Electrochemiluminescence of Ruthenium Polypyridyl Complexes in Solution and Solid-state

Submitted by

Gregory Joseph Barbante

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Department of Chemistry
School of Molecular Sciences
Faculty of Science, Technology and Engineering

La Trobe University, Victoria 3086
Australia

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In quella parte del libro della mia memoria, dinanzi alla quale poco si potrebbe leggere, si trova una rubrica la qual dice: *Incipit Vita Nova.*

*Dante Alighieri*

*1293-1295*
Statement Of Authorship

Except where reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from a thesis submitted for the award of any other degree or diploma.

No other person's work has been used without due acknowledgement in the main text of the thesis.

The thesis has not been submitted for the award of any degree of diploma in any other tertiary institution.

Signature ..............................

Date ..............................
**Abstract**

Electrochemiluminescence (ECL), where light emission is generated electrochemically, is of increasing interest in analytical science. Because the luminophore is typically not consumed in the ECL cycle, an attractive alternative to the conventional solution phase mode of ECL detection, is one where the luminescent reagent is immobilized directly on the working electrode surface. This allows for the development of reagentless sensors suitable for real-world applications where the active form of the luminophore is constantly re-generated *in situ*.

In this project we have explored various approaches to the immobilisation of ECL active ruthenium complexes based on derivatives of 1,10-phenanthroline and 2,2′-bipyridine. An important aspect of the work has been the tailoring of the properties of these compounds in order to facilitate their attachment to surfaces. Furthermore, the extent to which the electrochemical and photophysical properties of such species can be customised for optimal ECL and emission colour is examined.

To this end, the solution phase properties of a series \([\text{Ru}(\text{bpy})_2(L)](\text{PF}_6)_2\) of complexes were evaluated, where \(L\) is a 2,2′-bipyridine derivative. This study showed that emission could be tuned within a substantial wavelength range while keeping the oxidative power of the complex approximately constant. In other words the lowest unoccupied molecular orbital (LUMO) could be tuned independently of the highest occupied molecular orbital (HOMO). These findings were supported with DFT calculations.

The solid state electrochemistry, specifically the attachment in the form of microparticles, of Ru(II) complexes to electrode surfaces is described. In this work redox behaviour, spectroscopic and ECL properties in the solid-state were investigated. The ability to study ECL in the solid-state is crucial to practical applications such as novel analytical and light emitting devices and is valuable as it may provide valuable fundamental insights into radiative charge recombination in solids.
The electrochemical and surface properties of functionalized Ru(II) luminescent materials immobilized by covalent attachment are also described. Stable multilayers of complexes were covalently attached to glassy carbon electrode surfaces by electrografting using diazonium chemistry. Other complexes were attached to carboxylated carbon nanotubes using conventional coupling chemistry, before or after drop coating onto an electrode. The potential of some of these systems for ECL sensing applications was also demonstrated with certain analytes of interest.


Simultaneous control of spectroscopic and electrochemical properties in electrochemiluminescent tris(2,2'-bipyridine)ruthenium(II) derivatives. Analyst, 2011, Gregory J. Barbante, Conor F. Hogan, David J.D. Wilson, Naomi A. Lewcenko, Fredrick M. Pfeffer, Neil W. Barnett, Paul S. Francis
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Per i miei nonni amorevoli Camella, Guisseppi, Jose e Edilo. So che stai cercando dopo di noi. Ti amo così tanto!

Special thanks to uncle Frank who was there for me over the years and has played a key role in developing me into the person I am today.

I would like to explicitly thank these people in my life for their unique friendship and support.

James Robert Cram
Rocky and Erin Bernardi
Nathan O’Brien
Arlen Cram
Eden Cram
Marvs
Nhi Nguyen
Marky Mark
A Journey of a thousand miles begins with one step!

Chinese proverb

If you learn only methods, you'll be tied to your methods, but if you learn principles you can devise your own methods.

Ralph Waldo Emerson

Don't wait until everything is just right. It will never be perfect. There will always be challenges, obstacles and less than perfect conditions. So what. Get started now. With each step you take, you will grow stronger and stronger, more and more skilled, more and more self-confident and more and more successful. ~ Mark Victor Hansen

One must learn by doing the thing, for though you think you know it, you have no certainty until you try.

Aristotle

There ain't no rules around here! We're trying to accomplish something!

Thomas Alva Edison
Abbreviations

2-(dibutylamino) ethanol – (DBAE)
2,2′-bipyridine – (bpy)
Anodic peak potential – (E_{p,a}) – (V, mV)
Charge transfer diffusion coefficient – (D_{CT}) – (cm^2 s^{-1})
Boron doped diamond – (BDD)
Cathodic peak potential – (E_{p,c}) – (A)
Chemically modified electrodes – (CMEs)
Chemiluminescence – (CL)
Chronoamperometry – (CA)
Concentration – (C) – (mol cm^{-3})
Constant phase element – (CPE)
Cyclic Voltammetry – (CV)
Density functional theory – (DFT)
Derivative cyclic voltabsorptometry – (DCVA)
Diffusion coefficient – (D) – (cm^2 s^{-1})
Double layer capacitance – (C_{dl})
Effective fixed site concentration – (C_o) – (mol cm^{-3})
Effective-core potential – (ECP)
Electrochemiluminescence – (ECL)
Electrochemiluminescent quantum yield – (\Phi_{ECL})
Electrode area – (A) – (cm^2)
Electrons transferred – (n)
Faradaic charge – (Q) – (C mol^{-1})
Faraday constant – (F) – (C)
Formal potential – (E°) – (V, mV)
Full width half maximum – (FWHM)
Gas constant – (R) – (J mol⁻¹ K⁻¹)
Glassy Carbon – (GC)
Heterogeneous rate constant – (k°)
Highest occupied molecular orbital – (HOMO)
Indium tin oxide – (ITO)
Limit of Detection – (LOD)
Lowest unoccupied molecular orbital – (LUMO)
Metal centred transition – (MC)
Metal to ligand charge transfer – (MLCT)
Molecular orbital – (MO)
Multi-Wall Carbon Nanotubes – (MWCNT)
Peak current – (iₚ) – (A)
Peak potential difference – (ΔEₚ) – (V, mV)
Photoluminescence – (PL)
Photoluminescent quantum yield – (Φₚ)
Photomultiplier tube – (PMT)
Photon – (hν)
Physical diffusion – (D_{phys})
Polarisable continuum model – (PCM)
Scan rate – (ν) – (V s⁻¹)
Scanning Electron Micrograph – (SEM)
Screen Printed Electrode – (SPE)
Self-assembled monolayers – (SAMs)
Self-exchange rate constant – (k_{SE})
Single Wall Carbon Nanotubes – (SWCNT)
Solution phase resistance – (R_s) – (Ω)
Surface coverage – (Γ) – (mol cm^{-2})
Temperature (Kelvin) – (T) – (K)
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Chapter 1.0 Modified electrodes

The ability to control the chemical properties of the electrode solution interface through modification of the electrode surface has been a revolutionary advance (or series of advances) for the field of electrochemistry and indeed for science in general. Activity in this area has been continuously growing since its establishment over three decades ago.\textsuperscript{1,2} In the 1970s,\textsuperscript{3} interest arose in the modification of electrode surfaces by covalent attachment of monolayers of different species to electrode surfaces. Electrodes modified with thicker polymeric films and inorganic layers were introduced later.\textsuperscript{3} Due to the variety of applications for such systems and the fundamental insights gained from them, chemically modified electrodes (CMEs) continue to be the focus of intense research. The range of applications envisaged for these electrodes is very large and their unique properties are exploited in such diverse areas as chemical sensors, heterogeneous catalysts, biosensors, molecular electronic devices and energy harvesting devices.

An important aspect of CMEs is the manner in which the desired molecules are attached to the substrate in order to impart their properties. A number of reviews discussing the preparation, characterisation, and electrochemical behaviour of CMEs are available.\textsuperscript{3} The desired properties imparted by the immobilized species may be electrochemical, optical, physical or chemical. Modified electrodes can be prepared in a variety of different ways, as discussed in Section 1.1, including irreversible adsorption, self-assembly or covalent attachment of a monolayer, as well as coating the electrode with films of polymers or other materials. One approach which has enjoyed a significant resurgence quite recently is electrochemically assisted attachment using diazonium species.\textsuperscript{4,5}
1.1 Literature survey

Introduction

Electrochemiluminescence (ECL) has been a growing area of research interest since the phenomenon began to be studied in detail in the 1960s. The majority of ECL systems that have been investigated have involved freely diffusing species, with emission originating from a reaction layer near the electrode surface. However, ECL has also been generated in films constrained or chemically attached to the surface of an electrode. The ECL of [Ru(bpy)₃]²⁺ and its derivatives have received considerable attention. [Ru(bpy)₃]²⁺ was the first inorganic complex to show ECL,⁶ it is arguably still the most important in both fundamental studies and analytical applications.⁷ The ECL and chemiluminescence⁸ of [Ru(bpy)₃]²⁺ has been reviewed several times.⁹⁻¹³

