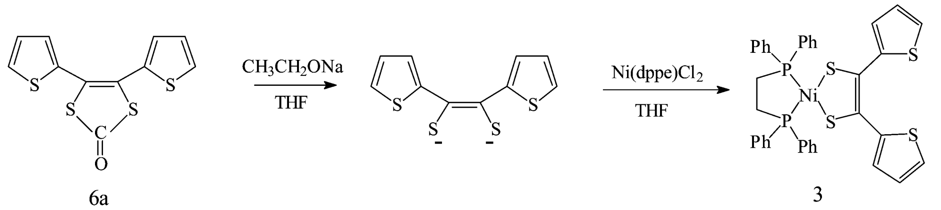
Results and discussion

Synthesis of complexes

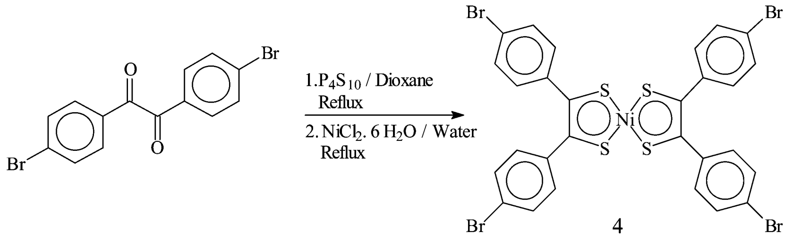
The synthetic routes employed are outlined in Schemes 1–3. Complexes **1** and **2** were prepared from the corresponding bis(aryl)ethynes (**5a** and **5b**) *via* 1,3-dithiol-2-ones **6a** and **6b**. The 1,3-dithiol-2-ones were obtained by following a general procedure described by Gareau and Beauchemin.[12] Generation of the dithiol dianion with base (Na in ethanol) and



Scheme 1



Scheme 2



Scheme 3

complexation with Ni^{2+} gave the anionic bis(dithiolene) complexes ([Et_4N]**1** and [Et_4N]**2**), which could be oxidized to the neutral complexes by I_2. The structures of the complexes were confirmed by X-ray crystallography of the Et_4N^+ salts of the anions ([Et_4N]**1** and [Et_4N]**2**).

Complex **3** was prepared (Scheme 2) from [1,2-bis(diphenylphosphino)ethane]dichloronickel(II) [Ni(dppe)Cl_2] and the dithiol dianion generated from **6a**, while complex **4** was obtained following an older route (Scheme 3)[13] by heating commercially available 4,4′-dibromobenzil with P_4S_{10} in 1,4-dioxane, followed by addition of $NiCl_2·6H_2O$ in water. Complex **4** could presumably be prepared in higher yield *via* a 1,3-dithiol-2-one route (as used for **1** and **2**), but this was not tried.

Crystal structures

The crystal structure of compound [Et_4N]**2** is presented in Fig. 2, while that of [Et_4N]**1** is available as a CIF in the ESI. In both cases, the single tetraethylammonium ion per complex indicates a lone negative charge on each complex. The crystal structure of [Et_4N]**2** reveals that the ligands are oriented in a "*trans*" arrangement across the complex. Knowledge of the ligand orientation is important for predicting the structure of polymers formed from this complex.

Both of the structures obtained reveal a degree of disorder within the close-packed structure of the crystal. This disorder is evident from the thiophenes shown in Fig. 2, where both the 1 and 3 positions were found to display sulfur character. This can be attributed to the thiophenes having two different conformations with very similar energies. This disorder is not likely due to rotation of the thiophene rings in the solid state, since this would cause elongation of the other two carbon atom ellipsoids, which is not evident in the crystal structures. The 1

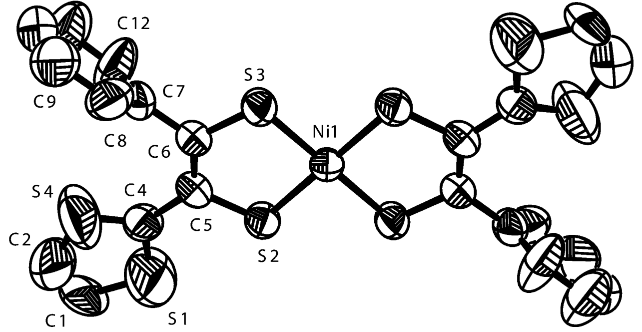


Fig. 2 X-Ray crystal structure of [Et_4N]**2**.

and 3 positions were therefore modeled as partial occupancy S atoms, with the occupancy set to refine and then fixed for the later stages of refinement. The S/C ratio was then calculated from the S occupancy.

