

For Dad

"Do not follow where the path may lead. Go instead where there is no path and leave a trail."

- Ralph Waldo Emerson

Authors Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy by research and thesis, is entirely my own work and has not been taken from work of others, save and to the extent that such work has been cited within the text of my work.

Signed: _____
Yvonne Halpin

Student I.D. No.: 52037475

Date: 20th January 2010

Acknowledgements

First and foremost I would like to thank my supervisor, Prof. Han Vos for his continuing support and guidance throughout the last three and a half years. I also want to thank you Han for convincing me that doing the PhD was the right thing to do when I almost backed out way back in the summer of 2006...I am eternally grateful!!

To Dr. Wesley Browne (I remembered the ‘e’ ;)), thank you for giving me the opportunity to work alongside you in Groningen over the last few years. I still don’t know how or why you put up with me and all my silly questions – thanks for that!

To Dr. Danilo Dini, I really appreciate all the help you gave me in preparing this thesis. You are an absolute gentleman...sono molto grata! To everyone past and present within HVRG: Bill, Lynda, Rob, Hamid, Laura, Nadia, Soraj, Gurmit, Avi, Jane – thank you for any help you have given me.

Sonia, Jane and Debbie – I cannot thank you enough for your love and friendship throughout the PhD (and as undergrad). You have all been there for me through the laughter and tears...and the odd bottle of vodka here and there ;) I only hope I can do the same for you. Love x

To Noeleen, thank you for everything! You are a great friend and roommate – fun times! Elmo x

To everyone else in DCU who have made the last few years so good...Emma H., Nikki, Jamie, Colm, Alan, Brian M, Emma W., James L., Richard, Mags...and anyone else I may have forgotten to mention (apologies!). To the technicians...Veronica, Ambrose, Vinnie and John...thank you for all the help!

To ‘the girls’...Edel, Grainne, Avril, Dee, Grace and Ruth...some of my best memories are of times with you...I love you guys...here’s to many more!

To James, I know it hasn’t been very long but you have helped me a lot throughout these last few months – more than you realise...thank you! Tidy...obviously! ;)x

To all my friends in the Frisbee circle...Laura, Liz, Michéal, Sparky, Katie, Sean, Dominick, Dónall, John, Brona, Emer and everyone else whom I have not mentioned...there literally isn’t enough room on the page. Thank you!

To my family: Betty, Karol, Paul, Edel, Hayley, Patrick, Catriona, Sarah, Dennis and Abi. I apologise for my incessant moaning and ‘pity me’ attitude over the last year (and longer I know). It’s nearly over I promise. You are the most important people in my life and I cannot thank you enough for all your support, not just with my PhD but in every part of my life. I would be lost without you!xx

Finally, to Dad...I dedicate this thesis to you because you have been my shining light throughout my life so far. You are the strongest person I have ever had the pleasure of knowing. If I can be even half the person you are then I would be very happy! I love you more than life itself. My hero...

“Lose a summer...gain a life!!” – Dr. J.K. Lovatt

Abstract

A focus of this thesis is the study of intramolecular interaction in compounds with a view to adapting these materials for use in the area of molecular electronics. Chapter 1 introduces the concept of intercomponent interaction, in particular the electronic coupling between metal centres across a bridging ligand. A concise synopsis of each results chapter is also included. Specific introductions to the different sections in this thesis are included at the start of each chapter.

Chapter 2 is primarily concerned with introducing the theory and practical aspects of this thesis. The experimental techniques employed (mainly cyclic voltammetry, differential pulse voltammetry and spectroelectrochemistry) in the studies presented in the later chapters are discussed as well as the featured materials and methods.

Chapter 3, the first of the results chapters, is concerned with a series of ruthenium and osmium mononuclear complexes which may be potentially useful as molecular transistors and as precursors to molecular diodes. These complexes have been characterised using electrochemistry, oxidative and reductive spectroelectrochemistry and Raman spectroscopy. The formation of the monolayers of each compound on platinum and gold surfaces has led to the investigation of their surface confined properties which have shown that these monolayers are stable under aerobic conditions in aqueous electrolyte.