Ruthenium polypyridine systems display excited state and their electrochemical properties that make them well suited for ECL. However, the synthetic versatility associated with polypyridine ligands is also crucial to the study of these systems. Key objectives in the design of ECL active molecules include enhanced luminescence, reversible electrochemistry and in some cases suitable layer forming / attachment properties essential for a stable functional sensor. Several notable reviews¹⁴⁻¹⁷ have illustrated the great diversity of 2,2ʹ-bipyridyl type ligands that have been synthesized to enhance and modulate the photophysical and electrochemical properties of such species for a large range of applications in solution phase and solid-state format. It should be noted, however, that the chemical variety in this area is very rich and there are many other types of ligands which have been investigated. For example, phenanthrolines, terpyridines and tertrazolates,¹⁸ to name a few which have been used to synthesize monometallic, bimetallic and dendrimeric metal complexes.
Modified electrodes, based on immobilisation of electrochemically active luminescent species such as [Ru(bpy)$_3$]$^{2+}$ and its derivatives on the electrode surface, have been investigated for a variety of applications including the development of light emitting devices, but the primary interest has been for sensing applications. Solid-state ECL or ECL from immobilised materials in general provides several potential advantages over solution-phase ECL, such as reducing consumption of expensive reagents, simplifying experimental design and enhancing the ECL signal. As a result, a variety of immobilisation strategies for ECL-active materials have been reported. This often involves attachment to or entrapment within a passive matrix. Examples include electrostatic binding to ionomers such as Nafion, layer by layer (LBL), covalent attachment to polymeric species such as polyvinyl pyridine and dispersion within sol-gels and sol-gel composites. Nanomaterials have also been utilised in such films. Modification of electrode surfaces with films of the luminescent moiety alone have also been demonstrated in the form of Langmuir-Blodgett films, self-assembled monolayers, solid deposition and electropolymerisation of vinyl-containing luminescent monomers. The use of diazonium chemistry is, however, relatively unexplored, as is the use of functionalised nanomaterials. They too have become the focus around the development of ECL sensing strategies. Thus, quite a number of different methods and materials have been developed to immobilize [Ru(bpy)$_3$]$^{2+}$ and its derivatives to an electrode substrate.
ECL systems using immobilised reagents

Polymers and composites

Immobilisation within an Inert Matrix

Polymer films play key roles in diverse areas including sophisticated sensing devices. Immobilisation of luminescent species in an inert ion-exchange polymer matrix such as Nafion and Nafion-SiO2 composites represents one of the earliest and simplest strategies.

The first report of immobilisation of \([\text{Ru}(bpy)_3]^{2+}\) on an electrode surface using Nafion was by Rubinstein and Bard. The layers were formed by dip-coating a pyrolytic graphite electrode with the polymer generating a film thickness of ~7 µm and subsequently immersing it in \([\text{Ru}(bpy)_3]^{2+}\) solution to “load” the ionomer. This produced layers of high surface concentration (2-4 x 10^{-6} \text{ mol cm}^{-2}) and moderately good stability. Upon catalytic oxidation of oxalate co-reactant in aqueous electrolyte, ECL was observed from immobilized \([\text{Ru}(bpy)_3]^{2+}\). Generation of ECL in the absence of oxalate or similar co-reactants, by repetitive pulsing between the 1+ and 3+ oxidation states of the complex in solutions containing >20% acetonitrile was also demonstrated. However, emission was short lived due to extensive dissolution of the film in these media.

In subsequent papers, the same authors reported results of more detailed investigations into both the ECL reaction of the film with oxalate and the nature of the catalytic reaction. In 1982, Martin et al. and others also demonstrated the charge transport properties of \([\text{Ru}(bpy)_3]^{2+}\) in Nafion films. In a landmark paper in 1992 Downey and Nieman demonstrated that this system can be used to detect oxalate, alkylamines and NADH in flowing streams with detection limits of 1 µM, 10 nM, and 1 µM, respectively.

The early ECL work by Rubinstein, Bard and others using the cation-
exchange polymer Nafion has been extended by many other researchers.\textsuperscript{25,30-35} Furthermore, it has been recognized that these systems suffer certain drawbacks related to the reagent leaching into electrochemically inaccessible regions of the film\textsuperscript{31} and the long rise time of the luminescence caused by slow diffusion of reactants.\textsuperscript{36} Matrices such as hydrogels (e.g., polyhydroxyethylmethacrylate, polyHEMA) and sol gels are frequently used for the non-covalent immobilisation of biomolecules. Sol gels are transparent porous silica xerogels which have good chemical and thermal stability and high resistance to abrasion.\textsuperscript{36} PolyHEMA is easily obtainable by UV exposure of a monomer mixture\textsuperscript{32} and sol gels are obtained from a one-phase solution. However, both of these matrices can exhibit leaching effects and structural problems. Michael et al.\textsuperscript{32} demonstrated the fabrication of a reagentless sensor by combining two different materials for the non-covalent immobilisation of \([\text{Ru(bpy)}_3]^{2+}\) onto an electrode surface. The complex was immobilised into a sol-gel matrix, which was then subsequently ground to powder and then entrapped into a polyHEMA membrane. The sensor was tested for the detection of tripropyl amine (TPrA) and codeine (Limit of detection, LOD = 20 \(\mu\)M). The ECL activity was constant over a seven-day period and then decreased rapidly after a week of ECL sensing. ECL sensing strategies have also been observed in other sol-gel derived glasses.\textsuperscript{23,36}

Directly synthesizing the polymer-containing Ru reagent at the surface is another mode of immobilisation. Compared to physical entrapment procedures covalent immobilisation has certain advantages. It ensures homogeneous distribution of the reagent within the matrix while preventing reagent leaching, resulting in reduced analysis costs, reproducible analyte responses and extended sensor lifetimes.\textsuperscript{37} Sykora and Meyer\textsuperscript{24} reported the ECL of an amide derivatised sol gel polymer of \([\text{PS-CH}_2\text{CH}_2\text{NHCO-(Ru}^{2+})_{18}]^{36+}\) (Figure 1.0), in the presence of oxalate ions.
Bright orange luminescence was observed during annihilation but the ECL lifetime was short (3-5 min). It is believed that the oxidation of chloride (counter ion) was the cause since it interfered with the potential needed for Ru$^{3+}$ generation. More recently Greenway et al.$^{37}$ demonstrated the covalent attachment of 4,4′-bis[(3-triethoxysilylpropyl)amide]-2,2′-bipyridine]bis(2,2′-bipyridine)ruthenium(II) dichloride onto a silica surface by simple hydrolysis of the triethoxysilane moieties. The organosilicate sol gels were prepared by a mixture of tetramethyloxysilane and the Ru(II) derivative where they were hydrolysed in 0.1 M HCl, followed by base catalysed gelation. They demonstrated the ECL activity of this derivatised sol-gel coated on a glassy
carbon electrode towards the detection of codeine (1 \times 10^{-3} \text{ M}) and report that there was no leeching effects of the luminescent moiety since the Ru(II) complex is covalently attached rather than physically entrapped into a matrix. Forster and Hogan\(^{38}\) developed a new kind of metallopolymers modified solid-state ECL electrode based on [Ru(bpy)\(_2\)(PVP)\(_{10}\)]\(^{2+}\) (bpy denotes 2,2\(^{′}\)-bipyridine; PVP denotes poly(4-vinylpyridine)) (Figure 1.1). The luminescent ruthenium centres are covalently attached to the preformed polymer backbone, where PVP is poly(4-vinylpyridine). Although the system showed outstanding selectivity for oxalate, the broader analytical application was limited by the inhibition of mass transport within the polymer.

\[ \text{Figure 1.1 Electrochemiluminescent redox polymer, [Ru(bpy)\(_2\)(PVP)\(_{10}\)]\(^{2+}\).} \]

(From reference \(^{38}\)).

The ECL and charge transport properties have been observed from electropolymerised films of [Ru(bpy)\(_3\)]\(^{2+}\) derivatives.\(^{22,38}\) They notably have attractive ECL properties but their analytical usefulness has been recognised to be limited due to inhibited mass transport and poor analyte permeation.\(^{38}\) The earliest report of ECL using electropolymerised films was by Abruna and Bard.\(^{39}\) They showed the electro-initiated polymerization of tris(4-vinyl-4\(^{′}\)-methyl-2,2\(^{′}\)-bipyridyl)ruthenium(II) (Ru(v-bpy)\(_3\))\(^{2+}\) onto a platinum electrode surface. The films were prepared by electro-reduction of [Ru(v-bpy)\(_3\)]\(^{2+}\) in an acetonitrile solution onto the platinum electrode surface following the
procedure of Murray and coworkers. They reported films from ~40 Å to ~ 1 μM thick containing Ru(II) centres distributed along hydrocarbon chains originating from vinyl groups and surfaces coverages of 2-6 x 10⁻⁸ mol cm⁻². The surface ECL was short lived (~20 min) with continuous cycling and showed a blue shift (~15-20 nm) relative to both luminescence and solution phase ECL in acetonitrile. In this work the decay mechanism was not fully known, although they found no dissolution of the Ru(II) complex in solution and suggest that it is probably due to some decomposition of the polymer.

Recently, Venkatanarayanan et al. described the aryl oxidative electropolymerisation of [Ru(aphen)₃](PF₆)₂ where aphen denotes 5-amino-1,10-phenanthroline from in an ionic liquid, 1-butyl-2,3-dimethylimidazoliumbis-[(trifluoromethyl)sulfonyl]imide (BDMITFSI). From an analytical sensor perspective, the loading of the luminescent materials into the film is important for an increase in limits of detection. It is suggested that electropolymerisation is considerably faster in ionic liquids and thicker films are produced compared to acetonitrile since the deposition decreases as the film grows. Results showed that the deposition was more than an order of magnitude faster, with more desirable morphological properties than attained in conventional solvents such as anhydrous acetonitrile and sulfuric acid. The charge transport through films grown in ionic liquids was (6.4 ± 1.2) x10⁻⁹ cm² s⁻¹, which is approximately 2 orders of magnitude faster than that found for films deposited from acetonitrile. Thin electropolymerized films from acetonitrile, sulfuric acid and ionic liquid were compared. The generated ECL in the presence of TPrA as a co-reactant were similar in magnitude for sulfuric acid and ionic liquid (BDMITFSI) depositions however, the signal from acetonitrile depositions, were far less intense. This is consistent with the higher D_CT values obtained for the films formed in sulfuric acid and BDMITFSI, compared to the substantially lower D_CT value found for acetonitrile deposition.

