Chapter 1

Introduction

A brief introduction to molecular electronics including reported examples of molecular transistor and diode type compounds is given in this chapter. Electronic coupling between metal centres in the mixed valence state of dinuclear complexes is considered advantageous in the realisation of a molecular diode. For this reason the theme of electronic interaction between metal centres in dinuclear species is addressed. A series of reported examples of bimetallic ruthenium and osmium complexes exhibiting interaction between the metal centres is discussed as well as a brief introduction to the different mechanisms of electron transfer between the metal centres across a bridging ligand. Finally, the content of each of the different areas studied in this thesis are introduced at the end of this chapter.

1.1 History of Molecular Electronics

Since the early ages mankind has focused on the design and development of novel machines and devices; improvements and upgrades of which are constantly being introduced. In the latter half of the 20th century, and continuing to the present day, the idea of miniaturization of these devices has captured the minds of scientists around the world especially in the area of information storage and processing.[1] In a technologically advancing world there has been an increasing demand for faster and more efficient computers leading to the development of the silicon based computer industry. This area of semiconductors has experienced a remarkable miniaturization trend, in particular in the last 40 years or so.[2, 3] In 1965 a scientist, Gordon Moore, envisaged that in order to progress in the semiconductor industry the number of transistors per chip would need to double by reducing the functional area by a half every couple of years, with each new technology generation.[4] This concept became known as Moore’s Law.

The silicon chip has impacted our lives far more than most people even realise. Silicon forms the backbone of electric circuits in most electronic devices from microprocessors in computers, to mobile phones and portable audio devices. Replacing the older more primitive electric circuits, it wasn’t long before the potential of electric circuits imbedded in silicon was realised. However, despite such advances observed in solid-state electronics on a regular basis, the major disadvantage is that the silicon based devices cannot be scaled down indefinitely as a result of physical, as well as monetary limitations. An example of a physical barrier that exists with downsizing the silicon chips is charge leakage from the oxide layer at such a small scale.[5]

The thirst for faster and increasingly powerful electronic devices such as computers etc. is ever more forcefully testing the limits of the silicon based integrated circuits. It cannot be denied that modern technology is approaching these limits and it is this which drives the search for novel ways of achieving the desired miniaturization targets in the semi-conductor industry. In recent years the idea of molecular scale components, replacing the silicon chip in electronic circuits, has been explored.

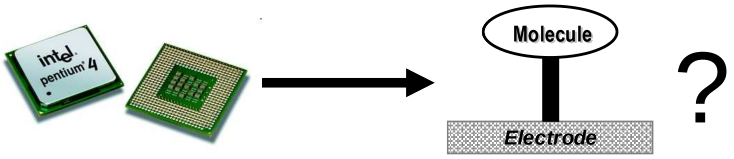


Figure 1.1: *Illustration of the possible progression from the recent silicon based integrated circuits* [6] *to innovative circuit components based on the "bottom-up" approach.*

Molecular electronics is concerned with the concept of using one or more molecules mounted on a surface (capable of conducting and switching electric currents and storing information) as a means of replacing electronic devices, such as transistors, wires and diodes.[5] Molecules are extremely attractive building blocks for electronic devices. Molecules exist in a vast and diverse array of shapes and sizes, each of which bears different properties to the next. There are definite advantages in considering molecules for the construction of innovative and revolutionary electronic devices; referring to nature, all electronic processes are governed by molecules. The most obvious advantage is the size of a molecule: depending on the number of atoms in the molecule it can range from 1 – 100 nm.[7] Using molecules on the smaller end of this scale to assemble an integrated circuit could lead to more cost effective production with improved functionality. Manipulation of the intermolecular interaction can give rise to the opportunity to form self assembled ordered structures on an electrode surface. Through control of the electronic and redox properties of the molecules, switching or rectifier behaviour, akin to that of electronic devices, may be observed. The extent of conductance through the molecule can also be altered by synthetically varying the nature of the different sites within the molecule.[7]

The idea of beginning with an interface, and assembling a system comprised of a molecule supported on the surface to establish a nanoscale device, was first introduced by Richard P. Feynman[8] in an address entitled "*There is plenty of room at the bottom*". This became known as the "bottom-up" approach and it is this concept that is providing an ideal alternative in the task of realizing novel and innovative electronic devices.

1.2 Molecular Diodes and Transistors

Recent years have witnessed a substantial effort in the development of molecular electronic devices. The concept of the “bottom-up” approach has led to a considerable amount of research in the area of molecular wires [3 - 5, 9, 10] transistors [11, 12, 13] and diodes [14, 15, 16]. In electronic devices, the wire plays one of the more simple roles in that its purpose is to facilitate the passage of current between two points. A transistor on the other hand, is capable of switching or amplifying electric current. Molecules are said to have transistor-like behaviour when the properties of the molecule can be alternated between conducting and insulating through a change in the physical, electronic or magnetic structure once an external gate signal has been applied. Alternating between these two states allows the molecule to control the flow of electricity acting like a switch in that the conducting state allows current to flow whereas the insulating state does not.

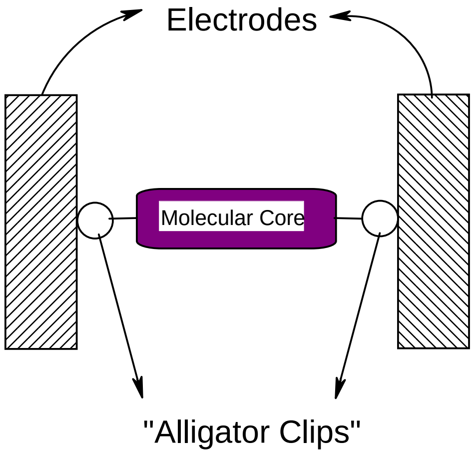


Figure 1.2: *Simplified schematic of a two terminal molecular electronic device.*

The function of a diode on the other hand is to regulate the direction of current. It is a two-terminal system that has a low resistance to current in one direction and high resistance in the other; thereby only allowing the current to flow in one direction. The two terminals of the diode act as entrance and exit points for the current flowing in and out and are usually referred to as the “source” and “drain”. Molecular-scale transistors operate on a three terminal principle. Like the diode, two of these terminals will act as a source and a drain with the third being that of the “gate”. In an electrochemical molecular electronics setup, the reference electrode is normally seen to act as the gate.

It wasn't until the second half of the 20th century that the concept of miniaturization to the molecular scale was realized. Two types of molecular scale diodes have been presented in the literature: rectifying diodes and resonant tunnelling diodes. The main aim of this project was to develop a rectifying diode, i.e. a unidirectional structure which allows current to pass through in one particular direction only, known as the *forward* direction. The "forbidden" direction is usually termed the *reverse* direction.

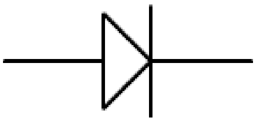


Figure 1.3: *Diagram to illustrate the symbol for a rectifying diode.*

The potential formation of molecular scale "diode" type components, capable of exhibiting rectifying behaviour, was first realised in the theoretical formulation of Aviram and Ratner in 1974.[17] The proposed structure of the Aviram and Ratner molecular diode was based on the operating principles of the solid state, bulk effect p-n junction diode.[18]

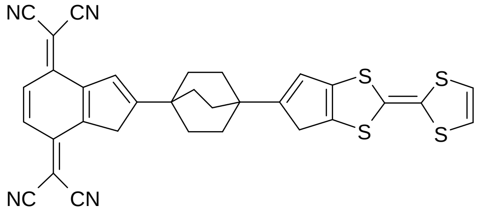


Figure 1.4: *Molecular structure of TTF-σ-TCNQ; a molecular rectifier proposed by Aviram and Ratner in 1974.*[17]

Following on from the work of Cowen *et al.* [19] in 1973, a donor-acceptor system exhibiting molecular conductivity was reported. Tetrathiafulvalene (TTF) was reported to form conducting cation radical complexes (donor) with the acceptor being that of a tetracyano-*p*-quinodimethane (TCNQ) anion radical complex. Aviram and

