

A rod-like polymer containing {Ru(terpy)}₂ units prepared by electrochemical coupling of pendant thienyl moieties

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Received (in Cambridge, UK) 15th November 2001, Accepted 4th January 2002

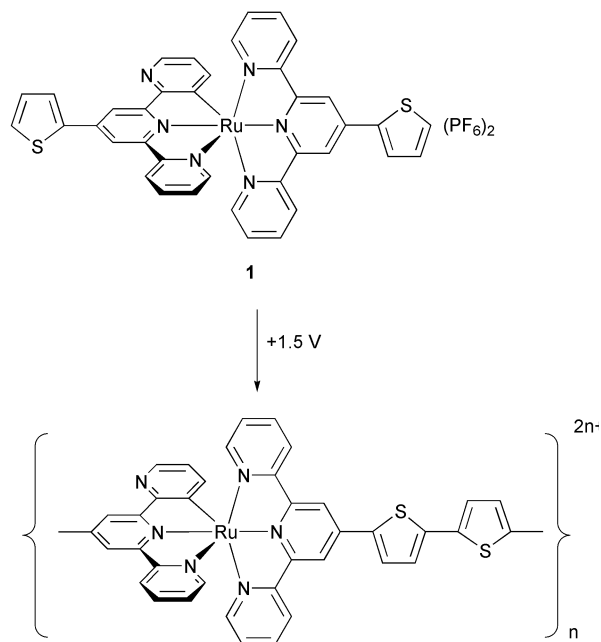
First published as an Advance Article on the web 23rd January 2002

A new rod-like coordination polymer consisting of {Ru(terpy)}₂ motifs bridged by bithiophene units has been prepared by electrochemical polymerisation in acidic organic medium.

Conjugated polymers containing transition metals in the backbone are an interesting class of materials. The metal is expected to modify the conductivity^{1,2} and may give rise to new optical and electronic properties; varying redox states can modulate the conductivity and electron-transfer rates. The incorporation of ferrocene units^{3,4} into polymers is well-established, with metal centres either in side chains or in the conjugated backbone.⁵ In this paper, we report a conjugated polymer in which {Ru(terpy)}₂²⁺ moieties are incorporated in the backbone. This motif is attractive because of the linear topography and useful optical and electronic properties.⁶ Photonic devices based upon conjugated ruthenapolymer of thienyl-functionalised terpy ligands are of interest since the ligand structure both modifies the luminescence behaviour⁷ and provides an electron transfer pathway along the polymer backbone.

The cyclic voltammogram (MeCN) of thienyl functionalised complex **1** exhibits quasi-reversible waves at +0.82 V (metal), -1.59 V (ligand), and -1.83 V (ligand) and an irreversible wave at $\approx +1.65$ V.^{7,8} The latter process is assigned to oxidation of the thienyl substituents to the radical cation.⁹ For scan rates, ν , between 20 and 500 mV s⁻¹ the metal-centred process gives a quasi-reversible response under semi-infinite diffusion control and plots of the peak current *vs.* $\nu^{1/2}$ are linear; the peak-to-peak separation is less than 86 mV and the anodic and cathodic peak currents are approximately equal. The electropolymerisation of thiophene involving radical cation intermediates to give conducting polymers is well established⁹ and we considered that complex **1** could react as a bithiophene with a metal-containing spacer which might be electropolymerised to a ruthenapolymer (Scheme 1).