Ceramic carbon materials (CCMs) are silica-carbon composite materials that are prepared by mixing carbon powder with sol-gel-derived ceramic binder.
They possess the versatility of the sol-gel properties and good conductivity from the carbon powder. CCMs allow diffusion, solid extraction of analytes and prevent fractures due to their accessible porosity and heterogeneity. This material has shown to be an ideal candidate for screen-printing technology. Bulk ceramic carbon electrodes (CCEs) can be renewed by simple polishing methods.\(^4\)\(^2\) For example, Shi et al.\(^4\)\(^2\) demonstrated the solid phase extraction of dioxopromethazine in urine for ECL sensing (1.0 \(\times\) 10\(^{-9}\) to 1.0 \(\times\) 10\(^{-4}\) mol L\(^{-1}\)) using a modified ceramic electrode, which contained Nafion for increased stability.

Interestingly, the exceptional properties of carbon nanotubes (CNTs) have enabled them to be dispersed into a range of polymer based ECL sensors. Carbon nanotubes possess high electrical conductivity, high chemical stability and high mechanical strength, which make them ideal for promoting electron-transfer reactions. For example, multi-walled and single walled CNTs were dispersed into mesoporous composite films of sol-gel titania and Nafion for the development of highly sensitive and stable ECL sensor incorporating [Ru(bpy)\(_3\)]\(^{2+}\) as the luminescent material.\(^4\)\(^3\) The study showed that the hydrophobic CNT in the titania–Nafion composite films which were coated on a glassy carbon electrode, increased the amount of [Ru(bpy)\(_3\)]\(^{2+}\) immobilized in the ECL sensor due to adsorption of [Ru(bpy)\(_3\)]\(^{2+}\) onto CNT surface. The electrocatalytic activity towards the oxidation of hydrophobic analytes, and the electronic conductivity of the composite films was also enhanced. A linear range of 50 nM to 1 mM was found with a detection limit of 10 nM (S/N = 3) for TPrA. The sensor showed outstanding long-term stability (no signal loss for 4 months with storage).

**Light emitting devices**

As early as the mid 1990s attention was focused on the development of light emitting devices based on electroluminescence\(^4\)\(^4\)-\(^4\)\(^7\) (EL) which is a closely
related phenomenon to ECL. ECL$^{48-52}$ devices have also been proposed and described in the literature. In particular, the area of light emitting electrochemical cells (LEECs) is currently a hot topic.$^8$ In these cases the proposed applications are for emissive panels and displays with low operating voltages.$^9$

One of the most widely used conjugated polymers with attached [Ru(bpy)$_3$]$^{2+}$ used for solid-state ECL devices is 4-methoxy-(2-ethylhexoxy)-2,5-polyphenylenevinylene.$^{53}$ With the intention of developing light emitting devices, Richter et al.$^{53}$ reported the ECL of a Pt electrode dip-coated with a layer (≈100 nm) of MEH-PPV. The electrochemistry of the polymer showed fairly reversible behaviour during repetitive scans. Orange luminescence is observed when the potential is stepped from +0.4 to -2.35 V. Although the ECL lifetime was short lived (1-2 min). A change in colour is observed, red, blue then black when used greater than its ECL lifetime as a light emitting device.

Wang et al.$^{54}$ prepared polymers with a variety of pendant iridium complexes as potential materials in organic-emitting diodes by employing click chemistry. In this contribution they took advantage of the 1,3-dipolar cycloaddition, which has high tolerance to functional groups, high reaction yields, and mild reaction conditions. The polymer used was based on two different co-monomers: styrene and N-vinyl carbozole. The styrene was functionalised with azide units for easy high yielding click reactions. N-vinyl carbozole was used due to its hole-transport properties and its high-energy singlet state. It also prevents self-quenching and aggregation of metal centres by decreasing the concentration of the Ir-complexes along the polymer backbone. The modified polymers gave 71-93% yields and the linker between the iridium complex and the polymer was a 1,4-disubstituted 1,2,3-triazole ring. The attachment of the iridium precursors to a polymer backbone did not affect their optical properties in solution phase and solid-state when compared to their small molecule analogues.
**Electrodes modified with solids**

Direct electrochemistry of solids following immobilisation by abrasive mechanical transfer or other approaches, as developed and used by Scholz, Bond and others, represents a powerful way to investigate the solid-state electrochemical properties of insoluble materials. Scholz and co-workers\textsuperscript{55} used the abrasive mechanical transfer of \([\text{Ru(bpy)}_3(\text{PF}_6)_2]\) on paraffin-impregnated graphite electrodes. In this report the electrochemical behaviour of \([\text{Ru(bpy)}_3(\text{PF}_6)_2]\) microparticles and its spectral changes upon oxidation and reduction were described. A range of osmium bipyridyl complexes have also been abrasively mechanically attached or added to an electrode in a paste form.\textsuperscript{56-58} In these contributions, the redox properties, overall charge transport dynamics, solvent effects and redox induced morphological changes were characterized.

More recently, Buda et al.\textsuperscript{59} used transparent indium tin oxide (ITO) electrodes to study the solid-state ECL properties of a spin coated film of \([\text{Ru(bpy)}_2(\text{LC})]^2_+\), where LC is \((4,4’-(\text{CH}_3(\text{CH}_2)_{12}\text{COO})\text{-bpy})\), a long alkyl chain bipyridine derivative that gives a water-insoluble ruthenium chelate. Cyclic voltammetry in aqueous solution of the Ru-LC film showed two reversible waves with peak potentials at 1.27 V and -0.97 V vs. Ag/AgCl. As shown in Figure 1.2 relatively strong ECL was observed during both oxidation and reduction, using both potential scans and potential step experiments. They also prepared two-electrode solid-state devices with Ga-In printing on the top of Ru-LC films. Furthermore, the authors claimed that they were similar to other \([\text{Ru(bpy)}_3]^2_+\) films that have been prepared previously with currents 3 orders of magnitude lower due to their low electron and hole mobilities.
Bard and co-workers\textsuperscript{18} looked at the solid-state ECL properties of Ru(II) complexes containing substituted tetrazolate ligands in search of novel materials for light emitting solid devices. Similarly, thin films of [Ru(dpp)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2}, (dpp = 4,7-diphenyl-1,10-phananthroline) have been spin coated onto ITO electrodes in search for stable light emitting electrochemical cells. This complex was chosen, as it exhibits photoluminescence quantum yields 6 times higher than [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} and is more robust towards substitution reactions.\textsuperscript{60,61} In this work, Ru(II) phenanthroline based complex showed promise as possible materials for stable single component solid-state light emitting cells.

Until recently, there have been no reports on the electrochemical and ECL properties of luminescent materials as micro-particles deposited onto an electrode surface. In chapter 4 of this thesis we will present novel work related

**Figure 1.2** CV and ECL for a Ru-LC film (~150 nm) spin-coated onto ITO. Scan rate: 200 mVs\textsuperscript{-1}; A~1 cm\textsuperscript{2}; solution: aqueous 0.1 M KClO\textsubscript{4}. (From reference \textsuperscript{59}).
to the deposition of 2,2′-bipyridyl and 1,10-phenanthroline based ruthenium complexes onto glassy carbon (GC), boron doped diamond (BDD) and ITO, demonstrating the voltammetry, spectroelectrochemistry, ECL properties and redox induced morphological changes monitored via in situ electrochemical atomic force microscopy (AFM).

**Monolayer modified electrodes**

The immobilisation of molecules into 2D films by adsorption / self-assembly or covalent deposition onto electrode surfaces is another attractive way to modify an electrode. These techniques are accepted methods for preparing electrodes for a variety of sensing applications. 62 Although there is a large number of monolayer systems described in the literature, the number of papers focusing on ECL sensing strategies are relatively few.

**Adsorbed Monolayers**

Monolayer formation techniques such as self-assembly (SAMs) have been used in electroanalytical chemistry for more than 2 decades. 62 SAMs are monomolecular layers which are spontaneously formed upon immersing a solid substrate into a solution containing amphifunctional molecules or by printing onto the metal surface using a stamp 62,63 (microcontact printing). The most widely studied are alkane thiols, which have an affinity for coinage metals such as gold, silver, platinum and copper via the formation of a metal-thiol bond. 64-66 Gold is the most common substrate used, due to its lack of stable oxide under ambient conditions. Attractive features of SAMs are molecular level control over the modification of the electrode surface, the incorporation of multiple molecular components within a monolayer, the fact that they can be used as a base for layer-upon-layer fabrication that allows the molecular level control to be extended into a 3rd dimension. SAMs have been used to monitor pH, 64 inorganic species 65,66 and organic molecules such as glucose 67 and lactate 68 using both chemical and biological recognition elements. Langmuir Blodgett (LB) and Langmuir Schaefer (LS) techniques can also offer the preparation of functional ultrathin films with a controlled
thickness at a molecular size providing a well-defined molecular orientation which has been seen with a wide range of compounds such as fullerenes, porphyrins, and luminescent materials.

The first report of ECL from monolayer systems was from a monolayer produced using LB techniques was published in 1988. In this work, Zhang and Bard demonstrated ECL for a derivative of tris(2,2'-bipyridine)ruthenium(II) \([\text{Ru(bpy)}_2(\text{bpy-C}_{19})]^2+)\) using oxalate ions as a co-reactant on various electrode substrates such as Pt, Au and In-doped SnO\(_2\). Although oxidative desorption was a significant problem, Bard and others subsequently studied more of these tris(2,2'-bipyridine)ruthenium(II) derivatives in SAMs and LB monolayers, and managed to fine tune the adsorption capabilities on various electrode substrates, improving stability and increasing ECL intensity.