Ratner, realising the potential of such a highly conducting organic complex, proposed a system whereby the TTF and TCNQ components were connected through a σ-bonded non-conjugated bridge, Figure 1.4.[17]

This theoretical model possesses characteristics akin to solid state devices: the electron-poor acceptor part of the molecule (TCNQ) and the electron-rich TTF donor make up the p-type and n-type components, respectively, which are found in solid state rectifiers employing p-n junctions. By modifying the substituents, in terms of their electron withdrawing/donating properties, the acceptor/donor profile of each component in the system can be altered. Current ideally would flow between the TTF and TCNQ units, through the non-conjugated σ-bonded bridge. Sufficient charge separation is achieved through use of such σ-bonds and the conductivity through the molecule is mediated by the delocalized orbitals of the π-bonds on the spacer unit.[20]

This model put forward by Aviram and Ratner proposed an ideal solution for achieving rectifying behaviour with molecules. For current to flow, it is required that the compound is sandwiched between two electrodes and at an appropriate potential the current flows between the electrodes via the HOMO and LUMO levels of the donor and acceptor which are in the charged separated state; TTF^{+}-σ-$TCNQ^{-}$. However, there is little evidence of this type of TTF π-donor-σ-π-acceptor (TCNQ) system with low HOMO-LUMO energy gaps. This is most likely due to synthetic problems associated with this model.

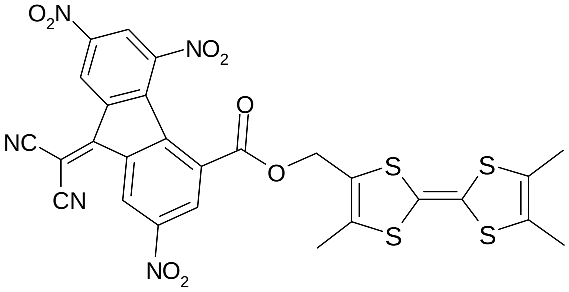


Figure 1.5: *Molecular structure of a molecular rectifier reported by Heath et al.*[23]

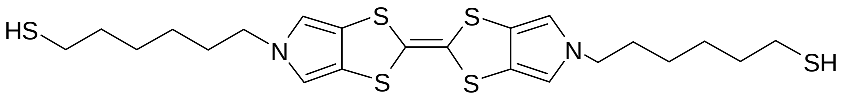
Adapted D-σ-A compounds have been reported exhibiting molecular rectifying behaviour.[21] Brady *et al.* [22] developed an organic molecular rectifier similar to that proposed by Aviram and Ratner where conductance was observed through the HOMO and LUMO levels of the D-σ-A system when under forward bias (at +0.5 V) . Under reverse bias a much lower conductance is observed and only at higher potentials (> +1.5 V). Heath *et al.* [23] achieved rectifier behaviour with a D-σ-A compound where the donor is a TTF derivative and the acceptor is a fullerene, Figure 1.5. The Aviram and Ratner predictions were based on a small energy gap in the region of 0.3 eV. This energy gap was found in the compound reported by Heath *et al.* and increased molecular conductivity was observed through construction of Langmuir-Blodgett films.

Several examples of organic molecular rectifiers based on this D-σ-A model have been reported in the literature.[20, 21, 22, 23] An alternative approach in the quest to develop molecular electronic transistor- and diode-type complexes, suitable for application in molecular electronics, is to consider redox active complexes where the conductivity may be measured as a function of the redox states within the molecule.

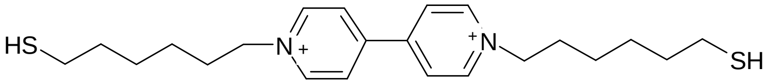
1.2.1 Redox Active Molecules in Molecular Electronics

Electron transfer in redox active compounds has been extensively studied as it plays a valuable part of many chemical processes. By assembling a molecule on a surface and *wiring* the other end of the molecule to a second electrode, the conductivity through the molecule can be measured. A third electrode is introduced in three terminal devices to allow for control of the current by switching between the redox states of the molecule.

Electrochemistry can play an important role in the development of such molecules. It has been reported that redox active molecules such as viologens [24] and oligo-anilines [25] can be electrochemically switched from one redox state to the next, and by combining this with other techniques such as scanning tunnelling microscopy (STM), the conductivity between the electrodes and the molecule can be measured simultaneously.[26]



6PTTF6



6V6

Figure 1.6: *Molecular structures of redox active molecules, 6PTTF6 [26] and 6V6 [24].*

The redox active molecules shown in Figure 1.6 have been reported to exhibit molecular conductivity.[24, 26] By assembling each molecule on a Au electrode, via a Au-S bond and tethering the other end to a Au STM tip, a four electrode configuration was used similar to the current solid state field effect transistors (FET). The reference electrode of the electrochemical *in situ* STM configuration acts as the *gate* electrode. The viologen molecule (6V6), which can be electrochemically switched to the monocation radical followed by the neutral compound, exhibits increased conductance upon sweeping to negative potentials. However, the resulting switching profile, “off-on”, is broad and is said to result from configurational fluctuations from the polymethylene chains.[24c] The tetrathiafulvalene derivative, 6PTTF6 is a redox active molecule exhibiting two stable redox states ($6PTTF6^{+}$ and $6PTTF6^{2+}$). The conductivity of the molecule was investigated by accessing the first oxidative process only, as the second more positive process falls outside the potential range where Au-S bonds are stable in aqueous electrolyte. An “off-on-off” switching profile was achieved which can be electrochemically controlled.

Molecular electronic devices, comprising of transition metal coordination complexes have been reported.[12, 27, 28] A benefit of using transition metals is that electron transfer can occur through well defined charge states of a single atom. Transition metals frequently exhibit stability when switching from one redox state to the next which makes them attractive starting points in the design of molecules for molecular electronics. Two transistors incorporating cobalt complexes have been synthesised and examined by McEuen and Ralph [12] where the cobalt atom is coordinated to two terpyridyl ligands in an approximately octahedral environment, Figure 1.7.

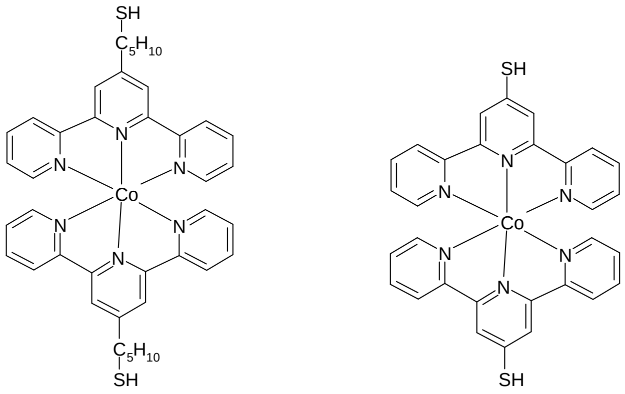


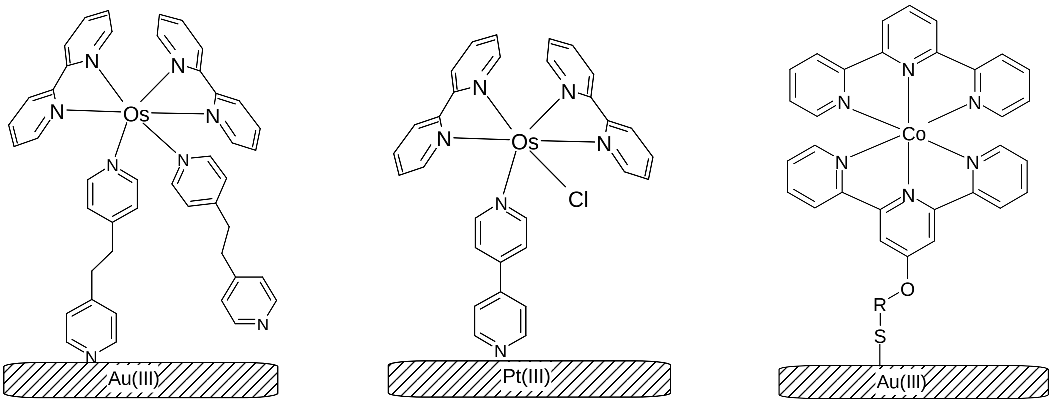
Figure 1.7: *Single molecule transistors developed by McEuen and Ralph.*[12]