Electrochemistry

Since complexes **1** and **2** are not soluble in acetonitrile, their electrochemistry was investigated in dichloromethane. The anionic complexes, $[Et_4N]$**1** and $[Et_4N]$**2** were soluble in CH_3CN, but their electrochemistry in this solvent was complicated by precipitation of the neutral species onto the electrode during oxidative scans. Since this process interferes with the anodic polymerization of the complex, which is the main subject of interest here, it was avoided by using CH_2Cl_2 as the solvent. The voltammetry of **1** has been presented elsewhere.[7]

Fig. 3 shows cyclic voltammograms of $[Et_4N]$**2** over various potential ranges. Like complex **1**,[7] it exhibits two reversible waves at low potential, and a third wave at *ca.* +1 V. Formal potentials for these waves are reported in Table 1, together with values for the other complexes. By comparison with literature values for similar complexes,[14] the wave at −0.75 V for **2** (−0.66 V for **1**) can be assigned to the $[NiS_4]^{1-/2-}$ redox couple, while the wave at +0.05 V (+0.13 V for **1**) is due to the $[NiS_4]^{0/1-}$ couple. The negative shift in the potentials of these two processes on substituting two of the thiophenes in **1** with phenyl groups in **2** indicates that the thiophene substituents stabilize the reduced species.

Based on the above assignments, the wave at +1.10 V (+1.08 V for **1**) must be due to formation of a cationic species. The absence of this wave for the tetraphenyl-substituted complex,[14] and the fact that it appears at almost the same potential for both **1** and **2**, strongly suggests that it is a thiophene-based wave. Indeed, repetitive potential cycling through this wave leads to an increasing voltammetric response (*e.g.* Fig. 3) that is characteristic of the electrochemical polymerization of a thiophene,[15,16] and results in film formation on the electrode.

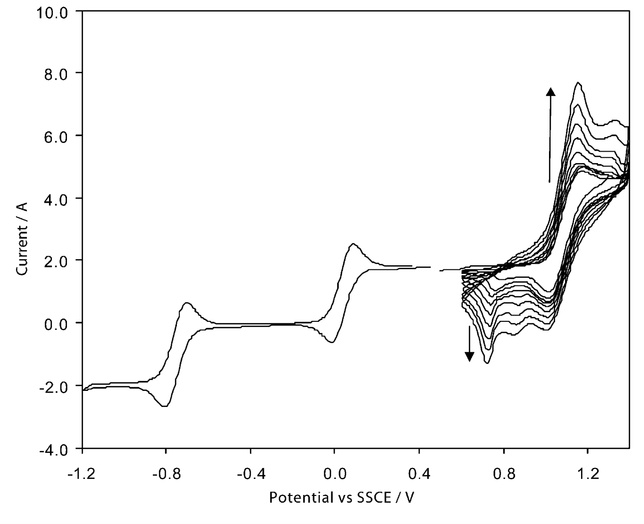


Fig. 3 Cyclic voltammetry (100 mV s^{-1}) of $[Et_4N]$**2** in CH_2Cl_2 containing 0.1 mol dm^{-3} $[Bu_4N]PF_6$. The initial scan between 0.5 and −1.2 V is shown, together with multiple scans between 0.6 and 1.4 V, during which currents increased with potential cycling.