In 1994, Xu and Bard demonstrated the ECL of adsorbed \([\text{Ru(bpy)}_3]^2+)\) on highly oriented pyrolytic graphite (HOPG), platinum and gold. Immersion of a HOPG electrode in a \([\text{Ru(bpy)}_3]^2+)\) solution followed by thorough washing produced a modified electrode as a result of strong adsorption of \([\text{Ru(bpy)}_3]^2+)\) on the graphite surface. They recorded a surface coverage of 2.5 x 10\(^{-10}\) mol cm\(^{-2}\), which is close to that of a closely packed monolayer (~1 x 10\(^{-10}\) mol cm\(^{-2}\)). The ECL emission obtained from TPrA in phosphate buffer decreased rapidly after three potential steps in a single experiment on a HOPG substrate suggesting desorption of the complex.

Apart from \([\text{Ru(bpy)}_3]^2+)\) based long chain alkanethiols, gold sputtered silicon electrodes have been coated with a SAM of lipoic acid. This electrode was then functionalized by covalently attaching a \([\text{Ru(bpy)}_2(\text{bpy'})]_2(\text{PF}_6)_2\) where bpy' is \([4-(4'-methyl-2,2'-bipyridin-4-yl)aminobutyl]\). The modified electrode results demonstrated intense ECL, which increased with increasing the oxidative potential for Ru\(^{3+}\) generation. However, the increased potential stripped the alkane thiol bond from the electrode surface.
Forster’s group\textsuperscript{73} reported the synthesis of a new surface-active Ru(II) complex, [Ru(bpy)\textsubscript{2}(bpySH)]\textsuperscript{2+}, where bpySH is 5,5′-bis(mercaptomethyl)-2,2′-bipyridine. Monolayers of [Ru(bpy)\textsubscript{2}(BpySH)]\textsuperscript{2+} have been formed on micro and macro platinum electrodes by spontaneous adsorption from micromolar solutions of the complex in 50:50 v/v water/acetone. Cyclic voltammograms of the Ru\textsuperscript{2+/3+} monolayers show a reversible redox couple at multiple scan rates, as depicted in Figure 1.3. They reported that adsorption of the complex was irreversible and saturation surface coverage was \((8.1 \pm 0.4) \times 10^{-11} \text{ mol cm}^{-2}\) when the complex concentration in the deposition solution is between 10 µM and 1.0 mM. They also determined that the system demonstrated a weak adsorbate-electrode electronic communication that lead to a relatively low standard heterogeneous electron-transfer rate constant, \(k^\circ\), of \((0.9 \pm 0.1) \times 10^4 \text{ s}^{-1}\), and slower quenching of the excited state by the electrode. Efficient ECL was generated using TPrA as the co-reactant.
Figure 1.3 Cyclic voltammograms for a spontaneously adsorbed monolayer of \([\text{Ru}(bpy)_2(bpySH)]^{2+}\) in 0.1 M TBAPF$_6$ in acetonitrile. Scan rates are (top to bottom) 100, 50, 10, and 5 Vs$^{-1}$. The radius of the platinum microelectrode is 50 µm. The monolayer surface coverage is \(8.1 \times 10^{-11}\) mol cm$^{-2}$. Cathodic currents are up. (From reference 73).

There are drawbacks to using Langmuir-Blodgett films, which are easily washed from the electrode surface. Thiol chemistry can be complicated when it comes to subsequent attachment of redox active molecules. The use of long-chain alkane thiols often results in a sharp decrease in electron transfer rates between the underlining surface and the redox active molecule. In addition, alkanethiols can be desorbed by oxidative and reductive process or from the use of high temperatures due to the weakness of the Au-thiol bond. These issues are a serious disadvantage to any real-world application. In particular for ECL where the level of oxidative stress is typically high, due to the necessarily high positive formal potentials of the luminophores used.
The use of organosilane monolayers for electrochemical applications is limited due to the requirement of an oxide layer to carry out the attachment chemistry. Moreover, the oxide layer may potentially restrict electron transfer to and from the electrode. Several research groups have attached luminescent complexes with potential ECL activity to oxide surfaces. Both the photochemistry and electrochemistry of these complexes have been undertaken, but the ECL properties of such systems have not been reported.

Wang’s group reported the synthesis of an ECL active organosilane monolayer on an ITO electrode which is transparent and readily allows access to the redox properties of the layer. The luminescent material was based on a ruthenium complex with an epoxy modified 1,10-phenanthroline ligand. The Ru(II) species was attached to the substrate via reaction with an aminated silane already immobilised at the electrode surface. The authors also reported the solid-state ECL response of a second type of layer with the same Ru(II) complex. This was formed whereby the complex was attached to gold nanoparticles through use of the epoxy chemistry which were subsequently attached to the electrode by the use of mercaptosilane. Although both layers exhibited strong ECL, the demonstration of the layer stability was restricted to only 10 CV cycles (~ 8 minutes), not enabling an appropriate comparison with other immobilisation methods. Furthermore, there was no report on analytical data such as limits of detection which makes the assessment of the layer’s suitability for ECL based sensing systems difficult.

ECL from Ru(II) bipyridylphosphonic acid complexes adsorbed to mesoporous TiO2 / ITO electrodes has also been observed where the TiO2 films provide an inert, robust support for the ECL active Ru(II) complex. The Ru(II) complex dyes used in this work are adsorbed to the surface through interaction of phosphonic acid moieties located on the 2,2’-bipyridyl ligands with TiO2. ECL was generated upon electrochemical oxidation in the presence of C2O42-. The ECL intensity decreased with time which is believed to be due to the migration of the oxidized form of the complex in the film via desorption and re-adsorption, leading ultimately to depletion of the complex at the electrode.
surface.
Forster’s group\textsuperscript{80} studied the electrochemical, photophysical and electrochemiluminescent properties of \([\text{Ru(bpy)}_2(\text{dcb})]^{2+}\) monolayers formed on optically transparent fluorine doped tin oxide (FTO) electrodes where, dcb is 4,4\textsuperscript{'-}dicarboxy-2,2\textsuperscript{'-}bipyridine. The surface coverages obtained were 2.5 x 10\textsuperscript{-10} mol cm\textsuperscript{-2} consistent with a closely packed monolayer. The monolayers were stable to voltammetric cycling and the Ru\textsuperscript{2+/3+} redox couple was electrochemically reversible. Interestingly, emission was observed despite the proximity of the complex to the electrode surface, which ought to quench the luminescence. This sensor was used to illustrate the ECL sensing capability with amino acids. The ECL and current responses increased linearly with increasing analyte concentration 0.2 < [Proline] < 1 nM while for hydroxyproline the dynamic range is from 1 to 10 nM.

\textit{Electrografted systems}

Unlike electropolymerisation where the monomer cross links under a potential bias and adheres to the electrode surface as it becomes insoluble, in electrografting the material being deposited forms a strong covalent bond to the electrode itself. Thus, it is considered another major approach to modifying electrodes and other surfaces at a monolayer and multilayer level. Carbon and metal surfaces can be modified by other means, namely by electrografting layers relying on the formation of radicals by either oxidation (as in the case for amines\textsuperscript{5,81,82} carboxylates,\textsuperscript{5,81-83} alcohols,\textsuperscript{82} Bunte salts\textsuperscript{4} and Grignard reagents\textsuperscript{84}) or reduction (as in the case of alkenes\textsuperscript{4,81,85} and diazoniums\textsuperscript{4,5,81,86}) of the attachment moiety.

Notably, only alkanethiol and diazonium attachment chemistries have found significant use in electrochemical sensing applications, with the other attachment chemistries mentioned often not being suitable. In the case of organosilanes, as mentioned, the oxide layer is often too insulating for electron transport, making them unsuitable for signal transduction to the electrode. Substrates modified with alkynes require high temperature
Chapter 1 Modified Electrodes and Theoretical Principals

treatment of up to 400 °C, alkene-based chemistries often require photochemical treatment, limiting these methods to molecules stable to high temperatures and radiation, respectively. Low yields have been reported for carboxylate chemistries.

Aryl diazonium salts have by far found the most widespread use compared to any other electrografting material. The electrochemical reduction of phenyl diazonium ions at a carbon electrode to form a covalently modified surface was first reported by Delamar et al. in 1992. Pinson and co-workers were the pioneers on the reductive adsorption of diazonium salts on electrode substrates and was further developed and reviewed by McCreery and co-workers, Downard group, and Gooding.

Electrochemical reduction of diazonium salts is an excellent electrode modification method as it offers irreversible attachment. It has the ability to covalently and stably attach a molecule with spatial control of the deposition on the electrode surface. Surface coverages can range from sub monolayer to values exceeding monolayer coverage.