Each complex is self-assembled on Au electrodes via a thiol group attached to each terpyridyl linker. By altering the length of the linker the degree of coupling between the molecule and the electrodes, and therefore the level of conductance, could be controlled. The cobalt metal centre was chosen as it is stable in both the Co^{II} and Co^{III} redox states and can be electrochemically switched between these redox states at low energy (~0.3 V *vs.* Ag/AgCl). The main difference between the two molecules is the length of the organic linker (alkyl chain that facilitates the coupling between the cobalt ion and the electrodes). Current *vs.* bias voltage plots were obtained and it emerged that the shorter chain allows for significantly larger conductance than that measured in the molecule with the larger alkyl chain. Both complexes, however, exhibit behavioural properties like those of single electron transistors.[12]

Major limitations accompany the single molecule electronic transistors and diodes reported to date; in order to operate successfully, these systems require cryogenic temperatures or ultra-high vacuum which are not ideal for practical devices.[12, 13] In 2005, Albrecht et al. reported osmium and cobalt mononuclear complexes for use as single-molecule transistors, the former novel in molecular electronics, Figure 1.8.[29] Extensive research into the electrochemical properties of these, and similar osmium complexes, has been carried out by Forster *et al.* evoking an interest in their application as molecular transistors.[30, 31, 32] This class of compounds includes the osmium complexes $[Os(bipy)_2(p2p)_2]^{2+/3+}$ and $[Os(bipy)_2(p0p)Cl]^{+/2+}$ and the cobalt complex $[Co(terpy)(terpy\text{-}O\text{-}(CH_2)_6\text{-}SAc]^{+/2+}$, where bipy = 2,2'-bipyridine, p2p = 1,2-bis(-4-pyridyl)ethane, p0p = 4,4-bipyridyl, tpy = 2,2',2"-terpyridine and

Ac=acetyl. The electrochemistry of these complexes has been studied and self-assembled monolayers have been formed on Au and Pt electrodes.

Characterisation of the monolayers using a range of electrochemical techniques reveals an almost ideal voltammetric response from the monolayers suggesting that electron transfer is mechanistically uncomplicated. The calculated surface coverages for the osmium complexes suggest that assembly on a metal surface results in a close to complete monolayer. The electron transfer rate constant for the $[Os(bipy)_2(p0p)Cl]^{+/2+}$ redox couple is in the range of 10^6 s^{-1} which is three orders of magnitude greater than the cobalt complex. This is because of the much stronger adiabatic electron coupling between the osmium complex and the electrode.



a **b** **c**

Figure 1.8: *Molecular structures of $[Os(bipy)_2(p2p)_2]^{2+}$ (a), $[Os(bipy)_2(p0p)Cl]^{+}$ (b) and $[Co(terpy)(terpy\text{-}O\text{-}(CH_2)_6\text{-}SAc]^{+}$ (c) bound to Au(III) and Pt(III) surfaces.*[29]

These complexes were analysed using a three electrode electrochemical *in situ* STM configuration which is very similar to three terminal transistors, where the substrate and tip electrodes correspond to the source and drain electrodes and the gate electrode relates to the reference electrode. These systems are capable of redox switching and amplification which leads them to be classed as “transistor”-type complexes.[29]

Interfacial electron transfer and molecular conductivity are at the forefront in the development of a molecular electron device. A principle concept in this area is to be able to design molecules with the appropriate properties for the intended function and to have the ability to assemble the molecules on a surface in an organized manner. The ability to control the function of the monolayer, so that the electrical conductivity and mechanisms of electron transport can be investigated, is desired. The aim of this project was to develop molecular transistors and diodes capable of functioning in an aerobic environment at room temperature.

1.3 Target Complex

The aim of this project was to develop mono- and dinuclear complexes that exhibited transistor and diode type properties capable of functioning at room temperature in the absence of a vacuum. The main focus, however, was to achieve diode type behaviour with dinuclear complexes that exhibited electronic interaction (electron or hole conduction) between the metal centres. The model candidate in this pursuit was a dinuclear complex, $[Os(bipy)_2(bpt)Os(py\text{-}tpy)Cl]^{2+}$, where bipy is 2,2'-bipyridyl, bpt is 3,5-bis(pyridin-2-yl)1,2,4-triazole and py-tpy is 4'(pyrid-4'''-yl) 2,2':6', 2'' terpyridine (Figure 1.9).

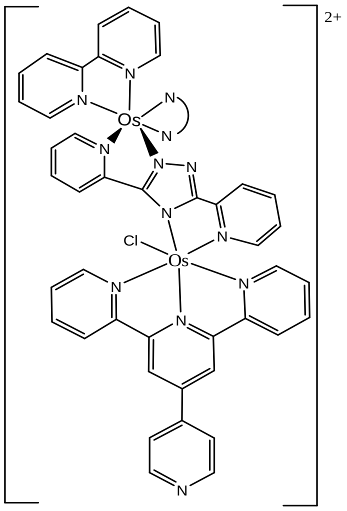


Figure 1.9: *Model transition metal complex,* $[Os(bipy)_2(bpt)Os(py\text{-}tpy)Cl]^{2+}$ *for the development of a molecular diode.*[33]

Depending on the electronic properties of the coordinated ligands, osmium complexes are known to exhibit oxidation potentials in a range suitable for (1) assembly on a Au metal surface (E_p < ~ +0.9 V, *vs.* SCE) [34] and (2) allowing conductivity to be measured in aqueous electrolyte. The Hbpt ligand is a good mediator of electron transfer from one metal centre to the other as it ensures strong coupling by mixing of the dπ orbitals of the metal with the π-orbitals of the bridging ligand.[35] The second osmium metal centre is coordinated to a functionalized tpy ligand providing an anchor to a metal surface.

Although the synthesis of this model complex was attempted several times within the research group, each effort proved unsuccessful.[33] Issues with which the purity of the starting material ([Os(tpy)Cl_3]) could be obtained, as well as severe reaction conditions for coordinating the osmium metal to the bridging ligand, prevented the successful synthesis of this complex. Tpy is a labile ligand and at the high temperatures required for osmium reactions, scrambling of the ligand occurs.

A series of homo- and hetero- dinuclear complexes have been previously synthesised within the research group.[33] These complexes were deemed suitable as precursors for molecule diode type complexes as the metal centres may “communicate” electronically when in a mixed valence state allowing a current to flow across the bridge leading to potential rectifier behaviour. While synthetic experiments are still underway to successfully add a linker ligand to these complexes thereby allowing for binding to a metal surface, the possibility of interaction and electronic coupling between the metal centres in each of the complexes was investigated. This was carried out via spectroelectrochemical measurements of each complex in the diffusion controlled solution-phase, the results of which are discussed in more detail in Chapter 4.

1.4 Mechanism of Interaction between Metal Centres

There has been extensive interest into the different mechanistic pathways of electron transfer considering its ubiquitous presence in chemical processes. Of particular interest is that of intramolecular electron transfer in multinuclear transition metal complexes because of the diversity offered through different coordination numbers, ligand chemistry and redox properties.[36] In the design of dinuclear systems where intermetallic communication is desired, one must consider the importance of the bridging ligand. Both the length and nature of the bridge can affect not only the probability of electron transfer from one centre to the other, but also the rate at which electron transfer proceeds. The electronic coupling between the centres is heavily dependent on the overlap of the wavefunctions of the donor and acceptor metals in dinuclear transition metal complexes. The nature of the bridge is also important in achieving intramolecular interaction. It has been shown that bridging ligands containing conjugated π-systems allow for fast electron transfer from the donor to the acceptor metal centres.[37]

“Communication” between metal centres is predominantly dependent on the electronic properties of the residing bridging ligand as well as the distance between the metal centres. Electron transfer can occur via a straightforward electron or hole hopping mechanism which is generally observed where the donor and acceptor are close together separated by a short bridge. Alternatively, where the length of the bridge prevents direct electron or hole hopping, the electron transfer occurs via a superexchange mechanism.

