Electrochemical polymerization of a bis(thienyl)bithiazole osmium complex

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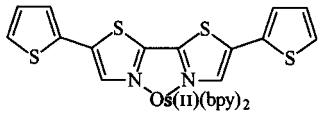
A novel and easily n-doped conjugated metallopolymer has been prepared by the electrochemical polymerization of $Os(bpy)_2[5,5'\text{-bis(2-thienyl)-2,2'-bithiazole}]^{2+}$.

2,2′-Bithiazole is an attractive component for conjugated metallopolymers[1] because of its structural similarity to bithiophene and high π-electron density relative to bipyridine. Thus, unlike (bi)pyridine containing polymers, bithiazole based materials can be stable when p-doped and can exhibit relatively high conductivities.[2–5] An appealing approach to well defined bithiazole based metallopolymers is *via* the electrochemical polymerization of complexes of bis(thienyl)bithiazoles such as **1**. However, we have found that such complexes {$Os(bpy)_2L^{2+}$ and $Ru(bpy)_2L^{2+}$, where bpy = 2,2′-bipyridine and L = 5,5′-bis(2-thienyl)-2,2′-bithiazole (bthbthz), 5,5′[bis(2-thienyl)-4,4′-dimethyl-2,2′-bithiazole, or 5,5′-bis[2-(3-methoxythienyl)]-4,4′-dimethyl-2,2′-bithiazole} can not be polymerized under conventional conditions. Zhu and Swager have found that complexes of the analogous bipyridine ligand, 5,5′-bis(2-thienyl)-2,2′-bipyridine, are also resistant to electrochemical polymerization.[6,7] These authors circumvented the problem by extending the terminal thiophenes to bithiophenes, which gave polymerizable complexes.



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The reason for the failure of complexes with single thiophene rings on the ligand to polymerize appears to be due to instability of the bithiophene linkages that are formed at the high potentials needed to drive the polymerization. As can be seen in Fig. 1, the oxidation of the bthbthz ligand of **1**,† does not begin until *ca.* +1.55 V *vs.* SSCE (E_{pa} = 1.68 V). This wave decreases rapidly with cycling (not shown), indicating that a passivating film is produced on the electrode. Interestingly, the Os(III/II) wave remains unchanged with extensive cycling, indicating that the passive layer contains electroactive Os centres. Indeed, a small Os(III/II) wave can still be seen when a passivated electrode is transferred to a blank electrolyte. Although the Os centres in the passivating layer can mediate the electrochemistry of Os(II) in solution, their redox potential is not high enough to mediate the oxidation/polymerization of the bthbthz ligand.

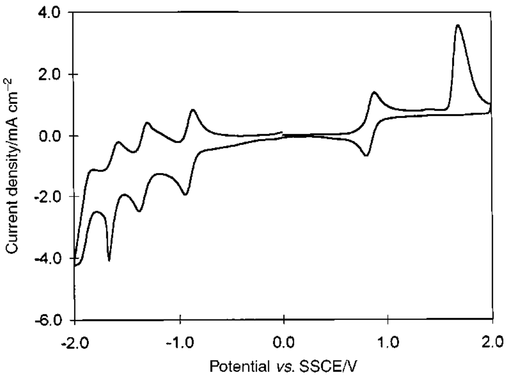

Fig. 1 Cyclic voltammetry (100 mV s^{-1}) of **1** in acetonitrile containing 0.1 mol dm^{-3} NEt_4ClO_4.

Reasoning that the passivating nature of the film formed by **1** was due to nucleophilic attack of residual water‡ on oxidized segments of the bithiophene-bithiazole backbone,[8] we added $BF_3{\cdot}OEt_2$ (Aldrich) to the acetonitrile–0.1 mol dm^{-3} NEt_4ClO_4 electrolyte solution. This reagent has been reported to be an excellent solvent system for the electrochemical synthesis of polythiophene.[9] The rationale for its use here is the deactivation of residual water by complexation with the BF_3. As shown in Fig. 2, compound **1** undergoes facile and sustained electrochemical polymerization in the $BF_3{\cdot}OEt_2$ containing electrolyte when the potential is cycled into the ligand oxidation wave at *ca.* 1.65 V. The Os(III/II) wave at a formal potential ($E°'$) of +0.85 V increases monotonically with cycling of the potential into the ligand oxidation wave, and new waves appear in the region between the Os and ligand waves. The number, positions, and intensities of these new waves are somewhat variable. They are in the expected potential region for oxidation and re-reduction of a conjugated polymer backbone formed from polymerization of the bthbthz ligand at the 5-positions of the thiophene end groups, and therefore provide evidence that the complex polymerizes in this way. A deep red–purple film was observed on the electrode following the cyclic voltammetry shown in Fig. 2.