Aryl diazonium salts are most widely used because they are particularly attractive for sensing applications due to their diverse reactivity towards a range of substrates. These include not only carbon surfaces (glassy carbon, graphite, nanotubes and doped diamond) but metals, silicon, and semiconductors such as indium tin oxide (ITO) and gallium arsenide. Previously, diazonium based films have proven useful in a range of electrochemical applications including biochemical, pH and gas sensing systems. Their utility also extends to applications such as lubrication of low-level electrical contacts, reversible trapping of ionic waste on reactive electrografted surfaces as an alternative to ion-exchange resins, junctions for molecular electronic devices corrosion protection.
In the field of biosensors and biofuel cells, Gooding and co-workers\textsuperscript{107} used SWCNTs adsorbed on glassy carbon electrodes which were modified with aryl diazonium salts generated \textit{in situ} from \textit{para}-aminobenzoic acid and \textit{para}-phenylenediamine. This work was done in effort to improve electron transfer rates between the active site of redox enzymes and electrodes to fully access the catalytic potential of the biocatalyst and achieve high current densities. The use of diazonium salts to attach metal complexes is an important step in the fabrication of the next generation of sensors. In the past, Liu et al.\textsuperscript{120} prepared electrodes by reduction of a carboxylated aryl diazonium salt on gold and GC, and subsequently attached ferrocenemethylamine to the surface, through amide linkage. Building on this concept, Leech and coworkers\textsuperscript{74} demonstrated that this surface derivatisation technique could thus be used to introduce terminal functional groups such as 3-(4-aminophenyl)propionic acid, which was formed from the in-situ generated diazonium salt of the above mentioned compound. From there, \textit{[Os(bpy)\textsubscript{2}(4-AMP)Cl]}(PF\textsubscript{6}) was covalently attached to the carboxylate acid-terminated GC modified electrode. The layer proved stable to pH, temperature, and storage conditions, retaining electroactivity for at least 6 months. Redox layers of osmium may have more advantages over ruthenium and iron due to the favorable redox potential of the Os(II/III) couple and the relative stability of complexes in the Os(III) oxidation state.\textsuperscript{74}

As this method of attachment results in a covalent bond between the electroactive moiety and the electrode, this could ultimately eliminate many of the degradation issues associated with other monolayer chemistries. Diazonium chemistry was used in one case to construct an ECL modified electrode.\textsuperscript{121} The electrode surface was first functionalised with a benzene sulfonic acid monolayer deposited from the diazonium salt and [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} was electrostatically attached to the electrode. The authors reported no loss of signal for a week when stored dry. However, the stability under oxidative stress was not reported.
A “one pot” modification procedure was reported, where the diazonium salt could be synthesized in situ and grafted subsequently in the same solution. Tour and co-workers have demonstrated on numerous occasions the side-wall modification of both SWCNTs and MWCNTs. They used the “one pot” method on SWCNTs and claimed that sidewall functionalization occurred causing the combination of an sp² carbon atom to sp³ hybridization, which was reversible upon heat treatment,¹²² and later showed improved functionalisation using ionic liquids in an inert atmosphere.¹⁰⁵ This group also showed that SWCNTs could be functionalized by grinding them for minutes at room temperature with aryldiazonium salts in the presence of ionic liquids and K₂CO₃.¹²³ The synthesis and electro-deposition of metal complexes containing diazonium moieties have been recently been described by Jousselme et al.,¹²⁴ who reported the deposition of the diazonium salt of bis(2,2''-bipyridyl)(p-amino-4''-phenyl-2,2''-bipyridyl)ruthenium(II), [Ru(bpy)₂(ph-bpy-N₂⁺)][PF₆]₃, as well as its terpyridine analogue, from acetonitrile solution. The objective of this work was to endow the electrode with properties suitable for optoelectronic applications. The system proved stable for an extended period of time with a 20% decrease in peak current (Ip) over 90 min. However, these films were fabricated using an organic solvent, which limits its potential in the field of microfluidics and screen-printed electrodes due to their preparation.

Recently, Piper, Barbante et al.¹²⁵ used an aminated bipyridyl ruthenium complex precursor similar to the diazonium of Jousselme et al. and reported a rapid and facile strategy for depositing stable sensing layers of the ECL active metal complex. The method relied on the in situ formation of the diazonium form of the metal complex shortly before electrochemical attachment to the electrode. The resulting covalently bound layer was demonstrated to be electrochemically stable and suitable for ECL sensing providing a wide linear range and low detection limits for several known ECL co-reactants such as 2-(dibutylamino)ethanol (DBAE) as a model analyte, which can be detected to a level of 10 nM with a linear range between 10⁻⁸ and 10⁻⁴ M. Their intention is to use this technique for the post modification on lab-on-a-chip type sensors for real world sensing applications.
It is important to mention that even though grafting aryl groups onto electrode surfaces via diazonium salts is widely used and can form direct C-C or C-M bonds. The radical intermediate usually leads to formation of multilayer structures ranging from 0.7 – 15 nm in height on the surface. This is not ideal for coupling redox molecules because it can cause an ill-defined electron path.\textsuperscript{126} To date, there are no reports on the immobilisation of luminescent moieties or [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} derivatives for that matter, to an electrode surface via click chemistry where the ECL properties have been explored. Recently, Hamers and Stahl et al.\textsuperscript{127} demonstrated a modular “click”-based functionalization scheme that allows inexpensive conductive diamond samples to serve as an ultra-stable platform for surface-tethered electrochemically active molecules stable out to ~1.3 V vs Ag/AgCl. They have cycled surface-tethered [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} where tpy is: 2,2':6',2\textquoteright"-terpyridyl to this potential more than 1 million times with little or no degradation in propylene carbonate and only slightly reduced stability in water and acetonitrile. Although, these authors did not report any ECL investigations for this immobilized Ru(II) complex.

Gooding’s group\textsuperscript{128} investigated click chemistry using aqueous and organic conditions on Si(100) surfaces immobilizing ferrocene to provide a detailed account of an optimized effort of a novel strategy. Other surface modification based on click cycloaddition chemistry to a surface includes linking electroactive alkynes with azide groups in self-assembled monolayers on Au electrodes.\textsuperscript{129-131} Devadoss et al.,\textsuperscript{126} graphitic carbon electrodes have been primed with azide groups (~ 1 x 10\textsuperscript{-10} mol cm\textsuperscript{-2}) by the addition of iodine azide, which are covalently attached across a double bond on a graphitic edge plane. The azide terminated surface was reacted in the presence of a Cu(I) catalyst with ethynylferrocene and gave a surface confined voltammetric response for ferrocene with a surface coverage less than a monolayer.
Nanomaterial based systems

The use of advanced materials such as carbon fibres, carbon nanotubes, nanoparticles or nanocomposite materials have shown to be useful in chemical, electrocatalysts, biochemical and luminescent sensors, transistors and devices and energy storage. Interest in nanomaterials received a major boost with the discovery of carbon nanotubes in 1991. This section will primarily focus on carbon nanotubes and other nanomaterials relevant to ECL applications.

Carbon nanotubes

Carbon nanotubes, nanoparticles CNTs, exhibit remarkable electronic, mechanical, optical and chemical properties. Different ways have been developed to covalently functionalise SWNTs and MWCNTs involving chemical (ultrasonication with organic materials, coordinatively unsaturated Vaska’s compound, diimide-activated amidation, 1,3-dipolar cyclo additions), photochemical and electrochemical processes. Non-covalent modification of CNTs has also played an important role in intracellular drug delivery or creating water-soluble SWNT polyelectrolytes. Electrochemical modification was previously described although, chemical modification is the most developed and has been used to help ease the purification step of the fabrication process or to improve their performance. For example, this approach has been used for the development of MWCNT-COOH modified screen-printed electrodes which has being commercialised by companies such as DropSens.

Gooding and co-workers prepared high-density, surface-mounted ferrocene using covalent immobilisation of an alcohol substituted ferrocene derivative to a pre-assembled single-walled carbon nanotubes directly attached via an ester bond to silicon(100) surface (SWCNTs-Si). The electrochemical results showed the surface concentration of ferrocenemethanol was $9.26 \times 10^{-8}$ mol cm$^{-2}$. The authors suggest that the high-density of ferrocene methanol on the SWCNTs-Si surface is attributed to the attachment of ferrocenemethanol both
onto the sidewalls as well as the free ends of SWCNTs. Furthermore, their results showed that their surfaces coverages were 500–1000 times greater than the experimentally measured coverage of ferrocene directly attached to flat Si(100) surfaces. The electrochemical data showed reversible one-electron wave of the ferrocene/ferrocenium couple at 490 mV versus Ag+/Ag. The apparent rate constant of electron transfer, $k_{app}$, was 21 s$^{-1}$. Thus, their results suggested that these ferrocene-modified electrodes are excellent candidates for molecular memory devices.

MWCNTs functionalised with COOH groups by immersing nanotubes into a H$_2$SO$_4$ / HNO$_3$ solution and dispersing them onto carbon surfaces has been used to immobilise aminated [Ru(bpy)$_3$]$^{2+}$ derivatives for ECL sensing. Tao et al.$^{142}$ demonstrated the surface characterisation, voltammetric and co-reactant ECL properties of a CNT-[Ru(bpy)$_2$(5-NH$_2$-1,10-phen)]$^{2+}$-modified GC electrode. The Ru$^{2+/3+}$ redox couple in the voltammetric scans shown were difficult to identify, as there were only shoulders visible in the CV for the Ru(II) modified CNT-GC electrode. Even though, there was a significant change in capacitive current and FTIR was used to help confirm the covalent attachment via an amide bond. The amount of Ru(II) on the electrode was calculated as 9.5 x 10$^{-9}$ mol. The ECL emission from TPrA was stable and reproducible under continuous cycling and gave a linear range from 1.0 x 10$^{-6}$ to 2.0 x 10$^{-3}$ mol L$^{-1}$ with a LOD of 8.8 x 10$^{-7}$ mol L$^{-1}$. Li et al.$^{143}$ claimed a LOD of 8.75 pM for their modified CNT electrode with the ruthenium(II) bipyridyl derivative [Ru(bpy)$_2$(AMbpy)]Cl$_2$ where (AMbpy) is 4,4'-aminomethyl-2,2'-bipyridine.