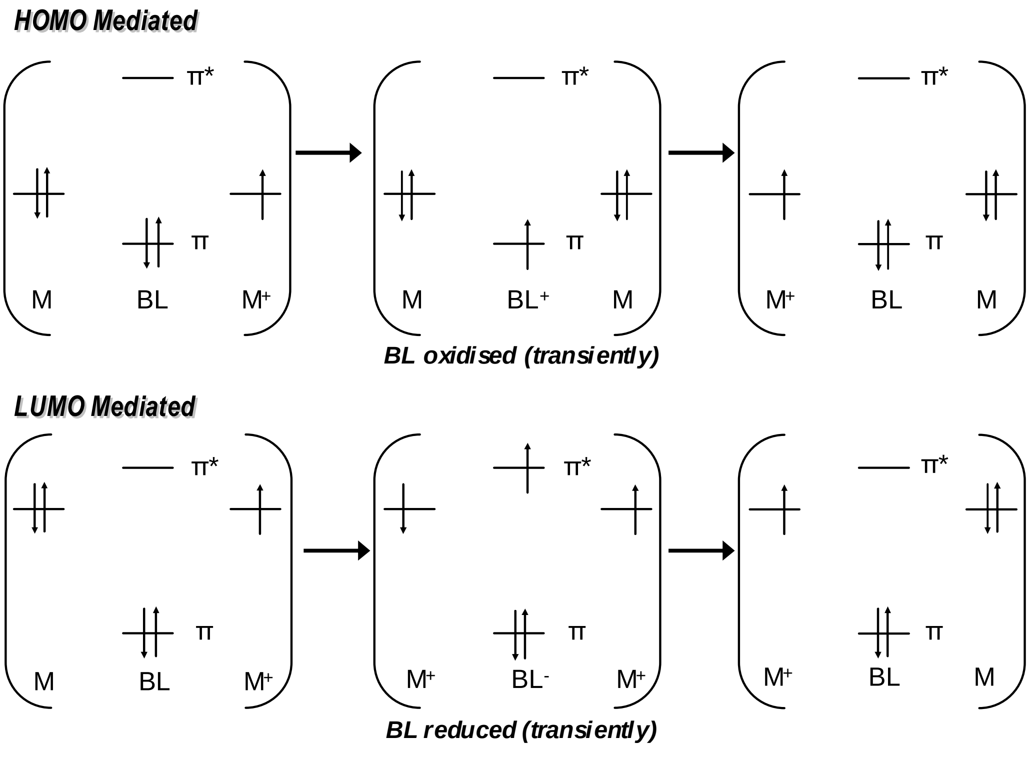


Figure 1.10: *HOMO mediated (top) and LUMO mediated (bottom) superexchange electron transfer mechanisms. M = metal and BL is bridging ligand. Adapted from reference 38.*

Electron transfer involves an interaction of the donor metal with the lowest unoccupied molecular orbital (LUMO) of the bridge. In order to facilitate electron transfer across the bridge it must possess low-lying π or π* orbitals that can accept and transfer the electron. Where the LUMO levels of the bridge are too high in energy to mediate electron transfer, hole transfer can occur (where the donor and acceptor are separated by a short distance) through the highest occupied molecular orbital (HOMO) of the donor and acceptor. The electronic coupling weakens exponentially with increased distance between the donor and acceptor and the mechanism of electron transfer will depend on the extent of resonance between the bridge energy levels and those levels of the donor and acceptor.[37]

HOMO mediated superexchange involves oxidation of the bridging ligand in order to reduce the oxidised metal (acceptor). The π-orbitals of the BL that are involved in this electron transfer process are then subsequently reduced through electron transfer from the donor metal. LUMO meditated superexchange on the other hand, entails reduction of the π*-orbitals of the bridge and transferral of the electron from there to the acceptor metal. HOMO mediated superexchange often occurs with electron deficient metal centres and electron rich bridging ligands, such as triazoles.[38]

1.5 Intramolecular Communication in Dinuclear Complexes

Owing to the first disclosure of intercomponent interaction within the Creutz-Taube ion (Figure 1.11), considerable attention has been paid to electronic interaction between metal centres in multimetallic transition metal complexes.[34] The Creutz-Taube ion [39] ($[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+}$, where pz is an aromatic pyrazine heterocycle) is an example of a molecule where interaction between metal centres occurs over a short bridging ligand distance.

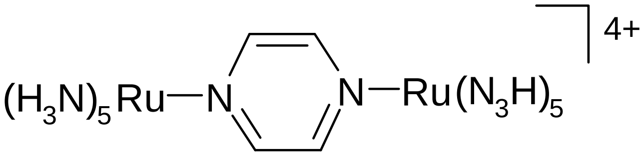


Figure 1.11: *Molecular structure of the Creutz-Taube ion.*[39]

The orientation of the bridging ligand orbitals allows for overlap with the dπ orbitals of the ruthenium metal centres according to Figure 1.12. Therefore the dπ orbitals of the metal are, in a sense, delocalised across the conjugated aromatic bridge and the metal centres can interact with each other. A first indication of the possible presence of interaction between metal centres lies in the separation between the oxidation potentials of the two metal centres. The overlap of metal orbitals, via the bridging ligand, facilitates communication between the metal centres. When the first metal centre is oxidised the second metal centre is aware of the presence of an increased positive charge and therefore is oxidised at a higher potential. The oxidation potentials of the Creutz-Taube ion ($Ru^{2+/3+}$ redox couples) are separated by 390 mV indicating possible interaction between the metal centres.[40]

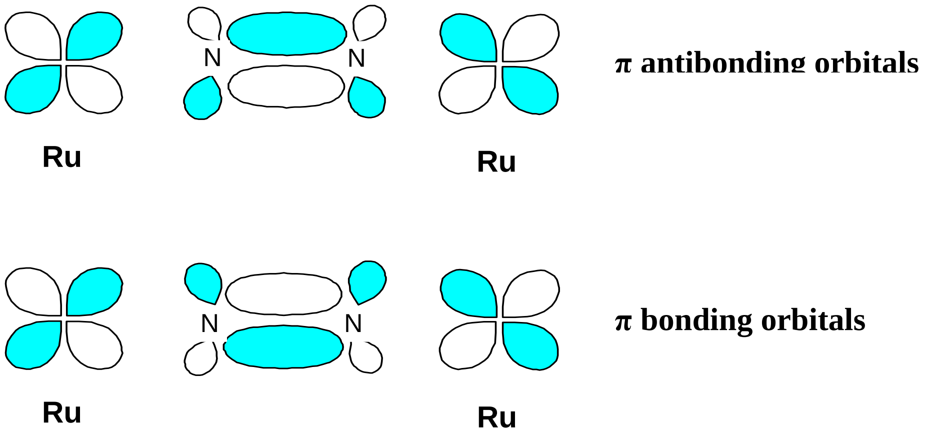
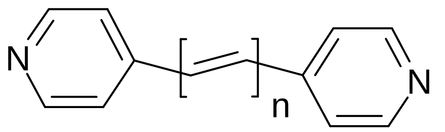


Figure 1.12: *π bonding and antibonding orbitals found in the Creutz-Taube ion. Adapted from reference 41.*

The Creutz-Taube ion has a comproportionation constant, K_c (a measure of the stability of the mixed valence state, see Chapter 4, section 4.1.4) in the range of 10^6 which is a direct measurement, from electrochemical results, of the stability of the mixed valence state. The pyrazine bridge offers a short metal-metal distance and leads to strong electronic coupling in the mixed valence state. The complex may be classed as having a Type III interaction where the unequal charge in the mixed valence state is delocalized over the metal-bridge-metal domain.

