A low band gap conjugated metallopolymer with nickel bis(dithiolene) crosslinks

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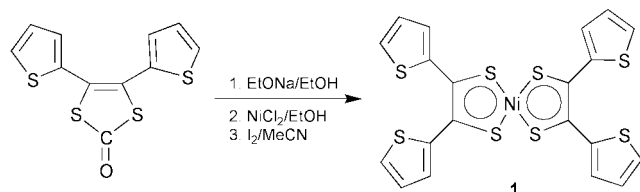
A low band gap conjugated metallopolymer has been prepared by the electrochemical polymerization of bis[1,2-di(2-thienyl)-1,2-ethenedithiolene]nickel.

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 the ease of reduction (n-doping) of the aromatic system. 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 report here on a dithiolene based conjugated metallopolymer prepared by the electrochemical polymerization of bis[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]

Fig. 1(a) shows a cyclic voltammogram of **1**† in solution. Reversible waves appear at formal potentials (*vs.* SSCE) of $E^{\circ\prime}(-1 \leftrightarrow -2) = -0.66\,V$, $E^{\circ\prime}(0 \leftrightarrow -1) = +0.13\,V$, $E^{\circ\prime}(+1 \leftrightarrow 0) = 1.08\,V$, and an irreversible oxidation (not shown) begins at *ca.* +1.26 V. The first two waves have been assigned as reductions of the aromatic metal dithiolene unit to the anion and dianion by analogy with the electrochemistry of other ditholene complexes.[9] The third wave ($E^{\circ\prime} = +1.08\,V$) must then be due to oxidation of the complex to the cation. The reversibility of
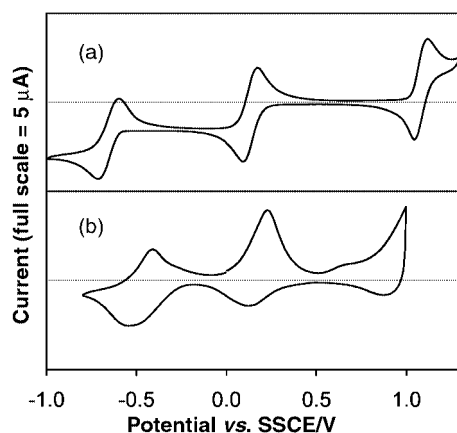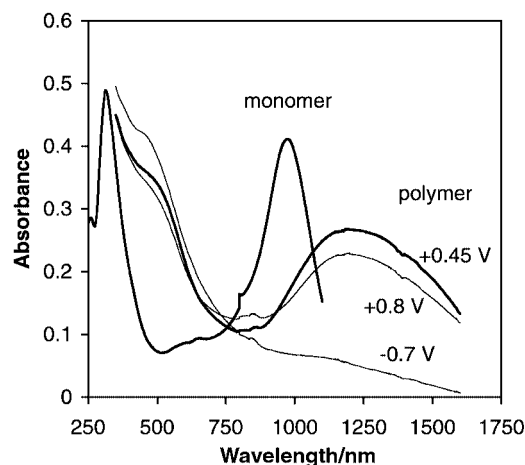
this wave suggests that the positive charge is localized on the metal dithiolene unit. However, since cycling into this wave leads to deposition of a polymer on the electrode surface, there is presumably some delocalization onto the peripheral thiophene rings. Cycling into the forth (irreversible) wave at higher potentials leads to more rapid polymer deposition and therefore this wave must correspond to oxidation of one or more of the thiophene rings.

Fig. 1(b) show cyclic voltammograms of a poly-**1** coated electrode‡ in the absence of **1** in solution. The new broad wave starting at +0.5 V is characteristic in both shape and position of a conjugated oligothiophene backbone, and provides clear evidence that anodic polymerization of **1** has occurred at the vacant α-positions of the thiophenes. The oxidation current increases sharply at potentials higher than the limit of +1 V used for Fig. 1(b), and this leads to loss of the polymer's electrochemistry, which is again consistent with an oligothiophene-based material. The two Ni–dithiolene based waves seen for the monomer (at −0.66 and +0.13 V) are both retained by the polymer, indicating that the Ni–dithiolene center remains intact. The anodic shifts of these waves (to −0.49 and +0.19 V) are due primarily to the change in junction potential (*ca.* 80 mV) on changing the electrolyte to MeCN + Et$_4$NClO$_4$. Their broadening and splitting into multiple overlapping waves can be attributed to the variety of slightly different Ni sites that would arise from factors such as coupling of different combinations of the four peripheral thiophenes, different conjugation lengths, and defects causes by the reaction of peripheral thiophenes with trace water in the solvent. The unusual voltammetric wave shapes observed for the polymer and the apparent lack of reversibility are presumably due to ion transport effects which commonly produce complex voltammetric behaviours for polymer films.