Table 1 Formal potentials (V *vs.* SSCE) for the monomer complexes from cyclic voltammetry

Complex	−1/−2	0/−1	+1/0	+2/+1
1	−0.66	0.13	1.08	1.35
2	−0.75	0.05	1.1	—
3	—	—	0.51	1.1
4	−0.71	0.09	—	—
7[a]	−0.82	0.12	—	—

[a] In CH_3CN.[14]

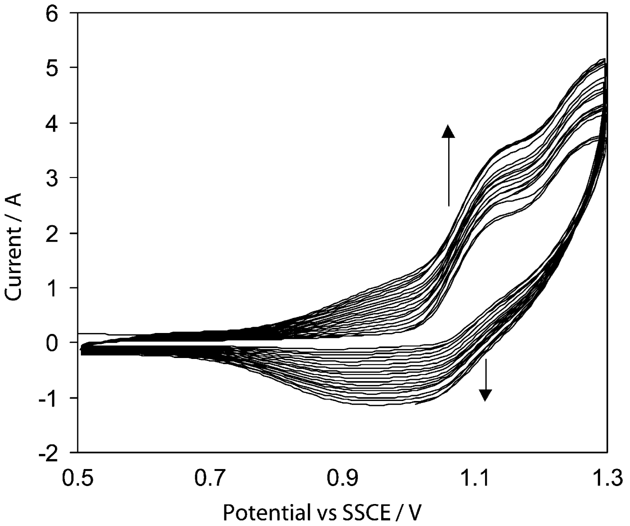


Fig. 4 Cyclic voltammetry (100 mV s^{-1}) of **1** in CH_2Cl_2 containing 0.1 mol dm^{-3} $[Bu_4N]PF_6$. Currents at all potentials increase with potential cycling.

Complex **1** was also found to polymerize when the potential was cycled through the +1.1 V wave, but more rapid polymer deposition was observed when the potential was cycled into a higher potential wave at *ca.* +1.3 V (Fig. 4). The current increases observed on successive scans are indicative of formation of an electroactive polymer film on the surface of the electrode.

The voltammetric behavior of complex **3** (Fig. 5) is quite different from that of either **1** or **2**. Oxidation waves are seen at + 0.51 and +1.1 V, but no reduction waves are seen. Clearly, the electron-donating power of the phosphine ligands has a very strong influence on the redox potentials of the complex, shifting the formal potentials for reduction to below −1.5 V. The oxidation wave at +1.1 V is at the same potential as the waves assigned to thiophene-based oxidations of **1** and **2**. Cycling through this wave does not lead to film formation on the electrode in CH_2Cl_2, but does in CH_3CN. It is therefore reasonable to assign it to a thiophene-based oxidation. The more reversible wave at +0.51 V would, therefore, appear to be due to an oxidation centered on the NiS_2P_2 core of the complex.

The voltammetric behavior of complex **4** (Fig. 6) is similar to

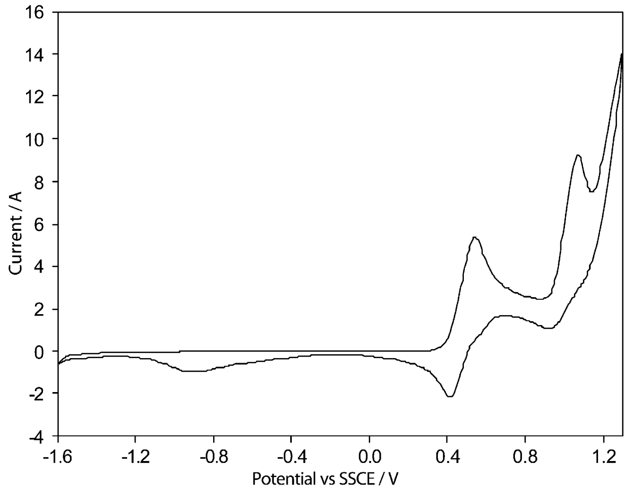


Fig. 5 Cyclic voltammetry (100 mV s^{-1}) of **3** in CH_2Cl_2 containing 0.1 mol dm^{-3} $[Bu_4N]PF_6$.

