

Preparation and Characterization of Redox Active
Conducting
Polymers Incorporating Ru(II) and Os(II) Polypyridyl
Complexes

Tim McCormac
Institute of Technology Tallaght
Advanced Smart Materials Research Centre
Dublin 24
Ireland

Conducting polymer films containing metal polypyridyl complexes, such as those of Co [1], Cu [2], Ru [3-5], Fe [5], Re [6] and Ni [7], covalently grafted to the polymer backbone have also received a lot of attention. The rationale for attachment of polypyridyl complexes stems from the fact that electropolymerised films of polypyridyl metal complexes are moderately permeable to ferrocene [5] and extremely permeable to small anions [3] such as the bromide ion, and as a result possess high ionic conductivities, but unfortunately exhibit poor to moderate electron transport properties. This covalent grafting of the molecular electroactive species to the conducting polymer backbone, via the nitrogen atom of the pyrrole for example, has been achieved through the use of short inflexible spacer arms, such as, 4-methyl-4'(2-pyrrol-1-ylethyl)-2,2'-bipyridine [1,3] and 3-(pyrrol-1-ylmethyl)pyridine [3,8].

Two metal (Os^{II} or Ru^{II}) substituted polypyridyl complexes, substituted by a pyrrole containing ligand, as depicted in Figure 1, have been synthesised. The complexes were characterised by both spectroscopic (UV-Vis, $^1\text{H}/^{13}\text{C}$ NMR) and electrochemical (cyclic voltammetry, spectroelectrochemistry) techniques. The electrochemical behaviour of the complexes exhibits a metal based redox couple associated with the reversible oxidation of the Ru(II) or Os(II) centres with a $E_{1/2}$ values of +0.485V and +0.050V (vs. Ag/Ag^+) respectively, an irreversible oxidative wave at +1.05V (vs. Ag/Ag^+) associated with oxidation of the pyrrole moiety and successive reversible one electron reductions for the bipyridyl ligands. It was found that stable conducting metallopolymer films could be obtained by cyclic voltammetry, chronocoulometry and a novel potential pulse method. The basic electrochemical behaviour of the films is presented with scan rate, stability and film permeability studies being carried out as a function of film thicknesses. Also preliminary work is presented concerning the substitution of the Ru(II) and Os(II) polypyridyl complexes through the 3-position of the pyrrole moiety.

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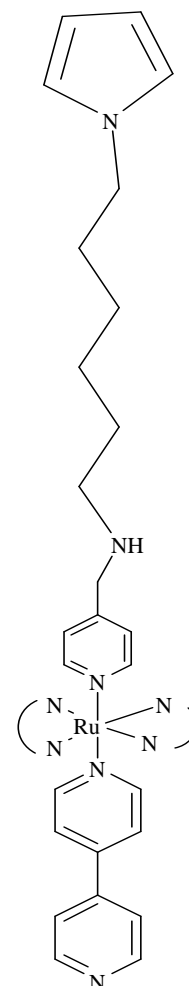


Figure 1. [Ruthenium-bis-N,N'-(2,2'-bipyridyl)-N-(pyridine-4-yl-methyl-(6-pyrrole-1-yl-hexyl)-amine)chloride] hexafluorophosphate