The effect of distance between metal centres on the intercomponent interaction can be investigated by varying the length of the bridging ligand. This can be seen by comparing the Creutz-Taube ion with analogous complexes with a longer metal-metal distance. The $[Ru(NH_3)_5]^{2+}$ fragment of such complexes is a strong σ-donor which makes it ideal for coordinating to strong π-acceptor bridging ligands like those shown in Figure 1.13. The dinuclear complexes, $[(NH_3)_5Ru(BL)Ru(NH_3)_5]^{n+}$ (BL = X, Y, Z; n = 4, 5, 6) [42], are ideal candidates for ascertaining the effect of distance on the intramolecular interaction.

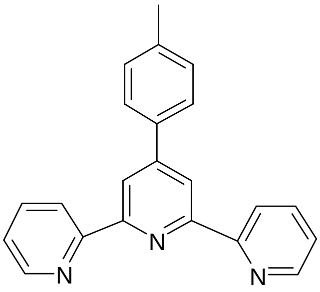


X (n = 2)
Y (n = 3)
Z (n = 4)

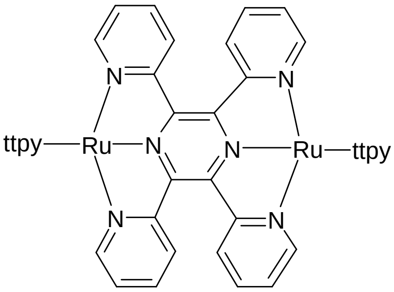
Figure 1.13: *Molecular structures of the dipyridyl polyene bridging ligands of* $[(NH_3)_5Ru(BL)Ru(NH_3)_5]^{n+}$.[42]

The metal centres in these complexes exhibit weak electrochemical interaction; oxidation of the metal centres occur at potentials very close to one another. However, despite this, spectroelectrochemical measurements give rise to intervalence charge transfer bands in the spectrum of the mixed valence state of each complex. A decrease in the degree of electronic coupling between the metal centres with increasing bridge length is observed. The electronic interaction, observed when n = 2 ($[(NH_3)_5Ru(X)Ru(NH_3)_5]^{4+}$), decreases by a minimum of 30 % for $[(NH_3)_5Ru(Z)Ru(NH_3)_5]^{6+}$ where the number of C-C double bonds in the polyene chain of the bridge is 4.

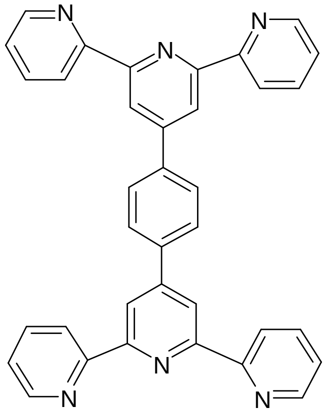
The rigidity of the bridging ligand can also affect the interaction between the metal centres in the mixed valence state. RuRu dimers, where the peripheral ligands are ttpy (4'-tolyl-2,2' ,6' ,2"-terpyridine), and the bridging ligands either tppz or ttpy-ph-ttpy, Figure 1.14.[43]



ttpy



$[(ttpy)Ru(tppz)Ru(ttpy)]^{4+}$



ttpy-ph-ttpy

Figure 1.14: *Molecular structure of RuRu dimers with tppz and ttpy-ph-ttpy bridging ligands.*[43] *These complexes exhibit long range intercomponent electronic coupling.*

The tppz bridging ligand, in $[(ttpy)Ru(tppz)Ru(ttpy)]^{4+}$ is a planar ligand. Two independent anodic processes are observed for this complex, separated by 300 mV, representing the successive oxidation of each of the metal centres. The introduction of the aromatic ring as a spacer between the two ttpy ligands in the bridging ligand ttpy-ph-ttpy, Figure 1.14, leads to a certain degree of conformational freedom and the bridging ligand can be twisted as a result. This lack of rigidity in $[(ttpy)Ru(ttpy\text{-}ph\text{-}ttpy)Ru(ttpy)]^{4+}$ leads to this complex having two metal centres that are electrochemically isolated from each other as only one anodic wave is observed which represents the simultaneous oxidation of each metal centre. However, intervalence bands are observed for each complex and it is noted that the degree of electronic coupling is weaker with the longer, less rigid ttpy-ph-ttpy bridging ligand. Introduction of a second conjugated aromatic spacer to the bridging ligand (ttpy-ph-ph-ttpy) results in even less electronic coupling between the centres.[43]

The homo- and hetero-dinuclear complexes discussed in this thesis (Chapter 4) are comprised of either ruthenium and/or osmium as the metal centres with the peripheral ligands being those of the strong π-acceptor bipyridyl ligands. The bridging ligands used in these dimers contain both azole 5-membered and azine 6-membered heterocycles (triazoles, pyridine and bipyridine). Triazoles are 5-membered heterocycles that exhibit strong σ-donor properties due to the negative charge on the ring. A triazole ring, as a component of a bridging ligand, is capable of facilitating

HOMO-mediated superexchange as a result of mixing of its π-orbitals with the dπ orbitals of the Ru/Os metal centre. Homo- and hetero- ruthenium and osmium complexes incorporating the Hbpt ligand, where electronic interaction between the metal centres has been observed, have been reported in the literature.[35c, 44]

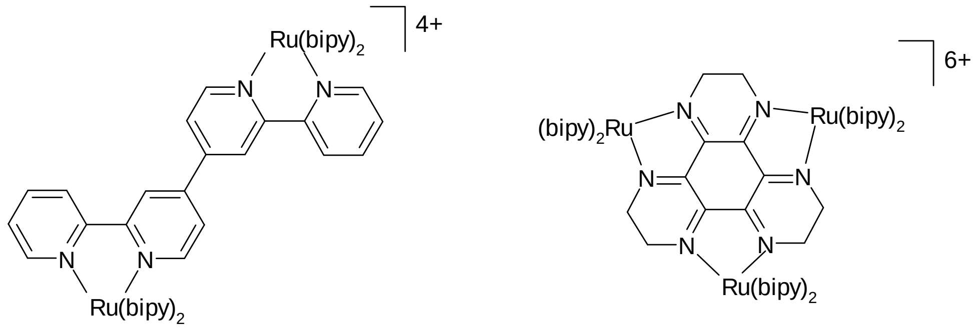
Two anodic processes are observed in the cyclic voltammetry of four complexes of this type representing the independent oxidation of each metal centre, Table 1.1. This indicates that the metal centres may be interacting electrochemically across the bridging ligand. The largest separation between the oxidation potential (Δ*E*) is observed for the mixed-metal RuOs and OsRu dimers – this is partly due to the redox asymmetry in each complex.

Compound	**Oxidation Potentials, $E_{½}$ (V *vs.* SCE)**		**$\Delta E_{½}$ / mV**
$[(bipy)_2Ru(bpt)Ru(bipy)_2]^{3+}$ (RuRu)	+1.04	+1.34	300
$[(bipy)_2Os(bpt)Os(bipy)_2]^{3+}$ (OsOs)	+0.64	+0.85	210
$[(bipy)_2Ru(bpt)Os(bipy)_2]^{3+}$ (RuOs)	+0.73	+1.20	470
$[(bipy)_2Os(bpt)Ru(bipy)_2]^{3+}$ (OsRu)	+0.65	+1.30	650

Table 1.1: *Oxidation potentials of a series of ruthenium and osmium bpt bridged dinuclear complexes.*[35c, 44]

Intervalence charge transfer bands have been observed for each of these complexes. Interestingly, the greatest electronic coupling between the metal centres is observed for the RuRu dimer with the OsRu analogue exhibiting the weakest interaction. The mechanism of charge transfer in the $M^{II}M^{III}$ state is proposed to occur via a HOMO mediated superexchange involving the dπ orbitals of the oxidised metal and the π-orbitals of the bridging ligand. The greater electronic coupling observed for the RuRu complex suggests that the Ru^{III}(dπ) – π(BL) interaction is dominant in the intervalence process rather than that of Ru^{II}(dπ) – π*(BL).[35c]

The intramolecular interaction in ruthenium and osmium metal complexes, designed using strong π-accepting bridging ligands, has also been investigated.[38, 45, 46, 47, 48] A tridentate bridging ligand, illustrated in Figure 1.15, has been shown to facilitate electron transfer in the mixed valence state. The HAT ligand (1,4,5,8,9,12-hexaazatriphenylene) was originally reported by Kirsch-de Mesmaeker *et al.* [47a] and the intervalence charge transfer was later investigated by Keene *et al.*.[47b]



$[((bipy)_2Ru)_2(qpy)]^{4+}$

$[((bipy)_2Ru)_3(HAT)]^{6+}$

Figure 1.15: *Molecular structures of* $[((bipy)_2Ru)_2(qpy)]^{4+}$ [48] *and* $[((bipy)_2Ru)_3(HAT)]^{6+}$ [47].