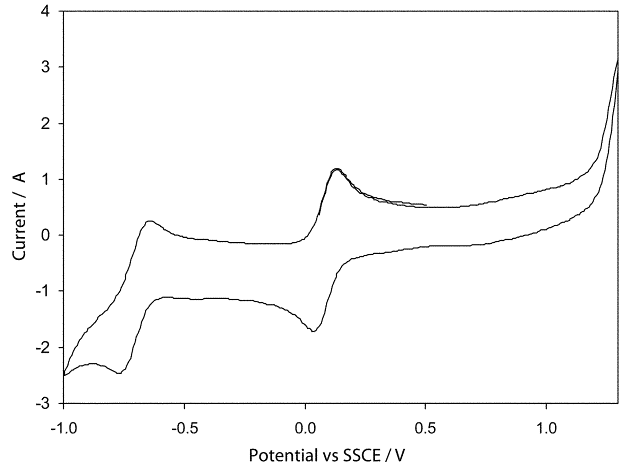


Fig. 6 Cyclic voltammetry (100 mV s^{-1}) of **4** in CH_2Cl_2 containing 0.1 mol dm^{-3} $[Bu_4N]PF_6$.

that of the unsubstituted tetraphenyl complex (**7**),[14] exhibiting reversible $[NiS_4]^{1-/2-}$ and $[NiS_4]^{0/1-}$ waves at −0.71 and +0.09 V, respectively (Table 1). These potentials are only slightly different from those of complexes **1** and **2**. The key difference is that complex **4** does not exhibit any oxidation waves and, therefore, cannot be anodically polymerized. Films of poly-**4** were prepared by cathodic polymerization[11] with Ni(2,2′-bipyridine)$_3$ as catalyst.

Electronic absorption spectra of monomer complexes

Bis-1,2 dithiolene complexes have unique electronic spectra with intense absorptions occurring at low energy in the visible and near infrared regions. These absorptions are due to π* transitions between orbitals that are delocalized over the NiS_4C_4 core of the complex. Data for complexes **1**–**4** and bis(*cis*-1,2-diphenyl-1,2-ethenedithiolene)nickel (**7**) are presented in Table 2.

As expected, addition of Br substituents to the peripheral phenyl rings of **7** to give **4** does not have a significant effect on the π* transition. However, replacement of the phenyl groups with thiophene significantly decreases the energy of this transition, with a larger effect being observed with four thiophenes (**1**) than with two (**2**). Thus, the thiophene substituents lower the HOMO–LUMO gap of the monomer and offer better prospects for generating low band gap polymers. This lowering of the HOMO–LUMO gap is consistent with the electrochemical results, in which thiophene substituents make the complex easier to reduce (lower LUMO) and easier to oxidize (higher HOMO).

Complex **3** does not exhibit a low energy π* transition. This is consistent with the electrochemical results, which show the absence of a low energy unoccupied state by the absence of an accessible reduction wave. Thus, the spectroscopic data support the assignment of the redox potentials in Table 1.

Cyclic voltammetry of polymer films

Fig. 7 shows a cyclic voltammogram of a poly-**1**-coated electrode in acetonitrile. The electrode was coated with a thin film of poly-**1** by constant potential electrolysis of **1** at +1.2 V in a *ca.* 2 mM solution of **1** in CH_2Cl_2 containing 0.1 M $[Bu_4N]PF_6$, then rinsed with acetone and transferred to the CH_3CN electrolyte solution. The voltammetry shown in Fig. 7 clearly shows that a Ni dithiolene complex has been deposited on the electrode. The three main redox waves were persistent for many cycles, although the peak currents did decay with potential cycling. The onset of oxidation at *ca.* +0.6 V indicates that the thiophene-based oxidation has shifted to lower potentials, and this is consistent with the formation of a polymer containing linkages at the peripheral thiophenes. Spectroscopic data and other observation support the conclusion that the film is polymeric.[7]

Table 2 Electronic spectral data for complexes **1**–**4** and **7**

Complex	λ_{max}/nm	ε/M^{-1} cm^{-1}
1	976	38 820
2	931	37 661
3	585	588
4	866	29 816
7[14]	866	30 900