Covalent attachment of an inorganic ruthenium metal complex, [ruthenium(4,4'-dicarboxy-2,2'-bi-pyridine)(2,2'-bipyridyl)$_2$](PF$_6$)$_2$, ([Ru(dcbpy)(bpy)$_2$](PF$_6$)$_2$), to amino functionalized MWCNTs for interconnecting CNTs was described, which could be used in sensing or transistor applications.$^{136}$ The emission and absorption properties were analysed and AFM showed that the nanotubes interconnected in the form of T and Y junctions but the ECL properties were not recorded.
Metal / Silica nanoparticles

An effective immobilisation of $[\text{Ru(bpy)}_3]^{2+}$ on an electrode surface was developed using gold nanoparticles.\textsuperscript{144} This process involved two steps (see Figure 1.4): the electrostatic interactions with citrate-capped gold nanoparticles (AuNPs) of $[\text{Ru(bpy)}_3]\text{Cl}_2$ in aqueous medium, where they were used to fabricate $[\text{Ru(bpy)}_3]^{2+}$–AuNP aggregates (Ru–AuNPs). In the second step, Au–S interactions between as-formed Ru–AuNPs and sulfhydryl groups were used to effectively immobilise the Ru–AuNPs on a sulfhydryl-derivatised ITO electrode surface. The modified ITO electrode showed good stability, and exhibited excellent ECL behaviour.

Zhang and Dong\textsuperscript{145} recently showed that ECL sensors could be developed where $[\text{Ru(bpy)}_3]^{2+}$ was doped in silica nanoparticles. This sensor had a LOD of 2.8 nM for TPrA, which was three orders of magnitude lower than that observed for Nafion based systems. The sensors were relatively stable over
several ECL reaction cycles. The use of these particle based systems, as viable sensors is quite an interesting direction of investigation.

**Theoretical principles**

1.2 *General electrochemical principles*

**Cyclic voltammetry**

Cyclic voltammetry is an electrochemical technique, which applies a triangular potential waveform to a working electrode immersed in an unstirred solution. It is used to examine electrochemical characteristics with respect to redox-induced current response. It can be used to determine qualitative, quantitative, kinetic and mechanistic information about the redox processes. A typical solution phase cyclic voltammogram (CV) is shown in Figure 1.5. The potential is scanned from an initial potential $E_i$ and at the end of its linear sweep, the direction of the potential scan is reversed, usually stopping at the initial potential $E_i$ (or it may commence an additional cycle). Oxidation has occurred during the forward sweep (reaction 1) and reduction on the reverse sweep (reaction 2).

The CV shown in Figure 1.5 is typical for a redox couple that is chemically and electrochemically reversible. The system is said to be chemically reversible if the oxidized and reduced species are both stable and $i_{p,a}$ and $i_{p,c}$ peak magnitudes are identical. If electron transfer is fast compared to the experimental timescale then the system is said to be electrochemically reversible. The peak potentials, $E_{p,c}$ and $E_{p,a}$ are independent of the scan rate, $ν$ (V s$^{-1}$) under this condition and the separation between $E_{p,c}$ and $E_{p,a}$ is 57 mV / n for an n-electron couple however, depends on ohmic effects and slow heterogeneous kinetics. $E^o$ is positioned midway between $E_{p,c}$ and $E_{p,a}$, i.e. $E^o = (E_{p,a} + E_{p,c})/2$. 
A $\rightarrow$ A$^+$ + ne$^-$ (oxidation) \hspace{1cm} (1.)

B$^+$ + ne$^-$ $\rightarrow$ B (reduction) \hspace{1cm} (2.)

\textbf{Figure 1.5} Typical reversible cyclic voltammogram for a solution phase redox couple.

If the electrochemical reaction is reversible and diffusion controlled, then the magnitudes of the peak currents, $i_{p,a}$ and $i_{p,c}$, are given by the Randles-Sevcik equation (1)

$$i_p = 0.4463 n F A C (n F v D / R T)^{1/2}$$

$$i_p = 2.69 \times 10^5 n^{1/2} A^{1/2} v^{1/2} C \text{ at } 25 \degree C$$

where $n$ is the number of electrons transferred, $F$ is the Faraday constant (C mol$^{-1}$), $A$ is the electrode area in cm$^2$, $C$ is the concentration in mol / cm$^3$, $v$ is
the scan rate $V \text{s}^{-1}$, $D$ is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, $R$ is the gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $T$ is the temperature in Kelvin.

**Chronoamperometry**

This is a technique in which the potential of the working electrode is stepped and the resulting Faradaic current is measured as a function of time. The charging current generated by chronoamperometry decays exponentially with time. The Faradaic current decay, due to electron transfer events, can be described by the Cottrell equation (2) for a diffusion controlled system.

$$i = \frac{nFAC\sqrt{D}}{\sqrt{\pi t}} \quad (2)$$

**Electrochemistry of Modified Electrodes**

The framework used to describe solution phase species can also be used to characterize modified electrodes. For example, the theory for the response due to the exhaustive electrolysis of a thin layer of solution (the finite diffusional condition) can readily be extended to electrodes with immobilized thin films or layers, although the electro-active material is not actually diffusing in most cases. Under these conditions, the composition of the layer is in thermodynamic equilibrium with the electrode potential (Nernst condition). This will be observed for all electrochemically reversible reactions at sufficiently slow scan rates during a cyclic voltammetric scan, where all electro-active centres on the electrode surface undergo redox transformations on the time-scale considered. Thus, the peak voltammetric current ($i_p$) for a reversible system under these conditions is given by;
\[ i_p = n^2 \frac{F}{2} \frac{A \Gamma_T V}{4RT} \]  \hspace{1cm} (3)

\[ \Gamma_T \] the total electroactive surface coverage (mol cm\(^2\)); the voltammogram for the surface confined redox couple will ideally also have the following features:

\[ E_{p,c} = E_{p,a} \]  \hspace{1cm} (4)

\[ FWHM = \frac{90}{n} \text{mV (at 25°C)} \]  \hspace{1cm} (5)

\[ \frac{i_{p,c}}{i_{p,a}} = 1 \]  \hspace{1cm} (6)

The FWHM is defined as the full width at half maximum, \( R \) the gas constant and \( T \) the temperature. The other parameters are described in Figures 1.5 and 1.6.
Figure 1.6 Ideal cyclic voltammetric response for a surface confined species. 

When the modified electrode is under conditions of exhaustive oxidation / reduction, the Faradaic charge \( Q \) under the current potential curve from the modified layer gives the quantity \( \Gamma \), \((\text{mol cm}^{-2})\) according to the following expression;

\[
\Gamma = \frac{Q_{\text{a,c}}}{nFA} \tag{7}
\]
In Figure 1.6 the charge measured will use a simple current base line which assumes that any dispersion in the double layer capacitance current that may influence the surface ionic charge from the oxidation / reduction processes is insignificant.

For electrodes with thin films under finite diffusional conditions, a plot of scan rate versus current will be linear. At high scan rates there may be a transition to semi-infinite diffusional type behaviour where the response is governed by the Randles-Sevcik equation and a \( \nu^{1/2} \) dependence on peak current is observed. Thus, in the absence of ohmic effects or slow electron transfer kinetics for thin film conditions, features typically associated with solution phase responses are observed. For example, a \( \Delta E_p \) of 57 / n mV is observed and the peak has a tailed appearance as with the case for a freely diffusing species. The reason for this behaviour is that the means by which charge is transported through the layer, electron hopping, is a diffusion-like process obeying Ficks laws.

Fixed oxidised and reduced locations within the film show a concentration profile that is characterized by the dimensionless parameter \( D_{ct} \tau / d^2 \), where \( D_{ct} \) is the charge transport diffusion coefficient, \( \tau \) is the experimental time-scale, (related to the time for a potential scan to traverse the wave), and \( d \) is the film layer thickness. The surface type behaviour described previously is seen when all electro-active positions inside the film are in equilibrium with the electrode potential. This occurs when \( D_{ct} \tau / d^2 \) is greater than 1 and the thickness of the diffusion layer is approximately that of the overall film. When \( D_{ct} \tau / d^2 \) is less than 1 the thickness of the diffusion layer is less than that of the film and there is a semi-infinite charge diffusion condition. The oxidizing scan direction is swapped before oxidation of reduced sites occurs at the outer boundaries of the film.
1.3 Spectroscopic and photochemical properties of ruthenium polypyridyl Complexes

Background

Ruthenium metal was first reported in 1884 by Karl K Klaus at the University of Tartu in Estonia and was named after the Latin name for Russia, Ruthenia. It is one of the rare noble metals, along with osmium, rhodium, iridium, palladium and platinum. It has rich coordination chemistry with oxidation states ranging from II to VIII, making ruthenium a metal of great interest in the field of inorganic chemistry.

Ruthenium(II) polypyridine complexes have received significant attention since the 1950s, when [Ru(bpy)$_3$]$^{2+}$ luminescence was first reported. In the early 1980s ruthenium(II) complexes gained in popularity due to their potential for applications in energy transformations and electron-transfer processes. The remarkable chemical stability and photophysical properties of Ru(II) complexes have resulted in applications in diverse areas, from solar energy related research to molecular wires, sensors and switches, machines, and also as therapeutic agents.

Ruthenium(II) polypyridyl compounds are typically stable low-spin d$^6$ species which can be oxidized by the removal of metal-localised electron or reduced by the addition of an electron to a ligand $\pi^*$ orbital. The reason for such great interest stems from a unique combination of chemical stability, redox properties, excited-state reactivity, luminescence emission, and excited-state lifetime. Ruthenium polypyridine complexes are good chromophores, feature relatively intense and long-lived luminescence, and can undergo reversible redox processes in both the ground and excited states. The purpose of this
section is to present some general concepts relating to the spectroscopic and 
photochemical properties of Ru(II) polypyrrole complexes which underpin the work presented in the later chapters.