Up to three one-electron anodic processes are observed depending on how many ruthenium metals are coordinated to the bridging ligand. The oxidation potentials are separated approximately 250 mV indicating the possible presence of intermetallic communication across the bridging ligand. Intervalence charge transfer bands are observed in the absorbance spectra of the dinuclear and trinuclear species when in the mixed valence states. Significant overlap of the $Ru^{II}(d\pi)$ and $Ru^{III}(d\pi)$ orbitals occurs as intense intervalence bands indicate strong electronic coupling between the metals. The complexes are believed to lie in the intermediate Type II/III classification of interaction. The different degrees of interaction are explained in more detail in Chapter 4.

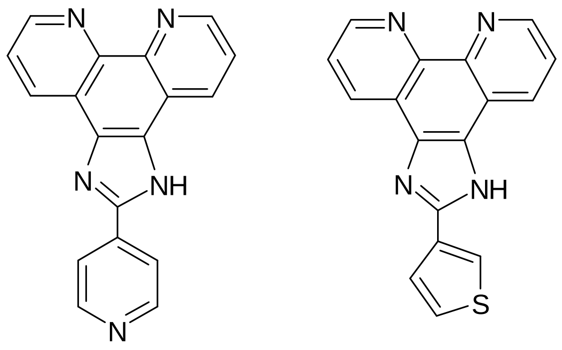
The electrochemical properties of the RuRu dinuclear complex bridged by the π-acceptor qpy ligand, where qpy is 2,2':4',4":2",2"'-quaterpyridine (Figure 1.15, right) have been reported by Steel *et al.*.[48] In contrast to $[((bipy)_2Ru)_3(HAT)]^{6+}$, the oxidation of the two metal centres in this dinuclear species is a simultaneous process occurring at a potential of +1.24 V (*vs.* SCE). The lack of separation between the metal centred oxidative processes suggests that they are isolated and that the electronic coupling is very weak. It is thought that this weak interaction arises from the lack of rigidity within the complex. Rotation around the 4'-4" bond which joins the two $[Ru(bipy)_3]^{2+}$ subunits can occur which would disrupt the overlap of the π-system across the conjugated bridging ligand.

1.6 Scope of Thesis

The main focus of this project was to develop dinuclear transition metal complexes which would be potentially useful as molecular diodes. When assembled on a metal surface, the conductivity between the molecule and the enclosing electrodes could be measured as a function of the redox chemistry of the complexes. Unfortunately, due to synthetic problems associated with forming a dinuclear osmium complex that was capable of binding to a surface, the formation of such a diode was not realised. However, it was possible to characterise a series of precursor molecules which could lead to the development of molecular rectifiers.

Chapters 3, 4 and 5 in this thesis introduce and discuss both inorganic transition metal complexes (3 and 4), as well as an organic TTF derivative (Chapter 5), which are potentially useful as molecular diodes or precursors thereof. The main electrochemical techniques, used in the aforementioned characterisation were cyclic voltammetry and differential pulse voltammetry. Spectroelectrochemistry was also used to investigate the electronic coupling between redox centres where possible.

The observation of transistor-type behaviour in a series of osmium mononuclear complexes (Figure 1.8) reported by Albrecht *et al.* [29] led to the synthesis of a series of novel ruthenium and osmium mononuclear polypyridyl complexes (by Laura Cleary, Prof. J.G. Vos research group, DCU). Two different linker ligands (L) were developed for these compounds (Figure 1.16) and using ruthenium or osmium as the metal centre, complexes of the type $[(bipy)_2M(L)]^{2+}$ were synthesised.



Pyrphen **Thimphen**

Figure 1.16: *Molecular structures of the pyrphen and thimphen ligands presented in Chapter 3.*

In order to be able to measure conductivity in such molecules, the assembly of monolayers on an electrode surface and characterisation of such monolayers must be carried out. Each of the complexes in Chapter 3 were assembled on either Au or Pt electrodes and the properties of these monolayers were investigated using cyclic voltammetry and surface enhanced Raman scattering spectroscopy (SERS). Monolayers of the osmium complexes on Pt and Au were stable in aqueous electrolyte and given that the associated metal centred oxidation potentials are less positive than that of H_2O, these compounds are ideal candidates for analysis via electrochemical *in situ* STM. Unfortunately due to time constraints characterisation using such a technique was not possible.

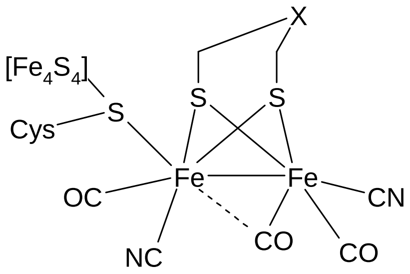
An important feature of a molecular rectifier is the presence of two stable redox centres. Chapters 4 and 5 discuss a range of complexes with two redox centres. A series of dinuclear ruthenium and osmium polypyridyl complexes were synthesised by Dr. Lynda Cassidy (Prof. J.G. Vos research group). The peripheral ligands consist of bipyridyl ligands in each complex. By maintaining this consistency with the peripheral ligands throughout the series, the electrochemical and spectroelectrochemical properties could be investigated as a function of the bridging ligand as well as the coordination geometry of the metal centres. Chapter 4 includes the characterisation of the redox properties of each of these dinuclear species using cyclic voltammetry and differential pulse voltammetry. Considering that the degree of electronic coupling between the metal centres, across the bridging ligand, cannot be determined from electrochemical results alone, the intermetallic interaction was investigated via spectroelectrochemical measurements where the degree of electronic coupling was determined by the presence and analysis of intervalence charge transfer bands in the NIR region of the absorbance spectrum.

In addition to the dinuclear complexes in Chapter 4, an alternative organic compound with two independent redox states was studied (Chapter 5). This compound, based on a TTF core was sourced from the Prof. J.D. Wallis research group in Nottingham Trent University, UK. Following on from reports of molecular conductivity within a TTF based molecule assembled on a Au electrode [26], this molecule was considered potentially useful as a molecular rectifier; mainly due to the appropriate redox chemistry as well as the possibility of binding to a surface through two possible sites on the compound. Two redox states are present within the molecule: the neutral compound undergoes a one-electron oxidation to the monocation radical followed by a subsequent one-electron oxidation to the dication. Assembly of this molecule on the surface of a Au or Pt electrode forming a monolayer that is stable in aqueous electrolyte, in air, would allow for the measurement of conductivity within the molecule.

Unfortunately, due to limited access to the necessary equipment, as well as stability issues with the monolayer in an aerobic environment, the STM studies proved inconclusive. However, the compound was characterised by cyclic voltammetry and differential pulse voltammetry, both in the solution-phase diffusion controlled state and on the surface of a Pt electrode. Spectroelectrochemical studies were also employed to investigate the stability of the redox intermediate monocation radical.

Chapter 6 discusses an isolated topic unrelated to the previous three chapters. As a result of current interest within the research group involving hydrogen production by metal catalysts, Chapter 6 explores a series of homo-nuclear diiron hydrogenase analogues. This work was carried out in collaboration with the Prof. W. Wiegand research group in the University of Jena, Germany. All compounds discussed in this chapter were synthesised in Jena by Ulf-Peter Apfel and all electrochemical analysis was carried out in Dublin City University.

In the quest to find a possible alternative to the current energy source which relies heavily on fossil fuels, there has been increasingly popular interest in the development of analogues of the naturally occurring hydrogenase enzymes.[49, 50, 51] The hydrogenase enzymes, found in biological microorganisms catalyse the reductive generation and oxidative uptake of molecular hydrogen at remarkable rates. A more detailed discussion of the catalytic process involved in the production of H_2 from the hydrogenase enzyme is given in Chapter 6.



