Chapter 7

Concluding Remarks and Future Work

7.1 Chapter 3

The electrochemical properties of a series of mononuclear ruthenium and osmium polypyridyl complexes have been analysed in chapter 3. Under both solution-phase and surface confined conditions, a single reversible metal centred oxidation is observed for each complex with the osmium metal complex oxidised at less positive potentials than that of the ruthenium analogue. Characterisation using reductive electrochemistry and spectroelectrochemistry suggests that the location of the first, least negative, ligand reduction is on the bipy ligand, and pyrphen ligand for the M(thimphen) and M(pyrphen) complexes respectively. Excited state resonance Raman spectroscopy indicates that the lowest lying excited states are bipy based in these complexes.

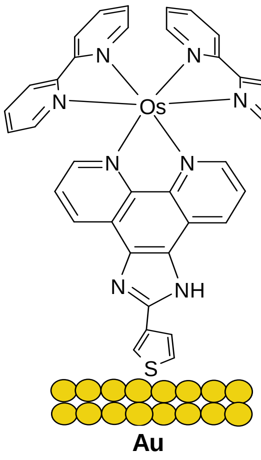

Figure 7.1: *Os(thimphen) assembled on a Au electrode.*

Monolayers of each of the four compounds have been formed on either Au or Pt electrodes and these monolayers have been analysed using cyclic voltammetry and surface enhanced Raman scattering spectroscopy. Os(thimphen) and Os(pyrphen) monolayers are formed on Au and Pt electrodes respectively and voltammetric sweeping in aqueous electrolyte reveals a stable monolayer. The osmium metal centre is oxidised at potentials less positive than that of the oxidation of the Au surface. This observation as well as the stability of the monolayer in aqueous electrolyte, suggests that this complex is an ideal candidate for a molecular transistor. Future work with these complexes includes the determination of the heterogeneous rate constant.

Analysis using scanning tunnelling microscopy to measure the molecular conductivity and investigate the mechanism for electron transfer to and from the molecule is also required.

7.2 Chapter 4

Chapter 4 is concerned with the electrochemical and spectroelectrochemical analysis of a series of homo- and hetero-dinuclear ruthenium and osmium polypyridyl complexes. The presence of intramolecular interaction in the mixed valence state may be an advantage in the design of molecular diodes. The electronic coupling between the metal centres in each of these complexes was determined as a function of the comproportionation constant, K_c, calculated using the peak to peak separation (ΔE) in the cyclic voltammogram, as well as the presence of intervalence charge transfer bands in the absorbance spectrum of the mixed valence state. Intervalence bands were observed for the symmetrically bridged $[(bipy)_2Os(bpbt)Os(bipy)_2]^{2+}$ and the asymmetrically bridged $[(bipy)_2Os(pytr\text{-}bipy)Os(bipy)_2]^{2+}$.

It was observed that the structural factors needed to facilitate the transfer of charge from the donor to the acceptor (oxidised) metal in the mixed valence state are the presence of osmium as the metal centre and the presence of at least one triazole moiety in the bridging ligand. A HOMO mediated superexchange mechanism is proposed for the charge transfer observed in both of these complexes. The greatest electronic coupling was observed for the asymmetrically bridged heteronuclear complex (Type II interaction). Proposal of the critical factors for intramolecular interaction allows for the systematic design of these types of complexes. With the addition of a linker ligand for binding to an electrode surface, these systems may prove useful in the realization of a transition metal based molecular diode. Formation of monolayers of these dinuclear complexes would allow for the investigation of the surface electrochemical properties as well as the potential molecular conductivity in the molecule.