Electropolymerisation of **1** in anhydrous CH₂Cl₂† (which stabilises cation radicals¹⁰) proceeded smoothly at Pt electrodes as illustrated in Fig. 1. The peak current of the metal-centered process increases in a linear fashion with each scan through the ligand oxidation wave, indicating the accumulation of an electroactive film at the electrode surface. After rinsing with MeCN and CH₂Cl₂ a smooth, transparent, deep red film was observed on the electrode. Polymer films were successfully deposited on platinum, glassy carbon, and fluorine-doped tin oxide electrodes (FDTO, Libbey–Owens–Ford). Continuous voltammetric cycling in MeCN solution containing 0.8 mM of **1** and 0.1 M NBu₄BF₄ results in the growth of a wave at +0.89 V and a collapse of the ligand oxidation wave. This behaviour suggests the formation of a passivating film on the electrode surface. The layer on the surface mediates the metal-based oxidation of the complexes in solution. Scheme 1 presents the coupling reaction and in the absence of detailed mechanistic data we simply propose that the key step involves the radical cation **1**⁺.⁹ Semi-empirical calculations (ZINDO/S) were carried out on [Ru(I)₂]ⁿ⁺ cations, which indicate a build-up of



Scheme 1 The coupling of **1** to give 2,2'-bithienyl-linked poly-**1**.

positive charge at the thienyl C5 position with the successive oxidation (3+/4+/5+) of the monomer, indicating that this is the favored position for coupling to give a linear rod-like redox-active polymer.

A near-ideal metal-centred wave can be seen in the voltammogram of a washed polymer-functionalised electrode in MeCN containing 0.1 M NBu₄BF₄ as supporting electrolyte. This allows the surface coverage to be determined by integration of the anodic wave at scan rates where the peak current

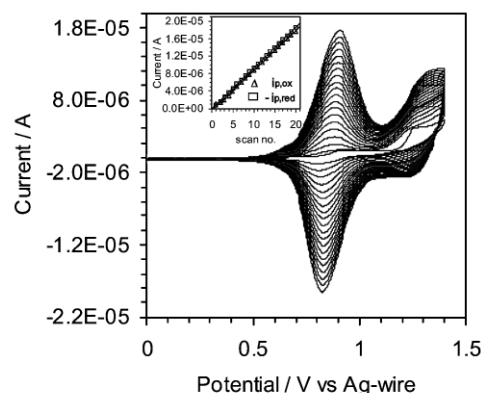


Fig. 1 Cyclic voltammogram recorded at 50 mV s⁻¹ with a platinum electrode in of CH₂Cl₂ solution containing a few drops of BF₃·OEt₂ and 0.5 mM **1**. The linear increase of the peak currents with scan number indicates the accumulation of the redox-active polymer poly-[Ru(I)₂]²⁺ onto the electrode surface.

is directly proportional to v . For example, ten voltammetric cycles at a platinum disk electrode at 50 mV s^{-1} with switching potentials being 0.5 and 1.4 V (vs. Ag-wire quasi reference electrode) gives an apparent surface coverage, Γ_{app} , of $1 \times 10^{-8} \text{ mol cm}^{-2}$, on platinum disk electrodes.† This corresponds to ≈ 100 monomer layers, assuming that one molecular layer consists of close-packed hard spheres 14 \AA in diameter.⁷ This corresponds reasonably well with AFM studies of poly-**1** generated at FDTO (Fig. 2) which shows a polymer film $\approx 100 \text{ nm}$ deep. Fig. 3 illustrates the cyclic voltammogram of a poly-**1** functionalised platinum electrode; scanning the potential in excess of 50 scans at 100 mV s^{-1} between 0.7 and 1.1 V results in less than a 5% loss of electroactivity, although repeated scanning to potentials $> +1.1 \text{ V}$ leads to more rapid degradation. The reduced state of the polymer appears to be much less stable than the oxidised state and the ligand reduction waves rapidly diminish upon continuous cycling between -1.1 and -2.0 V .