The presence of two accessible redox states in a compound is an advantage in the development of molecular diodes. In chapter 4 a series of dinuclear ruthenium and osmium transition metal complexes have been characterised electrochemically using cyclic voltammetry and differential pulse voltammetry. The interaction in a series of dinuclear complexes has been analysed using oxidative spectroelectrochemistry with the crucial factors for intramolecular communication examined. It is found that the overall change in energy involved in the IT transition (*i.e.* the difference in oxidation potentials of the metal centres), and the effect of the electron transfer on the relative energies of the HOMO associated with the binding units of the bridging ligand constitute the critical factors for the occurrence of IT.

Chapter five includes the electrochemistry and monolayer formation of an organic tetrathiafulvalene derivative (dipyrBEDT-TTF) which exhibits two independent redox centres – a requirement in the design of a redox activated molecular rectifier. The electrochemistry is dependent on both the solvent and atmospheric conditions. Monolayers of dipyrBEDT-TTF have been formed on a platinum substrate. The stability of the monolayer has been investigated in several solvents and electrolytes and the most stable monolayer has been obtained on a Pt electrode, in anaerobic conditions, using acetonitrile as the electrochemical solvent.

Finally, chapter six focuses on transition metal complexes using iron as the central metal atoms. This chapter deviates from the main thesis in terms of application as these complexes are designed to act as catalysts for the reduction of protons to molecular hydrogen. A series of diiron hexacarbonyl complexes have been investigated electrochemically and their catalytic ability has been examined using the weak acid, acetic acid as the proton source.

Table of Contents

Authors Declaration	ii
Acknowledgements	iii
Abstract	iv
Table of Contents	v
Chapter 1 Introduction	1
1.1 History of Molecular Electronics	2
1.2 Molecular Diodes and Transistors	4
1.2.1 Redox Active Molecules in Molecular Electronics	7
1.3 Target Complex	11
1.4 Mechanism of Interaction between Metal Centres	12
1.5 Intramolecular Communication in Dinuclear Complexes	14
1.6 Scope of Thesis	20
1.7 Bibliography	25
Chapter 2 Experimental Procedures and Introduction to Techniques	31
2.1 Electrochemistry	32
2.1.1 Introduction	32
2.1.2 Electrode/Solution Interface and the Double Layer	32
2.1.3 Differential Capacitance	35
2.1.4 Electron Transfer	37
2.1.4.1 Homogeneous Electron Transfer and the Marcus Theory	38
2.1.4.2 The Reorganizational Energy λ and Gibbs Free Energy of Activation	40
2.1.4.3 Diabatic and Adiabatic Electron Transfer	41
2.1.4.4 Heterogeneous Electron Transfer	43
2.1.5 Electrochemical Techniques	46
2.1.5.1 Cyclic Voltammetry	46
2.1.5.2 Reversible Redox Reactions – Solution Phase	49

2.1.5.3	Reversible Redox Reactions – Surface Confined Properties	51
2.1.5.4	Differential Pulse Voltammetry	53
2.1.6	Redox Chemistry of Ruthenium and Osmium Complexes	54
2.2	Electronic Properties of Transition Metal Complexes	57
2.2.1	Electronic Absorbance Spectroscopy	58
2.2.2	Luminescence	60
2.2.3	Electronic Properties of $[\text{Ru}(\text{bipy})_3]^{2+}$	62
2.3	Raman Spectroscopy	63
2.4	Experimental Methods	66
2.4.1	Electrochemical Cell Setup	66
2.4.2	Experimental Conditions	70
2.4.2.1	Cyclic Voltammetry and Differential Pulse Voltammetry	70
2.4.2.2	Monolayer Formation	72
2.4.2.3	Oxidative Spectroelectrochemistry	72
2.4.2.4	Reductive Spectroelectrochemistry	73
2.4.2.5	Raman Spectroscopy	73
2.4.2.6	Compounds within This Thesis	74
2.5	Conclusions	75
2.6	Bibliography	76

Chapter 3 Electrochemistry, Spectroelectrochemistry and Monolayer Formation of Mononuclear Ruthenium and Osmium Polypyridyl Complexes 79