7.3 Chapter 5

An organic molecule, based on the well known TTF core, featuring two accessible redox states is analysed and discussed in chapter 5. The redox chemistry involves the oxidation of the neutral compound, dipyrBEDT-TTF to the monocation radical and subsequently to the dication. Cyclic voltammetry and differential pulse voltammetry were carried out in a range of solvents. The stability of the redox intermediate monocation radical is dependent on the donor number of the electrochemical solvent; the comproportionation constant, K_c, varies from 33 (in DMF) to 3.75×10^5 (CH_2Cl_2). Further analysis of the absorbance bands is needed in order to assign each process in the molecule. Spectroelectrochemical measurements under argon are required in order to conclusively determine the extent of interaction between the redox centres.

The electrochemical properties were also analysed in the both the presence and absence of oxygen. Continuous cycling in an aerobic environment, oxidising both redox centres, results in a Faradaic current that decreases with time. It is suggested that degradation of the species arises from a reaction of the dication with oxygen. Degradation of the compound is not observed under anaerobic conditions where continuous cycling reveals a stable system; oxidation to the dication is reversible.

Monolayers of the compound have been formed on a Pt electrode. As was observed for the solution-phase diffusion controlled electrochemistry, the stability of the monolayer is greatly improved under anaerobic conditions in acetonitrile. STM studies of the monolayer on Pt proved unsuccessful due to the requirement of an oxygen free environment and an organic electrolyte. Optimisation of the experimental STM conditions for this type of system is required in order to measure the molecular conductivity in the molecule. The orientation of the molecule on the surface is as of yet unclear. Techniques such as x-ray photoelectron spectroscopy may be employed in order to elucidate the mechanism of binding and orientation of the molecule on the electrode.

7.4 Chapter 6

Chapter 6 presents a series of diiron hydrogenase analogues analysed for potential use as metal catalysts in the production of molecular hydrogen from protons. Each complex is based on the active site of the hydrogenase enzyme which resembles that of the synthetic organometallic complex, $[Fe_2(CO)_6(\mu\text{-}SR)_2]$. The electrochemical properties of each complex have been examined using cyclic voltammetry under argon with the target being that of the catalytic production of hydrogen using a weak acid (acetic acid) as the proton source. The naturally occurring diiron hydrogenase enzyme produces hydrogen from a low valent state, a property which is desired from these systems. Complexes **1 – 5**, bearing a functionalised carbon atom as the central atom of the dithiolate bridge, are proposed to catalytically produce hydrogen from an $[Fe^0Fe^0]$ state and the mechanism is proposed to be that of an EECC (complexes **2 – 5**) or an ECEC route (compound **1**).

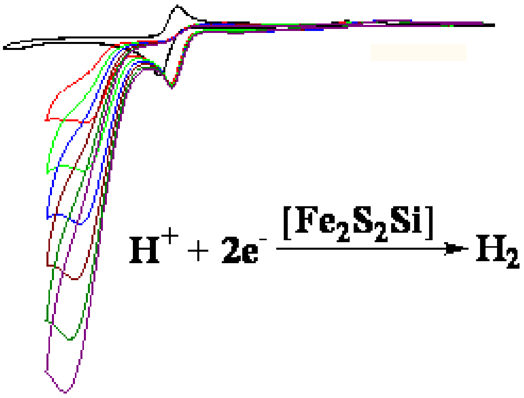

Figure 7.2: *Electrocatalytic production of molecular hydrogen from protons using a diiron hydrogenase analogue as the catalyst.*

The next five compounds, **6 – 10**, have a silicon atom in replace of the carbon as the central atom of the dithiolate bridging unit. The introduction of the silicon atom influences the catalytic pathway to hydrogen production. The basicity of the sulphur atoms is increased which allows for a direct protonation of the bridgehead sulphur atom in an acidic environment. The electrochemistry of a tetra-iron hydrogenase analogue bearing two active sites is also discussed in this chapter with hydrogen production proposed to follow a CECE mechanism. Analysis of these complexes via *in situ* electrochemical gas chromatography experiments would provide an ideal opportunity for the detection of hydrogen gas produced by these catalysts. The measurement of turnover numbers is also required in order to determine the impact of such catalysts in today’s quest for alternative fuel sources.