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A new family of conjugated metallopolymers from electropolymerised bis[(terthiophene)dithiolene] complexes

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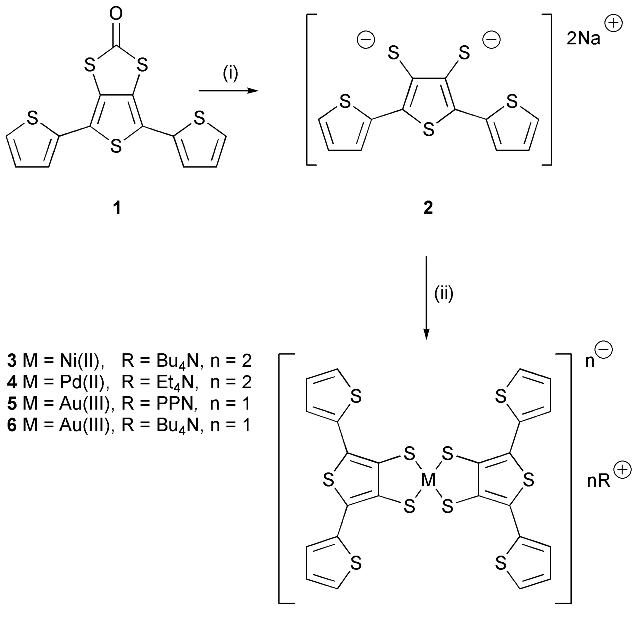
Bis(dithiolene) metal complexes incorporating fused terthiophene units have been prepared; the nickel analogue undergoes electropolymerisation to afford a low bandgap material with very broad absorption characteristics.

The role of conjugated polymers with the structural or functional capacity for coordinating to metals is diverse. The incorporation of the metal can be accomplished at the monomer stage or post polymerisation and can influence the electronic properties of the uncomplexed polymer by perturbation of conductivity, structure and optical and electronic properties. Consequently, these materials have varied applications. For example, metal-free polymers can behave as selective and highly responsive sensors towards metal-containing analytes,[1] whereas metallopolymers can be used in catalysis[2] or as low bandgap materials.[3]

Electrogenerated metallopolymers have received particular attention over recent years, with pyrrole and thiophene derivatives as frequent monomers of choice.[2,4] Very recently, conjugated polymers have been prepared electrochemically, in which $[Ru(terpy)_2]$[5] and $[Ni(dithiolene)_2]$[3] units are present in the main chain of a polythiophene based material. As part of our studies into 3,4-dithio-substituted terthiophene species,[6] we now report the synthesis, electropolymerisation and characterisation of a new cross-linked polythiophene bearing nickel bis(dithiolene) units fused to the main chain.

The synthesis of the dithiolene monomer is shown in Scheme 1. Terthiophene **1**[6] was dissolved in THF and treated with 2.2 equivalents of sodium ethoxide under reflux to generate the dithiolate intermediate **2**. Addition of $NiCl_2$ and n-Bu_4NBr gave the corresponding nickel bis(dithiolene) complex **3** (50% yield), after precipitation with petroleum ether. Similarly, the Pd(II) analogue (**4**) was obtained from **2** by addition of $Na_2[PdCl_4]$–Et_4NBr (49% yield). Gold(III) complexes, **5** and **6**, were isolated from the reaction of **2** with $PPN[AuCl_4]$ (38% yield) and n-$Bu_4N[AuBr_4]$ (55% yield), respectively. Recrystallisation of **3** from THF–hexane afforded deep red crystals and the X-ray structure† of the complex can be seen in Fig 1. The asymmetric unit shows a mirror plane bisecting the metal centre of the bis(dithiolene) unit. Short intramolecular $S\cdots S$ contacts are observed between S(4)–S(5) and S(3)–S(1′), which are shorter than the sum of the van der Waals radii for two sulfur atoms (3.60 Å). Disorder in one of the peripheral thiophene rings leads to an equal distribution of all-*anti* and *anti*–*syn* conformations within the terthiophene unit. This disorder, together with the weakened $S\cdots S$ interaction, is responsible for the larger dihedral angle observed within [S(2)–C(5)–C(4)–S(1′)] compared to [S(5)–C(9)–C(8)–S(2)], at 26.2 and 9.2°, respectively. No significant intermolecular interactions were observed between the nickel bis(dithiolene) units.