3.1	Introduction	80
3.1.1	Mononuclear Transition Metal Complexes in Molecular Electronics	80
3.2	Results and Discussion	85
3.2.1	Redox Properties	85
3.2.2	Spectroelectrochemistry – Oxidative	99
3.2.3	Spectroelectrochemistry - Reductive	105
3.2.4	Raman Spectroscopy	110

3.2.5	Electrochemistry and Raman Spectroscopical Properties of Mononuclear Complexes Confined on a Surface	112
3.2.5.1	Electrochemical Properties of Surface Confined Complexes	112
3.2.5.2	Surface Enhanced Raman Scattering Spectroscopy of Os(thimphen) Assembled on Au Electrodes	129
3.3	Conclusions	132
3.4	Bibliography	134
Chapter 4	Electrochemistry and Spectroelectrochemistry of Homo- and Hetero-Dinuclear Ruthenium and Osmium Polypyridyl Complexes	138
4.1	Introduction	139
4.1.1	Supramolecular Chemistry	139
4.1.2	Spectroelectrochemistry and Mixed Valence Systems	140
4.1.3	Interaction in the Mixed Valence State	143
4.1.4	Electrochemistry and Comproportionation Equilibrium	148
4.1.5	Aim of this Chapter	150
4.2	Results and Discussion	156
4.2.1	Redox Properties	156
4.2.2	Comproportionation Constant as a Measure of Intermetallic Interaction	164
4.2.3	Spectroelectrochemistry – Oxidative	166
4.2.4	Interaction Parameters in Mixed Valence States	177
4.3	Conclusions	185
4.4	Bibliography	187
Chapter 5	Electrochemistry, Spectroelectrochemistry and Monolayer Formation of a Tetrathiafulvalene Derivative: 5,6-dehydro-5,6-di(pyrid-4-yl)-bis(ethylenedithio)tetrathiafulvalene	193
5.1	Introduction	194
5.1.1	Molecular Rectifiers	194

5.1.2	Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) Compounds	197
5.1.3	D- σ -A vs. Redox Controlled Conductance in Molecular Electronics	199
5.1.4	Self-Assembled Monolayers of TTF Derivatives	203
5.2	Results and Discussion	206
5.2.1	Redox Properties	206
	5.2.1.1 Solution-Phase Diffusion Controlled Electrochemistry	206
	5.2.1.2 Solvent Dependence Study	212
	5.2.1.3 Aerobic vs. Anaerobic Effects on Stability of the Redox Intermediate	219
5.2.2	Oxidative Spectroelectrochemistry	223
5.2.3	Comproportionation Constant, K_c	227
5.2.4	Electrochemical Properties of dipyrBEDT-TTF on a Surface	229
5.3	Conclusions	242
5.4	Bibliography	245

Chapter 6	Catalytic Proton Reduction using a Series of Hexacarbonyl Diiron Hydrogenase Analogues	251
6.1	Introduction	252
	6.1.1 Hydrogen as an Energy Source	252
	6.1.2 Hydrogenase Enzymes	252
	6.1.3 Key Cofactors of the [FeFe] Hydrogenases	256
	6.1.4 Diiron Dithiolato Hexacarbonyl Hydrogenase Analogues	259
	6.1.5 Substituted Diiron Dithiolates	262
6.2	Results and Discussion	266
	6.2.1 Hexacarbonyl Diiron Hydrogenase Analogues with a Substituted 1,3-Propanedithiolate (pdt) Bridge	268
	6.2.1.1 Electrochemistry of Substituted pdt-Bridged Hydrogenase Analogues	269

6.2.1.2	Electrocatalytic Proton Reduction of Substituted pdt-Bridged Hydrogenase Analogues	274
6.2.2	Sila-Substituted Hexacarbonyl Diiron Hydrogenase Analogues	280
6.2.2.1	Electrochemistry of Sila-Substituted Hydrogenase Analogues	282
6.2.2.2	Electrocatalytic Proton Reduction of Sila- Substituted Hydrogenase Analogues	293
6.4	Conclusions	300
6.5	Bibliography	303
Chapter 7	Conclusions and Future Work	307
7.1	Chapter 3	306
7.2	Chapter 4	307
7.3	Chapter 5	308
7.4	Chapter 6	309
Appendix	Refereed Publications	313