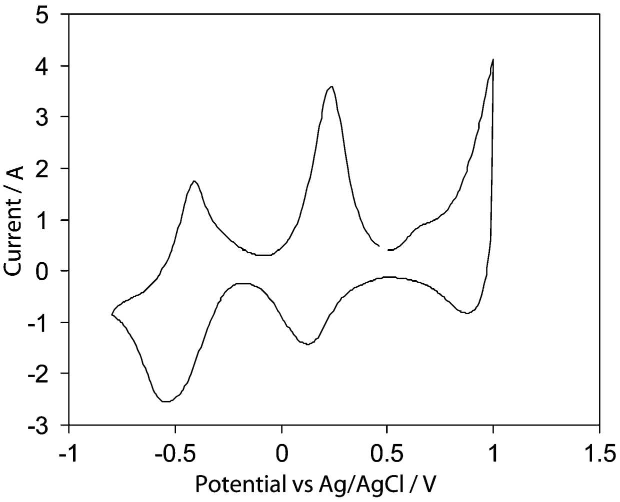


Fig. 7 Cyclic voltammetry (100 mV s^{-1}) of a poly-**1**-coated Pt electrode in CH_3CN containing 0.1 mol dm^{-3} $[Et_4N]ClO_4$.

Fig. 8 shows a cyclic voltammetric response for a poly-**2**-coated electrode. The waves at +0.06 and −0.68 V show that the complex has been deposited on the electrode in some way. The oxidation wave starting at *ca.* +0.65 V is irreversible and is, therefore, characteristic of neither the monomeric complex nor a polythiophene. This wave is quite different from the corresponding wave for poly-**1**, and the difference is consistent with the different polymeric structures that can be formed. In the expected structure of poly-**2** (Fig. 1), dimeric dithiolene ligands are linked by Ni centres to give a coordination polymer. The irreversibility of the thiophene oxidation wave of poly-**2**, which is characteristic of electronically isolated bithiophene

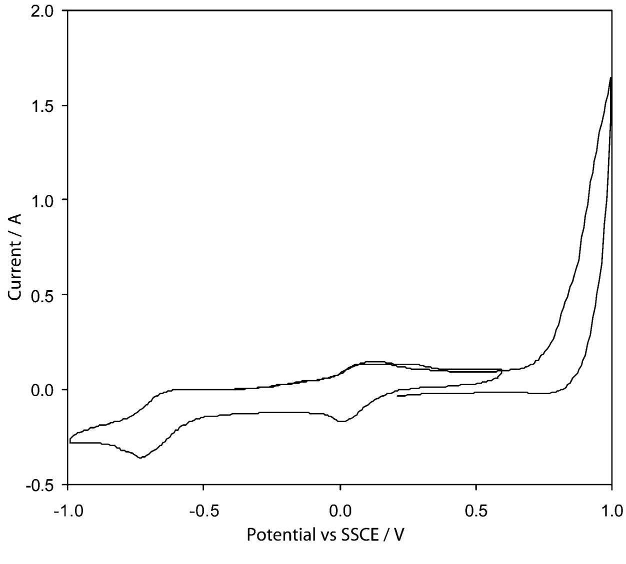


Fig. 8 Cyclic voltammetry (100 mV s^{-1}) of a poly-**2**-coated Pt electrode in CH_3CN containing 0.1 mol dm^{-3} $[Et_4N]ClO_4$.

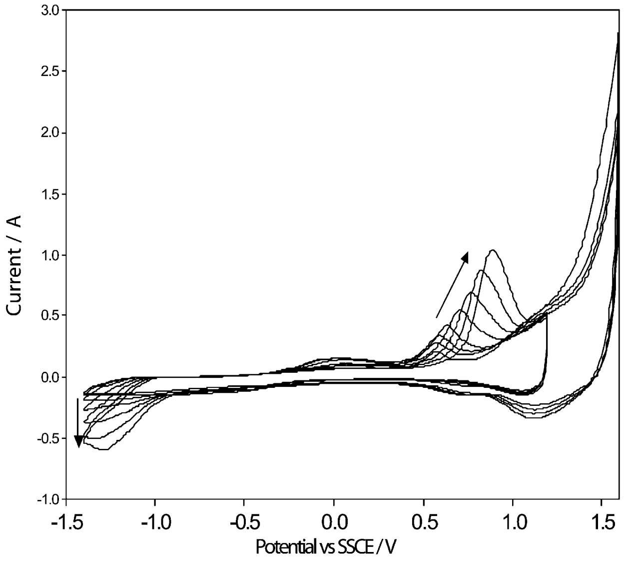


Fig. 9 Cyclic voltammetry (100 mV s^{-1}) of a poly-**3**-coated Pt electrode in CH_3CN containing 0.1 mol dm^{-3} $[Et_4N]ClO_4$. The potential was initially scanned between 0 and +1.4 V (not shown), and then the lower potential limit was decreased to −1.4 V and the upper limit increased to +1.6 V. The upper limit was decreased to +1.2 V when the waves at *ca.* −1.3 and +0.6 V began to grow.

