Electroactive Thin Films from the Anodic Electropolymerisation of Iron(II) and Ruthenium(II) Tris(*N*-bipyridylpyrrole) Complexes

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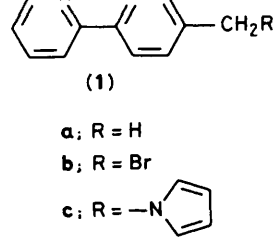
A platinum electrode was coated with an electroactive polypyrrole film containing tris(bipyridyl)-iron(II) or -ruthenium(II) redox centres and the film surface composition has been analysed by ESCA.

The electropolymerisation of substituted pyrroles has received considerable attention recently.[1—4] Poly(*N*-alkylpyrrole) films, in which the alkyl substituent contains a redox centre, are electroactively stable for potential ranges in which the polymer may be expected to be in either its insulating or conducting form.[1,2] We report the synthesis and anodic electropolymerisation of iron(II) and ruthenium(II) complexes of 5-(*N*-pyrrolylmethyl)-2,2′-bipyridine (**1c**) and an ESCA analysis of the resulting thin films.

Reaction of equimolar amounts of 5-methyl-2,2′-bipyridine[5] (**1a**) with *N*-bromosuccinimide in tetrachloromethane in the presence of one mole percent 2,2′-azo-bis(2-methylpropanonitrile), gave 5-bromomethyl-2,2′-bipyridine (**1b**). Direct reaction of (**1b**) with pyrrole *via* phase transfer catalysis,[6] using tetrahexylammonium bromide in 1:1 dichloromethane–50% aqueous sodium hydroxide, gave a colourless solid which was purified by chromatography on alumina to give (**1c**) in 75% overall yield [m.p. 88—89 °C, *m/z* (chemical ionisation, NH_3) 236 ($M^{\bullet +}$ + 1)]. Tris(bipyridyl) complexes from (**1c**) and iron(II) and ruthenium(II) were prepared using standard procedures.[7,8]†

Polymeric films were grown electrochemically in argon-purged anhydrous acetonitrile [0.1 M in tetrabutylammonium perchlorate (TBAP) or tetrafluoroborate (TBAT)] by cycling the applied potential at a platinum electrode between −0.2 and +1.5 V,‡ (Figure 1). A pre-wave to the major M^{2+}/M^{3+} anodic peak was observed for the first few cycles which merged into the major peak subsequently. Such behaviour has previously been noted for poly{$[Ru(bpy)_2L_2]^{2+}$} films where L was a pyridine *N*-substituted pyrrole (bpy = bipyridine).[9] The modified electrode was thoroughly washed and transferred to clean solvent and electrolyte. Cyclic voltammetry revealed that the isolated films exhibited a stable M^{2+}/M^{3+} couple related to that of the monomer.



(**1**)

For poly{$[(\mathbf{1c})_3Fe]^{2+}$} films grown over twenty cycles, differences were observed by varying the supporting electrolyte. Films formed in TBAP showed a linear dependence of peak current with sweep-rate v from 0 to 50 mV s^{-1}.

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† New compounds gave satisfactory analytical and spectroscopic data, consistent with their structures.

‡ Potentials are given relative to the saturated calomel electrode; under the experimental conditions used, $E_{\frac{1}{2}}$ ferrocene/ferricinium = 0.42 V.

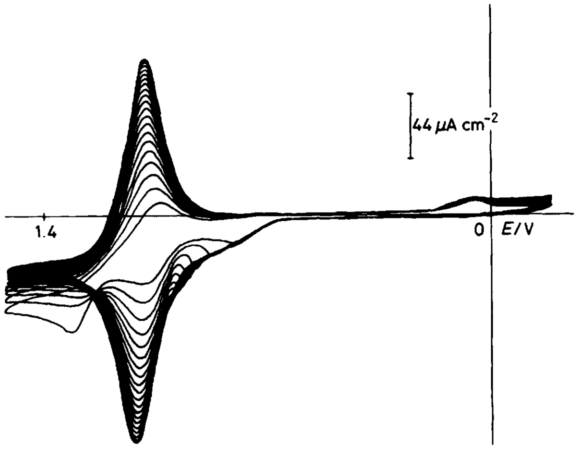

Figure 1. Cyclic voltammogram depicting the growth of the Fe^{2+}/Fe^{3+} peak during film formation from 1.75×10^{-4} M $[Fe(\mathbf{1c})_3]^{2+}(BF_4)_2$ in MeCN/0.1 M Bu_4NClO_4; sweep-rate $v = 50$ mV s^{-1}, electrode diameter = 1.70 mm; $E_{\frac{1}{2}}^{\circ} = 1.15$ V.