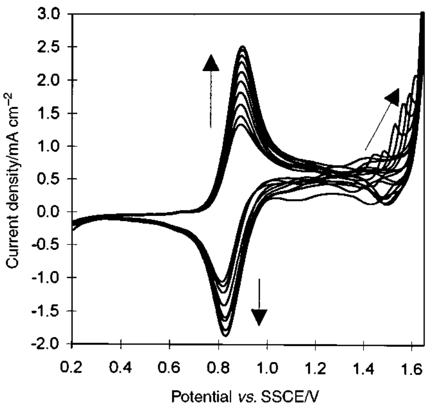

Fig. 2 Cyclic voltammetry (100 mV s^{-1}) of **1** in acetonitrile containing 0.1 mol dm^{-3} NEt_4ClO_4 and 0.45 mol dm^{-3} $BF_3{\cdot}OEt_2$. Arrows indicate changes with cycling.

Fig. 3 shows cyclic voltammograms of a poly-**1** coated electrode in the absence of **1** in solution. A reversible Os(III/II) wave appears at $E°'$ = 0.865 V and a series of reduction waves are seen in the region −0.5 to −2.0 V. Based on the first three redox potentials for reduction of $Os(bpy)_3^{2+}$ (−1.26, −1.45 and −1.76 V[10]), which are for ligand based reductions,[10] the most positive reduction wave ($E°'$ = −0.79 V) can be assigned to n-doping of the polymer backbone, while those at $E°'$ = −1.62 and −1.85 V can be assigned to bpy based reductions. The mild potential and reversibility of the polymer based reduction, and the good stability of the n-doped form (indicated by the lack of significant decay of peak heights on multiple scans), open up the possibility of applications in molecular electronics and the

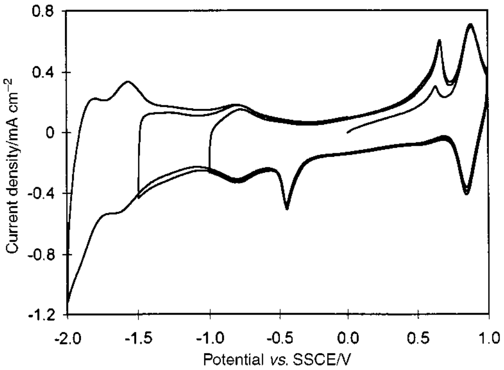

Fig. 3 Cyclic voltammetry (100 mV s^{-1}) of a poly-**1** coated Pt electrode in acetonitrile containing 0.1 mol dm^{-3} NEt_4ClO_4. Three consecutive scans to increasingly negative potentials are shown.

catalysis of reduction processes. The pre-peaks observed before the Os oxidation wave and the first reduction wave are typical of redox polymers based on bipyridine complexes.[11]

The Os(III/II) wave of poly-**1** is stable to multiple cycles extending down to −2.0 V, but decays rapidly when the potential is cycled to +2.0 V. Although no well defined polymer oxidation wave has been observed, it would appear that the polymer backbone is unstable to oxidation. Since the film remains visible on the electrode, the loss of the Os based electrochemistry implies that it is mediated by the polymer backbone. Since the backbone is not electroactive in the region of the Os(III/II) wave, electron transfer between Os sites presumably occurs *via* a superexchange interaction through the backbone.[1] Electron transport studies aimed at confirming these proposals, and establishing the influence of the metal (Os *vs.* Ru) and substituents on the polymer backbone are in progress. These studies can be expected to produce valuable guidance for the development of molecular electronics and electrocatalytic systems based on conjugated metallopolymers.

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Notes and references

† **1** was prepared by the reaction of $Os(bpy)_2Cl_2$[12] with 5,5′-bis(2-thienyl)-2,2′-bithiazole[3] at reflux in 70% aqueous ethanol. It was precipitated as the perchlorate salt and purified on a Sephadex LH-20/MeOH column.

‡ Acetonitrile was dried by distillation from CaH_2 immediately before use and NEt_4ClO_4 was dried at 120 °C under vacuum.

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