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# Synthesis and Electrochemical Characterisation of [Ru(2,2'-bpy)3]3[P2W18O62].15H2O

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Solid state electrochemical studies have recently become important due to their relevance in electrochemically based technologies. Solid state redox active materials play key roles in a wide variety of devices, ranging from optical detectors [1], redox supercapacitors [2] and sensors [3]. The study of redox reactions of solid materials by voltammetric techniques has been covered in recent reviews [4,5]. Cyclic voltammetry is a useful method for investigating the electrochemical behaviour of solid state particles and it has been applied to various systems [6-8]. Electrochemistry can provide direct information on the identity of the species present, the redox composition and the charge and transport mechanisms within the material. In this contribution, we present the synthesis, electrochemical behaviour and solid state voltammetry of the complex $[Ru(bpy)_3]_3[P_2W_{18}O_{62}]$ that have been mechanically attached to macroelectrodes. The complex combines the chemical stability, redox properties and excited state reactivity of Tris (2, 2' – bipyridine) ruthenium (II) with that of the Parent Dawson polyoxometallate, $K_6P_2W_{18}O_{62}.15H_2O$. Addition of $[Ru(bpy)_3][Cl_3]$ to $K_6P_2W_{18}O_{62}.15H_2O$ in aqueous solution resulted in the formation of the ionic complex $[Ru(bpy)_3]_3[P_2W_{18}O_{62}].15H_2O$ The complex was characterised by spectroscopic (UV/Vis, $P^{31}$ NMR, IR spectroscopy) techniques and cyclic voltammetry. Solution phase studies gave a range of redox couples associated with the $Ru^{2+/3+}$ and bipyridine ligands of the cationic $[Ru(bpy)_3]^{2+}$ moiety and the tungsten-oxo framework of the associated Dawson parent heteropolyanion, $[P_2W_{18}O_{62}]^{6-}$. The $[Ru(bpy)_3]_3[P_2W_{18}O_{62}].15H_2O$ was found to adsorb onto a glassy carbon electrode by potential cycling through the $Ru^{2+/3+}$ couple. Voltammetric studies of the adsorbed film were performed in pH's of 2.0, 4.5 and 7.0. The film was found to exhibit the same pH dependence for the tungsten-oxo framework of the heteropolyanion as in solution with the film also exhibiting better stability towards redox cycling in pH 2.00 as compared to pH 7.00. Mechanically attached solid state films of $[Ru(bpy)_3]_3[P_2W_{18}O_{62}]$ have also been formed on carbon macroelectrodes with the electrochemical behaviour of the microparticles in a variety of electrolytes being investigated. Upon redox switching between the $Ru^{2+/3+}$ redox states the solid-state charge-transfer processes are coupled to insertion/expulsion of anions from/to the aqueous solution phase.

**References**

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