To further characterise the films, we have performed XPS measurements on electrodes modified with poly-**1**. Samples display single N 1s, Ru $3d_{5/2}$ and S $2p_{3/2}$ peaks at 400.0, 281.0 and 164.0 eV, respectively, as expected for a material containing $\{\text{Ru}(\text{terpy})_2\}$ and thiophene units.¹¹ The electronic spectra of poly-**1** films deposited on FDTO reveal an MLCT band centered at 521 nm , red-shifted with respect to **1** which has

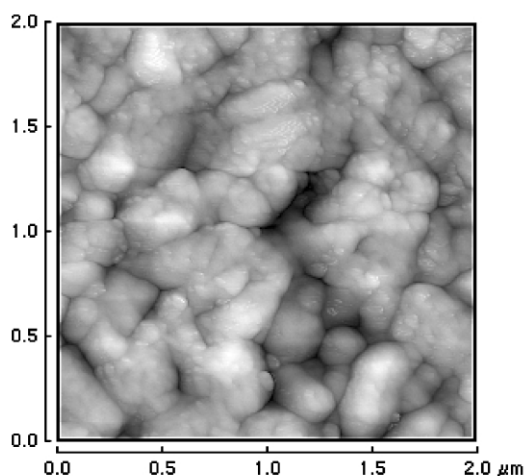


Fig. 2 Tapping mode AFM image of a poly-**1** modified particulate FDTO surface. The corrugation perpendicular to the surface indicates a poly-**1** depth of $\approx 100 \text{ nm}$.

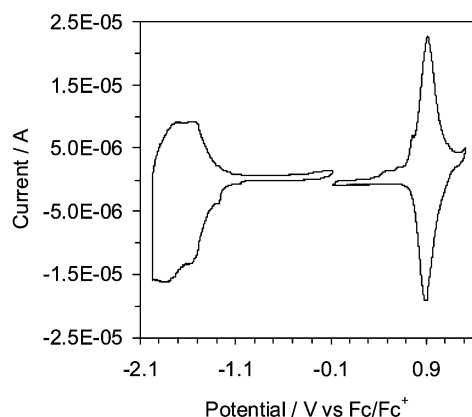


Fig. 3 Cyclic voltammetry of a poly-**1** modified Pt-electrode recorded at 50 mV s^{-1} in MeCN solution containing $0.1 \text{ M NBU}_4\text{BF}_4$ but no free **1**. The apparent surface coverage is $1.2 \times 10^{-8} \text{ mol cm}^{-2}$.

an MLCT band at 498 nm .⁷ The observed red shift of poly-**1** with respect to **1** is due to the extended conjugation arising from the bithienyl spacer.^{12,13} In the model compound $[(\text{terpy})\text{-Ru}(\text{II})\text{Ru}(\text{terpy})][\text{PF}_6]_4$ (**II** = 5,5'-bis(2,2':6',2''-terpyridin-4'-yl)-2,2'-bithiophene)¹⁴ the MLCT absorption maximum is shifted to 518 nm .

In conclusion, electropolymerisation of **1** in organic acidic medium offers a convenient route to rod-like coordination polymers where the $\{\text{Ru}(\text{terpy})_2\}$ units are linked by bithiophene units. Future investigations will focus on detailed charge transport investigations of systems in which the metal centres are linked by multiple thiophene units.

We gratefully acknowledge financial support from the University of Birmingham, EPSRC and the Swedish Natural Science Research Council (grant K 5104-20006267/2000). We also thank Dr Håkan Rensmo (Uppsala University) for XPS measurements, Professor Richard Palmer and Dr Quanmin Guo (University of Birmingham) for AFM measurements and Professor Robert Forster (Dublin City University) for fruitful discussions.

Notes and references

† CH_2Cl_2 solutions contained NBU_4BF_4 (0.1 M) **1** (0.5 mM) and a few drops of $\text{BF}_3\cdot\text{OEt}_2$ to ensure that the solution was water-free (B. J. MacLean and P. G. Pickup, *Chem. Commun.*, 1999, 2471; S. Jin and G. Xue, *Macromolecules*, 1997, 5753).

‡ The counter electrode was a coiled Pt-wire and the reference electrode was Ag/10 mM $\text{AgNO}_3 + 0.1 \text{ M NBU}_4\text{BF}_4 + \text{CH}_3\text{CN}$. The potential of this electrode was -0.08 V vs. the ferrocene/ferrocenium couple (Fc/Fc^+). All potentials are reported vs. Fc/Fc^+ unless otherwise stated.

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