The molecular orbitals of Ru(II) complexes can be represented as shown in Figure 1.7. Each molecular orbital (MO) is labeled as either metal (M) or ligand (L) according its predominant localization. The low energy σ-bonding MO's would result from a combination of metal and ligand orbitals with suitable symmetry which are therefore labeled as (L). This is due to most of the contributions coming from the ligand orbitals. When a transition metal complex is in its ground state configuration with its common oxidation state the \( \sigma_L \) and \( \pi_L \) orbitals are completely filled while the \( \pi_M \) orbitals are either partially or completely filled. As for the rest of the orbitals in the molecular orbital diagram, they are usually empty. The ordering of the orbitals described in Figure 1.7 may vary depending on the type of ligand used and the oxidation state of the metal centre. In the case of \([\text{Ru(bpy)}_3]^{2+}\) the \( \pi^*_L \) orbital is lower in energy than the \( \sigma^*_M \) orbital. The various electronic transitions for metal complexes such as those of ruthenium can be described based on the localization of the MO's available. There are various transitions which are possible, MC: metal centered (d-d transitions), LC: ligand centered (intraligand transitions). The other transitions between MO's of different localization cause the displacement of the electronic charge from the ligands to the metal or vice versa. These charge-transfer (CT) transitions are: MLCT (metal to ligand charge transfer) and LMCT (ligand to metal charge transfer). The relative energy of these levels may vary, depending on the nature of the interacting ligands. In ruthenium complexes such as \([\text{Ru(bpy)}_3]^{2+}\), the highest occupied molecular orbital (HOMO) is most commonly \( t_{2g} \) and the lowest unoccupied molecular orbital (LUMO) is the ligand \( \pi^* \) orbital.
Figure 1.7 Schematic energy-level diagram for an octahedral transition metal complex. (From references $^{158}$).

The absorbance spectrum of $\text{[Ru(bpy)$_3$]}^{2+}$ is shown in Figure 1.8. Each band in the spectrum can be appropriately assigned. The two bands at 240 and 452 nm are due to spin allowed MLCT $d \rightarrow \pi^*$ transitions. Shoulder peaks at 322 and 344 have been assigned to MC transitions. This is the lowest excited state for the complex. The intense band at 285 has been assigned to spin-allowed LC $\pi \rightarrow \pi^*$ transitions by comparison to a spectrum from a protonated bipyridine.$^{160}$ A peak at 185 nm (not shown in this Figure) is also present and it represents a spin-allowed LC $\pi \rightarrow \pi^*$ transition. Studies in ethanol:methanol glass at 77 K have demonstrated a shoulder peak at ~550 nm ($\varepsilon \sim 600$ M$^{-1}$ cm$^{-1}$) which is thought to be due to spin forbidden MLCT transition(s).$^{161}$

Even though Ru is regarded as a heavy atom, it is reasonable to assign the electronic transitions of $\text{[Ru(bpy)$_3$]}^{2+}$ as being due to “singlet” or “triplet” states.$^{159}$ A $\leq$ 10% singlet character has been established for the lowest lying excited state of $\text{[Ru(bpy)$_3$]}^{2+}$. $^{159}$
Figure 1.8 Electronic absorption spectrum of 10 µM [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN.

Emission properties

The important photophysical processes of [Ru(bpy)$_3$]$^{2+}$ are described in Figure 1.9. Its emission is dominated by an energy relaxation from the lower triplet states (emission quantum yield ($\Phi$) of 0.06). The observed lifetime ($\tau$) is given by equation (10) where $k_r$, $k_{nr}$, and $k_{dd}$ are the rate constants for the radioactive decay, non-radioactive decay, and thermal population of the nearby metal-centered ($^3$MC) state. The relationship between $\Phi$ and $k_r$ is given by equation (11) where $\eta_{isc}$ is the efficiency of intersystem crossing. Thus, measuring the lifetime and emission quantum yield, $k_r$ can easily be obtained.

\[
\frac{1}{\tau} = k_r + k_{nr} + k_{dd} \quad (10)
\]
\[
\Phi = \eta_{isc} \cdot k_r \cdot \tau \quad (11)
\]
Fast intersystem crossing from the singlet (^1MLCT) to triplet (^3MLCT) state (normally dipole forbidden) occurs with unit efficiency due to spin-orbit coupling. This unpairing of electrons is possible because the momentum needed to convert a singlet state into a triplet state is achieved due to the orbital contribution to the total spin momentum in heavy metals such as ruthenium. This then permits emission as phosphorescence from the triplet state to the ground state (k_r) or radiationless deactivation to the ground state (k_{nr}). An alternative deactivation is population of the ^3MC (metal centered) state. If this occurs the electron occupies an anti-bonding, metal-based orbital, resulting in distortion of the metal ligand axes and weakening the Ru-N bonds. This may cause photodecomposition of the complex, which manifests itself as ligand loss followed by co-ordination of a substitute ligand, often solvent or electrolyte.

Figure 1.9 Photophysical processes of [Ru(bpy)_3]^{2+} showing the formation the MLCT excited state and its deactivation pathways. (From reference ^162).
Redox behaviour of ruthenium complexes

The inter-relationships between the ground and excited states are best represented in the form of a Latimer-type diagram, as shown in Figure 1.10, for the MLCT excited state of [Ru(bpy)₃]²⁺. The spectroscopic and redox orbitals are the same with the \( \pi^* \) being the acceptor orbitals for both the reduction process and the charge transfer transition.

![Latimer-type diagram](Figure 1.10)

**Figure 1.10** Latimer-type diagram illustrating the energy and electron transfer processes of \([\text{Ru(bpy)}_3]^{2+}\). **[Ru(bpy)_3]^{2+}** indicates higher-energy spin-allowed excited states and *\([\text{Ru(bpy)}_3]^{2+}\) indicates the lowest spin-forbidden excited state (³MLCT). Reported potentials are in organic solution vs. ferrocene. (Adapted from reference ¹⁵⁹).
To help illustrate the relationship between the spectroscopic and redox properties shown in the Latimer-type diagram, Figure 1.11 shows the cyclic voltammogram (CV) of [Ru(bpy)_3]^{2+}. A reversible redox wave at 0.88 V vs. ferrocene (All redox potentials in this thesis are reported relative to the ferrocenium / ferrocene couple unless otherwise stated) for the Ru^{2+/3+} couple where an electron is abstracted from the metal centered orbital (d_\pi). There are also three closely spaced ligand-localized reductions at -1.74 V (Ru^{2+/+}), -1.93 V (Ru^{+/0}) and -2.17 V (Ru^{0/-1}) where an electron is added to the \pi^* orbital on each ligand.\textsuperscript{148,149} In the 3MLCT excited state, (formally [Ru^{III}(bpy)_{2}(bpy^{*\cdots})]^{2+}), the complex is both a stronger oxidant and reductant compared with the ground state. Thus, the excited state redox potentials can, to a first approximation be determined from the excited state energy (E^{0-0}) and the ground state potentials (eqs. 4 and 5).\textsuperscript{148,149} As shown in Figure 1.10, for [Ru(bpy)_3]^{2+}, the excited state energy is 2.12 eV (from the luminescence maximum), therefore the redox potentials for oxidation and reduction of the 3MLCT state are calculated to -1.24 and 0.38 V respectively.

\begin{align}
E^o(Ru^{3+/2+}) &= E^o(Ru^{3+/2+}) - E^{0-0} \\
E^o(Ru^{2+/+}) &= E^o(Ru^{2+/+}) + E^{0-0}
\end{align}
1.4 Fundamentals of electrochemiluminescence (ECL)

Introduction

Electrochemiluminescence or electro-generated chemiluminescence (ECL) is a phenomenon in which certain species emit light following heterogeneous electron-transfer reactions or more simply they partake in a chemiluminescence reaction having been electrochemically generated. The earliest report of the observation of light during electrolysis was in 1914, when Bancroft\textsuperscript{163} reported luminescence on electrolyzing halides at a mercury electrode. From there, in 1927, Dufford et al.\textsuperscript{164} demonstrated light emission from the electrolysis of Grignard compounds in anhydrous ether on application with high voltages of 500 to 1500 V. The name galvano-luminescence was suggested for this phenomenon after Harvey\textsuperscript{165} observed chemiluminescence of luminol in 1929 by electrolysis in aqueous alkaline solution at the anode with a potential of \(\sim 2.8\) V. In the mid 1960's, Chandross\textsuperscript{166} studied chemiluminescence of radical ions of polyaromatic hydrocarbons. This drove other
research groups such as Hercules,\textsuperscript{166} and others\textsuperscript{167,168} to publish papers describing the electrochemical generation of radical ion species with light emission.