[FeFe] Hydrogenase

Figure 1.17: *Molecular structure of the [FeFe] hydrogenase.*

The structure of the [FeFe] hydrogenase enzyme is very similar to the well known organometallic synthetic compounds of the formula $[Fe_2(CO)_6(\mu\text{-}SR)_2]$. A series of hydrogenase analogues bearing one or more diiron active sites, linked by a dithiolate bridge are discussed in Chapter 6. These hexa-carbonyl complexes are compared with several examples of hexacarbonyl diiron complexes from the literature.[52, 53] The main differences between these complexes lie in the nature of the central unit of the dithiolate bridge. For most of the complexes it is noted that the catalytic hydrogenesis proceeds via electron transfer as the first step of the reaction pathway and an ECEC (electrochemical-chemical-electrochemical-chemical) mechanism is often observed.

The electrochemistry of a series of novel analogues of the naturally occurring diiron hydrogenase enzyme was investigated using cyclic voltammetry and differential pulse voltammetry, the results of which are presented in Chapter 6. In the ground state the compounds are in the $Fe^{I}Fe^{I}$ redox state. Their ability to catalytically produce hydrogen from a low valent state using a weak acid (acetic acid) as a proton source is also discussed in Chapter 6. By varying the nature of the coordinated ligands on the diiron centres of these types of hydrogenase analogues, there is an opportunity to tune the catalytic properties of the complexes and explore the mechanistic pathways of hydrogen production.

Chapter 7 outlines the main concluding remarks from each chapter. The proposed future work for each of the different studies in the previous sections is also outlined in Chapter 7. A series of refereed papers have been published on the work presented in this thesis (Appendix A).[54]

1.7 Bibliography

---

1 Balzani, V., Credi, A., Venturi, M., *Molecular Devices and Machines - A Journey into the Nano World*, Wiley-VCH, Weinheim, Germany, **2003**.

2 Lundstrom, M, *Science*, **2003**, *299*, 210.

3 Packan, P. A., *Science*, **1999**, *285*, 2079.

4 Low, P.J., *Dalton Trans*, **2005**, 2821.

5 Tour, J.M., *Acc. Chem. Res.*, **2000**, *33*, 791.

6 http://www.intel.com/products/processor/pentium4/index.htm

7 Heath, J.R., Ratner, M.A., *Physics Today*, **2003**, 43.

8 Feynman, R.P., *Eng. Sci.*, **1960**, *23*, 22.

9 Reed, M.A., Zhou, C., Muller, C.J., Burgin, T.P., Tour, J.M., *Science*, **1997**, *278*, 252.

10 Bumm, L.A., Arnold, J.J., Cygan, M.T., Dunbar, T.D., Burgin, T.P., Jones, L., Allara, D.L., Tour, J.M., Weiss, P.S., *Science*, **1996**, *271*, 1705.

11 Zhitenev, N.B., Meng, H., Bao, Z., *Phys. Rev. Lett.*, **2002**, *88*, 226801-1.

12 Park, J., Pasupathy, A.N., Goldsmith, J.I., Chang, C., Yaish, Y., Petta, J.R., Rinkoshi, M., Sethna, J.P., Abruna, H.D., McEuen, P.L., Ralph, D.C., *Nature*, **2002**, *417*, 722.

13 Kubatkin, S., Danilov, A., Hjort, M., Cornil, J., Bredas, J.L., Stuhr-Hansen, N., Hedegard, P., Bjornholm, T., *Nature*, **2003**, *425*, 698.

---

14 Reed, M.A., *Proc. IEEE*, **1999**, *87*, 652.

15 Zhou, C., Deshpande, M.R., Reed, M.A., Jones, L., Tour, J.M., *Appl. Phys. Lett.*, **1997**, *71*, 611.

16 Metzger, R.M., *Chem. Rev.*, **2003**, *103*, 3803.

17 Aviram, A., Ratner, M.A., *Chem. Phys. Lett.*, **1974**, *29*, 277.

18 Ellenbogen, J.C., Love, J.C., *Proc IEEE*, **2000**, *88*, 386.

19 Ferraris, J., Cowan, D.O., Walatka, V., Perlstein, J.H., *J. Am. Chem. Soc.*, **1973**, *95*, 948.

20 Mizuseki, H., Igarashi, N., Majumder, C., Belosludov, R.V., Farajian, A.A., Kawazoe, Y., *Thin Solid Films*, **2003**, *438*, 235.

21 (a) Metzger, R.M., Panetta, C.A., *Molecular Electronic Devices*, Marcel Dekker, New York, USA, **1987**, (b) Ashwell, G.J., Sage, I., Trundle, C., *Molecular Electronics*, Wiley, New York, USA, **1992**, (c) Tsiperman, E., Becker, J.Y., Khodorkovsky, V., *Tetrahedron Letts.*, **2007**, *48*, 4161.

22 Brady, A.C., Hodder, B., Martin, A.S., Sambles, J.R., Ewels, C.P., Jones, R., Briddon, P.R., Musa, A.M., Panetta, C.A., Mattern, D.L., *J. Mater. Chem.*, **1999**, *9*, 2271.

23 Ho, G., Heath, J.R., Kondratenko, M., Perepichka, D.F., Arseneault, K., Pezolet, M., Bryce, M.R., *Chem. Eur. J.*, **2005**, *11*, 2914.

24 (a) Haiss, W., van Zalinge, H., Higgins, S.J., Bethell, D., Höbenreich, H., Schiffrin, D.J., Nichols, R.J., *J. Am. Chem. Soc.*, **2003**, *125*, 15294, (b) Haiss, W., van Zalinge, H., Höbenreich, H., Bethell, D., Schiffrin, D.J., Higgins, S.J., Nichols, R.J., *Langmuir*, **2004**, *20*, 7694, (c) Haiss, W., Albrecht, T., van

---

Zalinge, H., Higgins, S.J., Bethell, D., Höbenreich, H., Schiffrin, D.J., Nichols, R.J., Kuznetsov, A.M., Zhang, J., Chi, Q., Ulstrup, J., *J. Phys. Chem.*, **2007**, *111*, 6703.

25 Chen, F., He, J., Nuckolls, C., Roberts, T., Klare, J.E., Lindsay, S., *Nano Lett.*, **2005**, *5*, 503.

26 Leary, E., Higgins, S.J., van Zalinge, H., Haiss, W., Nichols, R.J., Nygaard, S., Jeppesen, J.O., Ulstrup, J., *J. Am. Chem. Soc.*, **2008**, *130*, 12204.

27 (a) Carroll, R.L., Gorman, C.B., *Angew. Chem. Int. Ed.*, **2002**, *41*, 4379, (b) Xiao, X., Brune, D., He, J., Lindsay, S., Gorman, C.B., Tao, N., *Chem. Phys.*, **2006**, *326*, 138, (c) Roth, K.M., Dontha, N., Dabke, R.B., Gryko, D.T., Clausen, C., Lindsey, J.S., Bocian, D.F., Kuhr, W.G., *J. Vac. Sci. Tech. B*, **2000**, *18*, 2359.

28 Albrecht, T., Guckian, A., Ulstrup, J., Vos, J.G., *IEEE Transactions on Nanotechnology*, **2005**, *4*, 430.

29 (a) Albrecht, T., Guckian, A., Ulstrup, J., Vos, J.G., *IEEE Transactions on Nanotechnology*, **2005**, *4*, 430, (b) Albrecht, T., Guckian, A., Ulstrup, J., Vos, J.G., *Nano Letters*, **2005**, *5*, 1451, (c) Albrecht, T., Guckian, A., Kuznetsov, A.M., Vos, J.G., Ulstrup, J., *J. Am. Chem. Soc.*, **2006**, 128, 17132, (d) Albrecht, T., Moth-Poulsen, K., Christensen, J.B., Guckian, A., Bjornholm, T., Vos, J.G., Ulstrup, J., *Faraday Discussions*, **2006**, *131*, 265.