Fig. 2 shows electronic absorption spectra of **1** in solution, and a poly-**1** film on an indium/tin oxide electrode at various

Fig. 1 Cyclic voltammetry (100 mV s^{-1}) of: (a) **1** in CH$_2$Cl$_2$ containing 0.1 mol dm^{-3} Bu$_4$NPF$_6$; (b) a poly-**1** coated Pt electrode in acetonitrile containing 0.1 mol dm^{-3} Et$_4$NClO$_4$.

Fig. 2 Electronic absorption specta of **1** in CH$_2$Cl$_2$ and a poly-**1** coated indium/tin oxide electrode at the indicated potentials in acetonitrile containing 0.1 mol dm^{-3} Et$_4$NClO$_4$.

potentials. Comparing the monomer spectrum with that of the polymer at +0.45 V (same oxidation state), it is seen that the monomer π–π* absorbance at 973 nm is shifted significantly to higher wavelength (1193 nm) in the polymer, which is consistent with the increase in energy of the HOMO that would result from its extended delocalization in the polymer and is evidenced by the decrease in potential of the thiophene based electrochemistry in Fig. 1. The new absorbance seen as a shoulder at *ca.* 450 nm for the polymer is consistent with an expected π–π* transition for a conjugated oligothiophene-like backbone.

Partial oxidation of the polymer (at +0.8 V) causes a partial bleaching of the complexes π–π* absorbance and an increase in absorbance at *ca.* 800 nm. These changes are consistent with partial depletion of the π band, and the formation of polaron or bipolaron states within the polymer's band-gap. Reduction of the polymer at −0.7 V causes bleaching of the Ni complex's π–π* absorbance, consistent with the filling of its LUMO (π*) band.

Preliminary conductivity measurements by impedance spectroscopy and using an interdigitated array electrode indicate that the electronic conductivity associated with the 0/−1 mixed valent state is *ca.* 10^{-6} S cm^{-1}, and that oxidation (p-doping) of the backbone at +1 V increases the conductivity to *ca.* 10^{-4} S cm^{-1}. Although these conductivities are disappointing, they should be regarded as lower limits that can be improved by optimization of the film forming procedure. The band gap of poly-**1**, estimated from the onset of the 1193 nm absorbance, is < 0.8 eV (*ca.* 0.35 eV based on the difference between $E^{0\prime}(0 \leftrightarrow -1)$ and the onset of the backbone oxidation at *ca.* +0.54 V), which offers significant promise for the development of intrinsic conductors.

The presence of four peripheral thiophene rings on **1** presumably results in a highly crosslinked polymer without extended linear chains. Better electronic conductivities may therefore be achieved by using **1** as a crosslinking agent in a linear polymer (*e.g.* by copolymerization with bithiophene), or by use of similar complexes with fewer thiophene substituents. Both of these approaches are currently being explored.

Notes and references

† **1** was prepared (in *ca.* 25% yield following CH$_2$Cl$_2$/silica column chromatography) by the reaction of 4,5-dithiophen-2-yl-1,3-dithiol-2-one[10] with NaOEt in EtOH, followed by addition of NiCl$_2$ in EtOH. The product was precipitated with Et$_4$NBr, dissolved in acetonitrile and oxidized to **1** with I$_2$. δ_H(500 MHz, CD$_2$Cl$_2$, ppm *vs.* TMS): 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: *m/z* 566 (M, 0.3%), 256 (36%), 190 (100%). Elemental analysis. Calc. for C$_{20}$H$_{12}$S$_8$Ni: C, 42.33; H, 2.13; S, 45.20. Found: C, 42.09; H, 2.16; S, 44.49%.

‡ Films of poly-**1** on electrodes were prepared by constant potential (+1.2 V) electrolysis of a solution of **1** in CH$_2$Cl$_2$ containing 0.1 mol dm^{-3} Bu$_4$NPF$_6$.

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 W. Freyer, *Z. Chem.*, 1984, **24**, 32.
8 A. Kobayashi, H. Tanaka, M. Kumasaki, H. Torii, B. Narymbetov and T. Adachi, *J. Am. Chem. Soc.*, 1999, **121**, 10
9 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.
10 E. G. Cammisa, *Synthesis of Low Band Gap Polymers*, M.Sc. thesis, Memorial University of Newfoundland, St. John's, Canada, 2000.