Scheme 1 Reagents and conditions: (i) THF, NaOEt, reflux, 15 min; (ii) metal salt (and R_4NBr for **3** and **4**).

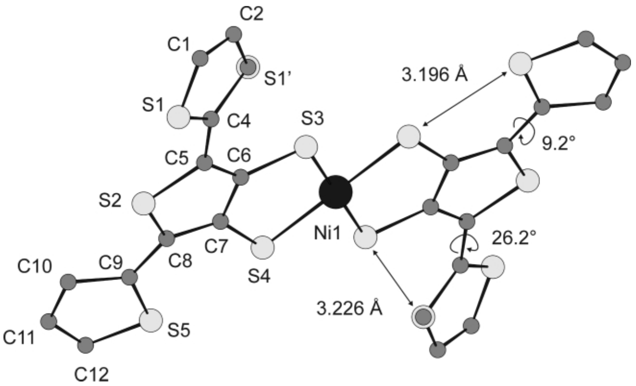


Fig. 1 X-Ray crystal structure of the nickel bis(dithiolene) complex **3**.

The redox properties of nickel bis(dithiolene) **3** have been studied by cyclic voltammetry (Fig. 2). Three electrochemical processes are observed, however, the nature of these waves are somewhat different to those reported for a related bis(dithienyldithiolene) complex.[3] The reversible redox wave at −0.13 V is due to oxidation of the metal dithiolene unit ($\mathbf{3} \leftrightarrow \mathbf{3}^{+\cdot}$); analogous peaks were observed for the remaining complexes in the series, albeit at higher potentials (+0.13 V, **4**; +0.64 V, **5**; +0.65 V, **6**). The peak at +0.46 V for **3** corresponds to the second oxidation of the dithiolene unit to the charge neutral complex and is irreversible. This process is not observed for the gold complexes **5** and **6** but occurs at a lower potential for **4** (+0.40 V) and is quasi-reversible. The irreversible reduction process at −1.16 V is due to the reduction of the terthiophene unit. Similar peaks are observed for the remainder of the series at −0.90 V

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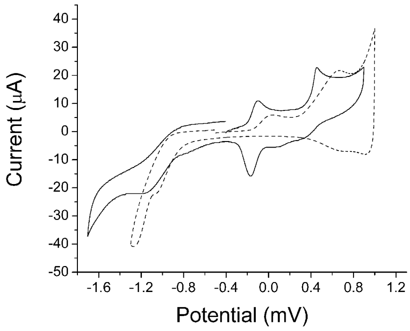

Fig. 2 Cyclic voltammogram of **3** (solid line) and poly(**3**) (dashed line) on glassy carbon working electrode, using Ag/AgCl reference and Pt counter electrodes, in CH_2Cl_2 for **3** (substrate *ca.* 10^{-3} M) and MeCN (monomer free) for poly(**3**) (n-Bu_4NPF_6 0.1 M as supporting electrolyte).

(**4**), −1.09 V (**5**) and −1.07 V (**6**). Unequivocal proof that this reduction process is independent of the metal centre comes from the CV (under identical experimental conditions) of 2,5-di(2-thienyl)-3,4-bis(methylsulfanyl)thiophene,[6] which displays a single electron irreversible reduction at −1.17 V.

Electropolymerisation for all complexes was conducted by repetitive cycling over the range 0.00 to +1.30 V on glassy carbon or ITO glass working electrodes; a typical experiment is shown in Fig. 3. During polymerisation, the successive oxidation of the monomer is accompanied by the growth of two new redox waves at *ca.* +0.5 and +1.0 V, which represents the electroactivity of a new material (*i.e.* the polymer). A plot of scan rate *vs.* peak current of E_{ox} for the polymer in monomer free solution (Fig. 3, inset), gives a linear fit ($R > 0.998$), confirming that charge transport through the film is not diffusion limited.[7]

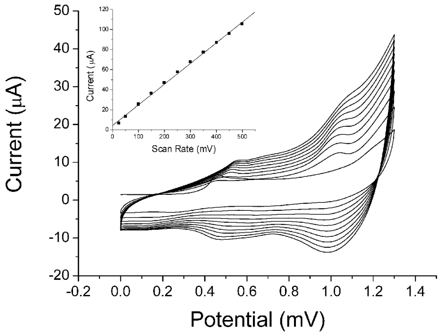

Fig. 3 Polymerisation of **3** on glassy carbon working electrode, under identical conditions as those for Fig. 2 in CH_2Cl_2. Inset: plot of scan rate *vs.* peak current from E_{2ox} for poly(**3**) in monomer free MeCN solution.