30 Forster, R.J., Faulkner, L.R., *J. Am. Chem. Soc*, **1994**, *116*, 5444.

31 Forster, R.J., Figgemeier, E., Lees, A., Hjelm, J., Vos, J.G., *Langmuir*, **2000**, *16*, 7867.

32 Forster, R.J., O'Kelly, J.P., *J. Electrochem. Soc.*, **2001**, *148*, 31.

33 Cassidy, L., *PhD. Thesis*, Dublin City University, Ireland, **2008**.

34 Balzani, V., Juris, A., Venturi, M., Campagna, S., Serroni, S., *Chem. Rev.*, **1996**, *96*, 759.

35 (a) van Diemen, J.H., Hage, R., Haasnoot, J.G., Lempers, H.E.B., Reedijk, J., Vos, J.G., De Cola, L., Barigelletti, F., Balzani, V., *Inorg. Chem.*, **1992**, *31*, 3518, (b) Hage, R., Haasnoot, J.G., Reedijk, J., Wang, R., Vos, J.G., *Inorg. Chem.*, **1991**, *30*, 3263, (c) Hage, R., Haasnoot, J.G., Nieuwenhuis, H.A., Reedijk, J., De Ridder, D.J.A., Vos, J.G., *J. Am. Chem. Soc.*, **1990**, *112*, 9245.

36 D'Alessandro, D.M., Keene, F.R., *Chem. Rev.*, **2006**, *106*, 2270.

37 Forster, R.J., Keyes, T.E., Vos, J.G., *Interfacial Supramolecular Assemblies*, John Wiley & Sons Ltd., Chichester, England, **2003**.

38 Browne, W.R., Hage, R., Vos, J.G., *Coord. Chem. Rev*. **2006**, *250*, 1653.

39 Creutz, C., Taube, H., *J. Am. Chem. Soc.*, **1969**, *91*, 3988.

40 Ward, M.D., *Chem. Soc. Rev.*, **1995**, *24*, 121.

41 Creutz, C., Taube, H., *J. Am. Chem. Soc.*, **1973**, *95*, 1086.

42 Woitellier, S., Launay, J.P., Spangler, C.W., *Inorg. Chem.*, **1989**, *28*, 758.

43 Collin, J.P., Laine, P., Launay, J.P., Sauvagea, J.P., Soura, A., *J. Chem. Soc. Chem. Commun.*, **1993**, 434.

44 (a) Hage, R., Dijkhuis, A.H.J., Haasnoot, J.G., Prins, R., Reedijk, J., Buchanan, B.E., Vos, J.G., *Inorg. Chem.*, **1988**, *27*, 2185, (b) Barigelletti, F., De Cola, L., Balzani, V., Hage, R., Haasnoot, J.G., Reedijk, J., Vos, J.G.,

Inorg. Chem., **1989**, *28*, 4344, (c) Barigelletti, F., De Cola, L., Balzani, V., Hage, R., Haasnoot, J.G., Reedijk, J., Vos, J.G., *Inorg. Chem.*, **1991**, *30*, 641.

45 Richter, M.M., Brewer, K.J., *Inorg. Chem.*, **1993**, *32*, 2827.

46 Fang, Y.Q., Polson, M.I.J., Hanan, G.S., *Inorg. Chem.*, **2003**, *42*, 5.

47 (a) Kirsch-De Mesmaeker, A., Jacquet, L., Masschelein, A., Vanhecke, F., Heremans, K., *Inorg. Chem.*, **1989**, *28*, 2465, (b) D'Alessandro, D.M., Keene, F.R., *Chem. Eur. J.*, **2005**, *11*, 3679.

48 Downard, A.J., Honey, G.E., Phillips, L.F., Steel, P.J., *Inorg. Chem.*, **1991**, *30*, 2259.

49 Tard, C., Liu, X., Ibrahim, S.K., Bruschi, M., De Gioia, L., Davies, S.C., Yang, X., Wang, L., Sawers, G., Pickett, C.J., *Nature*, **2005**, *433*, 610.

50 Gloaguen, F., Rauchfuss, T.B., *Chem. Soc. Rev.*, **2009**, *38*, 100.

51 (a) Liu, T., Darensbourg, M.Y., *J. Am. Chem. Soc.*, **2007**, *129*, 7008, (b) Hu, X., Brunschwig, B.S., Peters, J.C., *J. Am. Chem. Soc.*, **2007**, *129*, 8988, (c) Gloaguen, F., Morvan, D., Capon, J.F., Schollhammer, P., Talarmin, J., *J. Electroanal. Chem.*, **2007**, *603*, 15, (d) Capon, J.F., Gloaguen, F., Schollhammer, P., Talarmin, J., *J. Electroanal. Chem.*, **2004**, *566*, 241, (e) Gloaguen, F., Lawrence, J.D., Rauchfuss, T.B., *J. Am. Chem. Soc.*, **2001**, *123*, 9476, (f) Borg, S.J., Behrsing, T., Best, S.P., Razavet, M., Liu, X., Pickett, C.J., *J. Am. Chem. Soc.*, **2004**, *126*, 16988, (g) Felton, G.A.N., Vannucci, A.K., Chen, J., Lockett, L.T., Okumura, N., Petro, B.J., Zakai, U.I., Evans, D.H., Glass, R.S., Lichtenberger, D.L., *J. Am. Chem. Soc.*, **2007**, *129*, 12521.

52 (a) Chong, D., Georgakaki, I.P., Mejia-Rodriguez, R., Sanabria-Chinchilla, J., Soriaga, M.P., Darensbourg, M.Y., *Dalton Trans.*, **2003**, 4158, (b) Liu, T., Wang, M., Shi, Z., Cui, H., Dong, W., Chen, J., Akermark, B., Sun, L., *Chem.*

Eur. J., **2004**, *10*, 4474, (c) Capon, J.F., Gloaguen, F., Schollhammer, P., Talarmin, J., *J. Electroanal. Chem.*, **2006**, *595*, 47, (d) Hon Cheah, M., Tard, C., Borg, S.J., Liu, X., Ibrahim, S.K., Pickett, C.J., Best, S.P., *J. Am. Chem. Soc.*, **2007**, *129*, 11085.

53 (a) Gloaguen, F., Morvan, D., Capon, J.F., Schollhammer, P., Talarmin, J., *J. Electroanal. Chem.*, **2007**, *603*, 15, (b) Capon, J.F., Gloaguen, F., Schollhammer, P., Talarmin, J., *J. Electroanal. Chem.*, **2004**, *566*, 241, (c) Felton, G.A.N., Vannucci, A.K., Chen, J., Lockett, L.T., Okumura, N., Petro, B.J., Zakai, U.I., Evans, D.H., Glass, R.S., Lichtenberger, D.L., *J. Am. Chem. Soc.*, **2007**, *129*, 12521.

54 (a) Apfel, U.P., Halpin, Y., Gorls, H., Vos, J.G., Schweizer, B., Linti, G., Weigand, W., *Chemistry and Biodiversity*, **2007**, *4*, 2138, (b) Apfel, U.P., Halpin, Y., Gottschaldt, M., Gorls, H., Vos, J.G., Weigand, W., *Eur. J. Inorg. Chem.*, **2008**, 5112, (c) Cassidy, L., Horn, S., Cleary, L., Halpin, Y., Browne, W.R., Vos, J.G., *Dalton Trans.*, **2009**, 3923, (d) Halpin, Y., Cleary, L., Cassidy, L., Horne, S., Dini, D., Browne, W.R., Vos, J.G., *Dalton Trans.*, **2009**, 4146, (e) Apfel, U.P., Kowol, C.R., Halpin, Y., Kloss, F., Kübel, J., Görls, H., Vos, J.G., Keppler, B.K., Morera, E., Lucente, G., Weigand, W., *J. Inorg. Biochem.*, **2009**, *103*, 1236, (f) Halpin, Y., Dini, D., Ahmed, H.M.Y., Cassidy, L., Browne, W.R., Vos, J.G., *Inorg. Chem.*, Accepted Jan **2010**.