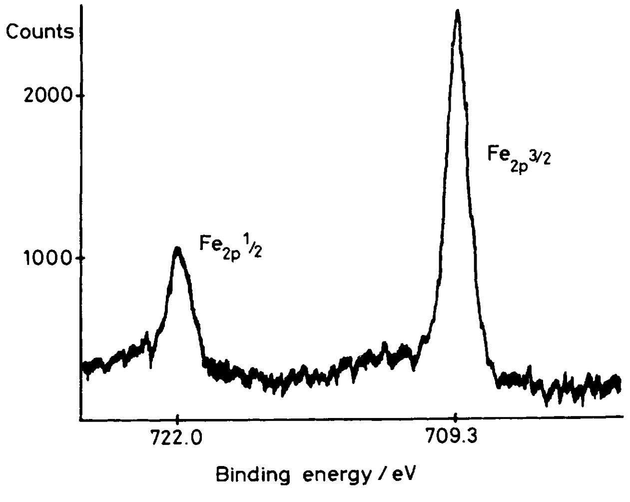

Figure 2. Fe_{2p} core level ESCA spectrum of poly$\{[(\mathbf{1c})_3Fe]^{2+}\}$; FWHM Fe_{2p} 3/2 = 1.3 eV. Binding energies are referenced to the main C_{1s} photoionisation peak at 285.0 eV.

Using a sweep-rate of 10 mV s^{-1} a peak separation of 15 mV was observed with an apparent molar coverage, $\Gamma_{app.}$, of 1.3×10^{-8} mol cm^{-2}. Films grown in TBAT exhibited a linear dependence of i_{pa} and i_{pc} with sweep-rate up to 150 mV s^{-1}, a peak separation of 10 mV at 10 mV s^{-1}, and $\Gamma_{app.}$ of 4.7×10^{-9} mol cm^{-2}. When $[Ru(bpy)_3]^{2+}$ units are incorporated into polymeric films, it has been established that deviations from linearity become progressively large with increasing film thickness.[10] *Negligible* loss of integrated peak current was observed after 200 cycles between −0.2 and +1.5 V at 50 mV s^{-1}, and only an 8% loss of integrated peak current was observed after storing the dried modified electrode in air for 24 hours.

$[(\mathbf{1c})_3Ru]^{2+}$ has been similarly polymerised and preliminary electrochemical studies reveal a square-root dependence of sweep-rate with peak current for sweep-rates greater than 25 mV s^{-1}. For a film grown over twenty cycles with 7.3×10^{-4} M monomer in TBAP, a peak separation of 25 mV was observed ($v = 25$ mV s^{-1}), with $\Gamma_{app.} = 1.1 \times 10^{-8}$ mol cm^{-2}. The half-wave potential was +1.34 V.

ESCA analyses were performed on films prepared on 1.8 cm^2 platinum foils. The Fe_{2p} core level spectrum of poly$\{[(\mathbf{1c})_3Fe]^{2+}\}$ formed in TBAP is shown in Figure 2. No multiplet splitting was observed, consistent with a film in which all of the iron is present in a low-spin d^6 configuration.[11] Using experimentally predetermined elemental sensitivity ratios, it is possible to evaluate the concentration of ClO_4^- or BF_4^- ions in the film from measurements of the N_{1s}/Cl_{2p} and N_{1s}/F_{1s} peak area ratios. Films formed in TBAT were essentially undoped since the N/F stoicheiometry indicated 4.5 nitrogen atoms for each tetrafluoroborate counterion. Such behaviour is in accord with that observed for poly(*N*-alkylpyrrole) in which the alkyl substituent is bulky.[12] For films grown in TBAP electrolyte, no B_{1s} or F_{1s} was detected. The N/Cl stoicheiometry was 3.0 indicating one positive charge for each monomeric unit. No high binding energy N_{1s} signal was observed indicating the absence of tetrabutylammonium cations. Moreover since a higher binding energy Fe_{2p} peak was not observed the possibility of a d^5Fe^{3+} complex charge compensating for the dopant perchlorate ions may be discounted. The oxidation reaction forming the polypyrrole chains in TBAP thus involves one positive charge for every three pyrrole rings.[13,14]§

Although the cathodic electropolymerisation of some tris(vinylbipyridyl) complexes has been reported,[15] this work represents a unique example of the anodic electropolymerisation of $[M(bpy)_3]^{2+}$ complexes. Further investigations of the polymeric films are in progress, exploring their potential as photosensitising coatings for semi-conductor electrodes and their possible use in molecular electronic devices.[16]

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§ The ruthenium containing polymer is less amenable to ESCA analysis as the most intense ruthenium photoionisation peak occurs close to the C_{1s} signal.