The cyclic voltammogram of poly(**3**) on glassy carbon electrode in monomer free solution is also shown in Fig. 2. Two reversible oxidaton waves are observed at +0.66 and +0.97 V and are attributed to the electroactivity of the dithiolene unit and polythiophene chain, respectively. The single peak at +0.04 V is also related to the oxidation of the metal dithiolene unit in the polymer; compared to the redox behaviour of the monomer, this process has lost reversibility and has been shifted to a more positive potential by 130 mV. Two irreversible reduction peaks are seen at −1.04 and −1.26 V. The electrochemical bandgap of the polymer is estimated to be *ca.* 1.4 eV (difference between the onset for the oxidation of the polythiophene chain and the onset of the reduction peak at −1.04 V). Conductivity measurements have been performed by impedance spectroscopy. The conductivities for the series of metallopolymers are *ca.* 10^{-6} to 10^{-5} S cm^{-1} in the range 0 to +1 V, similar to those reported for analogous bis(dithiolene) polymers.[3]

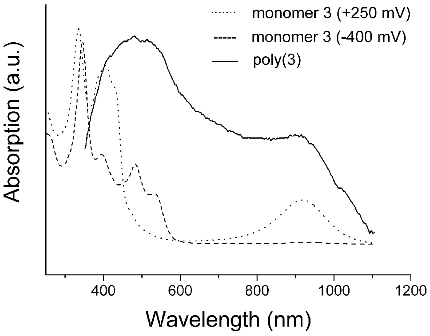

Fig. 4 Electronic absorption spectra for **3** in MeCN and poly(**3**) as a thin film on ITO glass.

The electronic absorption spectrum of the polymer grown on ITO glass, along with spectra of **3** at −0.40 and +0.25 V in MeCN, are shown in Fig. 4. A fresh solution of the monomer gives an identical spectrum to that obtained from a solution of **3** at −0.4 V (spectroelectrochemistry was conducted using an OTTLE cell). The complex oxidises after several days under ambient conditions, giving a spectrum that can be reproduced spectroelectrochemically at +0.25 V and which features an additional absorption peak at 917 nm, corresponding to the oxidised nickel dithiolene monoanion species.[8] In both oxidation states, the peaks at 335 and 342 nm correspond to a π–π* transition within the triaryl units, as seen for similar terthiophene systems.[6] For the polymer film, this transition is shifted bathochromically by *ca.* 150 nm, indicative of an increase in conjugation and providing further proof for the generation of a polymeric material. The peak for the monoanion dithiolene moiety remains at 908 nm, indicating that, under the electrochemical conditions employed, this is the preferred ground state of the polymer. The most remarkable feature of poly(**3**) is the extremely broad absorption of the material between 400–1000 nm. Conjugated polymers that cover such a vast range are extremely rare; since the maximum of the photon flux of the sun peaks around 700 nm (just out of the range of most conjugated polymers such as simple PPVs and polythiophenes), low bandgap polymers such as poly(**3**) could be extremely useful materials as light-harvesting components in plastic photovoltaic devices.[9]

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Notes and references

† *Crystal data.* $C_{56}H_{84}N_2NiS_{10}$, M = 1164.56, monoclinic, a = 8.5643(6), b = 20.0991(6), c = 17.8440(11) Å, β = 101.9540(10)°, U = 3005.0(3) Å^3, T = 120(2) K, space group $P2_1/n$, Z = 2, μ(Mo–K$_a$) = 0.707 mm^{-1}, 9829 reflections measured, 6238 unique (R_{int} = 0.0507) which were used in all calculations. $R1$ ($I > 2\sigma I$) = 0.0655 and the final $wR2$ (F^2) was 0.1219 for all data. CCDC 188996. See http://www.rsc.org/suppdata/cc/b2/b206243g/ for crystallographic data in CIF or other electronic format.

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