linkages,[17] therefore indicates that the Ni centres do not mediate conjugation between dithiolene dimers along the chain. The polythiophene-like nature of the thiophene oxidation wave for poly-**1** thus indicates that this polymer contains more extensive conjugation, presumably due to the formation of poly(dithienylvinylene) chains (structure **8**) of significant length. The electrochemistry of poly-**3** (Fig. 9), which can only form poly(dithienylvinylene) chains and shows oxidation waves that are characteristic of such a structure, supports this conclusion. There appears to be a Ni dithiolene-based oxidation wave for poly-**3** in the +0.5 to +1 V region. This wave began to grow, and move to more positive potentials, when the potential sweep was extended to −1.4 V, and a reduction wave appeared at *ca.* −1.3 V. This behavior indicates that the Ni dithiolene sites are electronically isolated, and that their electrochemistry is mediated by the polymer backbone.

The electrochemistry of poly-**4** (Fig. 10) is very different from that of any of the other polymers prepared in this work. An oxidation wave at +0.46 V was observed on the first scan to +1 V (heavy line in Fig. 10), but this was absent on subsequent scans until the lower potential limit was decreased to < −1.2 V to allow reduction of the film. This wave is presumably due to Ni dithiolene sites in the film. Its disappearance following the first scan, and reappearance following reduction of the film, indicate that the oxidized form is non-conductive, causing electronic isolation of the oxidized sites. The partially reversible reduction waves at *ca.* −1.6 V are presumably due to n-doping of a poly(diphenylenevinylene)-type backbone. There are no oxidation (p-doping) waves between +1 and +2 V.

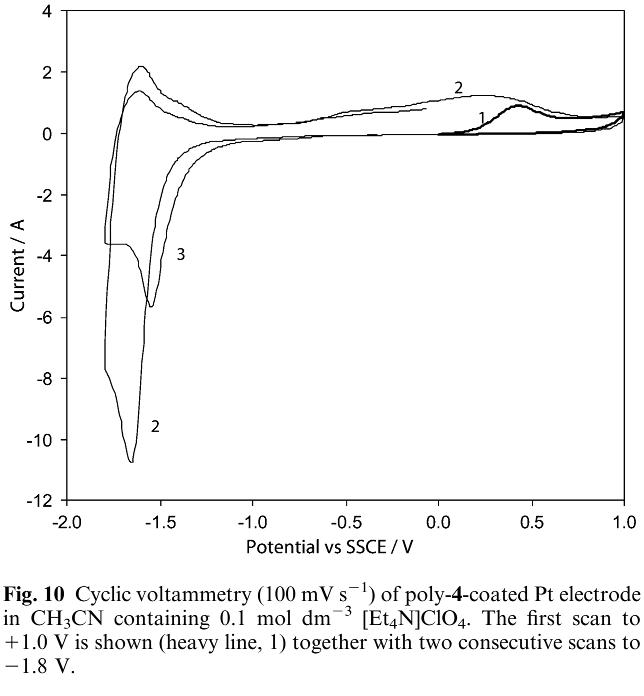


Fig. 10 Cyclic voltammetry (100 mV s^{-1}) of poly-**4**-coated Pt electrode in CH_3CN containing 0.1 mol dm^{-3} $[Et_4N]ClO_4$. The first scan to +1.0 V is shown (heavy line, 1) together with two consecutive scans to −1.8 V.

The differences between the electrochemistries of poly-**1** and poly-**4** are consistent with the behaviors of their expected poly(dithienylenevinylene) and poly(diphenylenevinylene) backbones. Poly(dithienylenevinylene) (structure **8**) is easily p-doped, exhibiting a formal potential for oxidation of *ca.* 0.2 V *vs.* Ag/Ag^+ in acetonitrile, but is difficult to n-dope, with a formal potential for reduction of *ca.* −1.9 V.[18] The observation that the backbone of poly-**1** can be easily p-doped (formal potential *ca.* +0.9 V) is, therefore, consistent with such a structure. On the other hand, poly(phenylenevinylene) is more difficult to p-dope (*ca.* 0.8 V)[19] than poly(dithienylenevinylene), and easier to n-dope (*ca.* −1.7 V). Thus, the electron-withdrawing effect of the Ni complex, which shifts the p-doping potential of the backbone of poly-**1** from *ca.* 0.2 to *ca.* 0.9 V, makes p-doping of poly-**4** inaccessible, while its n-doping is easily observed at *ca.* −1.6 V.

Conclusions

A series of electrochemically polymerizable Ni dithiolene complexes have been prepared. Their electrochemical and spectroscopic properties are consistent with their structures and expected modes of polymerization. The electrochemical properties of electrochemically deposited films of these complexes are consistent with the expected polymeric structures.

Comparison of the electrochemical properties of poly-**1**, poly-**2**, and poly-**3**, provides important insight into the structure of poly-**1**. The four potentially polymerizable thiophene substituents of **1** can lead to a variety of different structures, including the coordination polymer structure expected for poly-**2** and the poly(dithienylenevinylene)-type structure expected for poly-**3**. The observation of facile p-doping for poly-**1** and poly-**3**, but not for poly-**2** indicates that poly-**1** contains extended segments with the poly(dithienylenevinylene)-type structure. However, there may also be extensive cross-linking and/or branching *via* poly-**2**-type linkages. Further work is required to fully characterize the structures of the polymers, and to ascertain the relationships between structure and conductivity in these types of novel electronic materials.

Acknowledgements

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References

1 P. G. Pickup, *J. Mater. Chem.*, 1999, **8**, 1641.
2 R. P. Kingsborough and T. M. Swager, *Prog. Inorg. Chem.*, 1999, **48**, 123.
3 U. T. Mueller-Westerhoff and B. Vance, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 12, pp. 595–631.
4 M. N. Collomb, A. Deronzier, K. Gorgy and J. C. Lepretre, *New J. Chem.*, 2000, **24**, 455.
5 I. Malfant, N. Cordente, P. G. Lacroix and C. Lepetit, *Chem. Mater.*, 1998, **10**, 4079.

6 C. T. Chen, T. Y. J. Lin, C. H. Chen and K. J. Lin, *J. Chin. Chem. Soc.*, 2000, **47**, 197.

7 C. L. Kean and P. G. Pickup, *Chem. Commun.*, 2001, 815.

8 A. Kobayashi, H. Tanaka, M. Kumasaki, H. Torii, B. Narymbetov and T. Adachi, *J. Am. Chem. Soc.*, 1999, **121**, 10763.

9 E. G. Cammisa, *Synthesis of Low Band Gap Polymers*, M. Sc. thesis, Memorial University of Newfoundland, St. John's, Canada, 2000.

10 A. Carpita, A. Lezzi and R. Rossi, *Synthesis*, 1984, 571.

11 G. Schiavon, G. Zotti, G. Bontempelli and F. Lo Coco, *J. Electroanal. Chem.*, 1988, **242**, 131.

12 Y. Gareau and A. Beauchemin, *Heterocycles*, 1998, **48**, 2003.

13 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1965, **87**, 1483.

14 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49–221.

15 K. Tanaka, T. Shichiri, S. Wang and T. Yamabe, *Synth. Met.*, 1988, **24**, 203.

16 T. F. Otero and J. Rodriguez, *J. Electroanal. Chem.*, 1991, **310**, 219.

17 B. J. MacLean and P. G. Pickup, *J. Mater. Chem.*, 2001, **11**, 1357.

18 G. Zotti and G. Schiavon, *Synth. Met.*, 1994, **63**, 53.

19 M. Helbig and H.-H. Horhold, *Makromol. Chem.*, 1993, **194**, 1607.