ECL has been extensively investigated and there are many published works on the fundamentals and applications of ECL.\textsuperscript{13} There are several features which make ECL attractive for sensing applications, including the absence of a background optical signal, spatial and temporal control over the luminescence reaction, compatibility with solution-phase and thin-film formats, and opportunities to enhance intensity with nanomaterials such as metallic nanoparticles and nanotubes.\textsuperscript{9} These features allow ECL to be used as the basis for highly sensitive and selective analytical methods where a coreactant is the analyte or the electrochemiluminophore itself is used as a label on biological molecules for antibody or nucleic acid based assays.\textsuperscript{9,169,170} This also extends to the detection of pharmaceuticals, food and water testing, biological warfare agents\textsuperscript{169,171} and more recently, light emitting devices.\textsuperscript{59}

**General principles**

**ECL reactions of ruthenium polypyridyl complexes**

By far the greatest number of investigations in ECL have concentrated on ruthenium chelates, particularly \([\text{Ru(bpy)}_3]^{2+}\) and its derivatives. As mentioned the \([\text{Ru(bpy)}_3]^{2+}\) complex is commonly used as the basis of comparative studies of other ECL active species. There are two dominant pathways to ECL emission, which is the annihilation and co-reactant pathway. Each of these mechanisms offers different advantages and relies on different pathways to generate the electronically excited state that ultimately emits light.
General overview of annihilation ECL

In the annihilation pathway, two species are electrochemically generated; for instance, oxidised and reduced forms of the luminophore are produced by a potential step or sweep. These species then interact to produce both a ground state and an electronically excited state, which then relaxes by emission. Although the chemiluminescence of the chemically oxidized \((3+)\) species had previously been reported,\(^{175}\) the ECL emission of metal chelate systems such as \([\text{Ru(bpy)}_3]^{2+}\) in CH\(_3\)CN via an annihilation reaction (see reactions 1-4) was first reported in 1972.\(^9\)

The authors showed that on cycling the potential of a Pt electrode between the first oxidation and reduction potentials of a solution of the complex dissolved in CH\(_3\)CN, the same characteristic emission could be produced. The enthalpy of the charge transfer reaction between these two species was calculated from the peak potentials and it was noted that the energy of the reaction was quite sufficient to populate the excited triplet state of the complex.\(^9\)

The main advantages of the annihilation pathway are that it requires only the ECL species, solvent, and supporting electrolyte to generate the light reaction. However, the potential window of water is often not sufficiently wide to allow the luminophore to be both oxidized and reduced, making it necessary to use organic solvents such as CH\(_3\)CN and N,N-dimethylformamide (DMF).\(^9\)

**Annihilation System:**

\[
\begin{align*}
1 & \quad [\text{Ru(bpy)}_3]^{2+} \rightarrow [\text{Ru(bpy)}_3]^{3+} + e^- \\
2 & \quad [\text{Ru(bpy)}_3]^{2+} + e^- \rightarrow [\text{Ru(bpy)}_3]^+ \\
3 & \quad [\text{Ru(bpy)}_3]^+ + [\text{Ru(bpy)}_3]^{3+} \rightarrow [\text{Ru(bpy)}_3]^{2+} + [\text{Ru(bpy)}_3]^{2+} \\
4 & \quad [\text{Ru(bpy)}_3]^{2+} \rightarrow [\text{Ru(bpy)}_3]^{2+} + h\nu
\end{align*}
\]

Potential step methods such as chronoamperometry are often used to characterize ECL processes, as this is a convenient technique to perform annihilation.
experiments. The generation of ECL via this method, has been used to determine the ECL efficiency ($\Phi_{\text{ECL}}$), and equation 10 is used.

ECL emission studies are important to help gain a thorough understanding of the properties of these complexes.

**General overview of co-reactant ECL**

By adding certain species, called co-reactants into a solution containing luminophore species, ECL can be generated with a single potential step or by potential scanning at an electrode. Depending on the applied potential, both the co-reactant and the luminophore can be first oxidized or reduced at the electrode to form radicals, and intermediates formed from the co-reactant then decompose to produce a powerful reducing or oxidizing agent that reacts with the oxidized or reduced luminophore to produce the excited states that emit light. A key advantage of the co-reactant approach is that it facilitates ECL generation in aqueous solution, opening up a wide range of diagnostic applications including assays for molecules of biological relevance. While there are several molecules that exhibit ECL, [Ru(bpy)$_3$]$^{2+}$ and its analogues have received most of the attention due their excellent chemical, electrochemical, and photochemical properties even in aqueous media and in the presence of oxygen.$^9$

In 1977 Bards group$^{176}$ reported the first co-reactant ECL with oxalate ion, C$_2$O$_4^{2-}$, CH$_3$CN. In 1987, Noffsinger and Danielson$^{177}$ first reported the chemiluminescence of [Ru(bpy)$_3$]$^{2+}$ with aliphatic amines. Leland and Powell$^{178}$ were the first to report the ECL of [Ru(bpy)$_3$]$^{2+}$ with tri-propylamine (TPrA). Since these early developments, these analytes and others such as peroxidisulphate (reductive-oxidative co-reactant ECL) have become the most important co-reactants for ECL applications. For the oxalate system as for amines, the luminophore, [Ru(bpy)$_3$]$^{2+}$ operates in the oxidative-reduction mode with the co-reactant (reactions. 5-10). First, [Ru(bpy)$_3$]$^{2+}$ is oxidized at the electrode to the [Ru(bpy)$_3$]$^{3+}$ cation. This species can then oxidize the oxalate (C$_2$O$_4^{2-}$) in the diffusion layer at the electrode surface to form a oxalate radical ion (C$_2$O$_4^{-}$) which irreversibly decomposes to a highly reducing radical ion
(CO$_2^-$) and carbon dioxide. This CO$_2^-$ radical can either reduce the [Ru(bpy)$_3$]$^{3+}$ cation back to the parent complex in the excited state (reaction 8); or reduces [Ru(bpy)$_3$]$^{2+}$ to form [Ru(bpy)$_3$]$^{+}$, which reacts with [Ru(bpy)$_3$]$^{3+}$ (reaction 9) to generate the excited state [Ru(bpy)$_3$]$^{2+*}$, which emits light with $\lambda_{\text{max}} \sim 620$ nm.

**Oxalate System**

(5) Ru(bpy)$_3^{2+}$ $\rightarrow$ Ru(bpy)$_3^{3+}$ + e$^-$
(6) Ru(bpy)$_3^{3+}$ + C$_2$O$_4^{2-}$ $\rightarrow$ Ru(bpy)$_3^{2+}$ + C$_2$O$_4^{-}$
(7) C$_2$O$_4^{-}$ $\rightarrow$ CO$_2^{-}$ + CO$_2$
(8) Ru(bpy)$_3^{3+}$ + CO$_2^{-}$ $\rightarrow$ Ru(bpy)$_3^{2+*}$ + CO$_2$ (excitation pathway: 1)
(9) Ru(bpy)$_3^{2+}$ + CO$_2^{-}$ $\rightarrow$ Ru(bpy)$_3^{+}$ + CO$_2$ (Alternative pathway: 2)
(10) Ru(bpy)$_3^{2+*}$ $\rightarrow$ Ru(bpy)$_3^{2+}$ + h$\nu$

[Ru(bpy)$_3$]$^{2+}$ produces ECL with amines, especially tertiary amines such as tripropyl amine (TPrA). This is of particular interest due to the prevalence of the amine moiety in a large range of pharmaceutical compounds. The mechanism for the reaction of TPrA, with [Ru(bpy)$_3$]$^{3+}$ to produce its excited state is thought to be as follows:

**Tri-propyl amine System**

(11) [Ru(bpy)$_3$]$^{2+}$ $\rightarrow$ e$^-$ + [Ru(bpy)$_3$]$^{3+}$
(12) NPr$_3$ $\rightarrow$ Pr$_3$N$^+$
(13) Pr$_3$N$^+$ $\rightarrow$ Pr$_2$NCH$_2$Et + H$^+$
(14) [Ru(bpy)$_3$]$^{3+}$ + Pr$_2$NCH$_2$Et
(15) [Ru(bpy)$_3$]$^{2+*}$ + Pr$_2$N$^+$=CCH$_2$
(16) [Ru(bpy)$_3$]$^{2+*}$ $\rightarrow$ [Ru(bpy)$_3$]$^{2+}$ + h$\nu$

(where NPr$_3$ = TPrA, Pr = CH$_3$CH$_2$CH$_3^-$ and Et = CH$_2$CH$_2^-$)
There are other pathways for this system which have been discussed in great detail by Zu and Bard. Thus, TPrA can be oxidized either directly at the electrode or by [Ru(bpy)_3]^{3+} depending on the electrode material, applied potential and buffer additives. Studies have shown that at Pt and Au electrodes, the formation of surface oxides tend to inhibit direct oxidation whereas at GC electrodes the heterogeneous oxidation of TPrA is not blocked. The hydrophobicity of the electrode surface or in the presence of Triton X-100 and other nonionic surfactants have shown to improve the ECL emission. Finally, the ECL intensity depends on the solution pH with dramatic increases at ~pH > 5.5 and a maximum value at pH 7.5. This is particularly important in analytical applications because many analytes are of biochemical interest and their solutions, in vivo and for handling, are buffered. It is commonly found that there is an optimum pH level related to the pK_a of the co-reactant. However, pH values > 9 are undesirable as this often gives rise to competing reactions that decrease ECL emission or increase background.

**Kinetic requirements of ECL reactions**

According to the definition of ECL, the precursors participating in the homogeneous electron transfer leading to the light emitting excited state are generated at electrodes through heterogeneous electron transfer reactions. In organic ECL systems these precursors are often in the form of oxidised and reduced radical ions, whereas in inorganic systems they are typically the reduced and/or oxidised forms of the parent complex. The oxidised ion presents a “hole” in the HOMO, which enhances its oxidative properties. On the other hand, the reduced ion possesses an electron in its LUMO, which enhances its reducing capacity. In all cases the homogeneous reaction between these precursors is characterised by very fast (~10^{10} M^{-1}s^{-1}) very energetic (typically 2-4 eV) electron transfer.

In Figure 1.12 the two possible paths for the homogeneous reaction between the two electrogenerated precursors are illustrated. When the system follows the pathway
most favoured by thermodynamic predictions (B), the electron transfer takes place from the LUMO of the reduced radical to the HOMO (MO) of the oxidized one. Since this pathway is mostly favoured thermodynamically, if electron transfer is sufficiently rapid, this means that a large amount of energy would have to be dissipated over a very short time scale in vibrational modes. Here a kinetic manifestation of the Frank-Condon principle comes into play, and the path to electronically excited products becomes more favoured, because its demand for mechanical accommodation is not nearly so great.\textsuperscript{146} The luminescent pathway involves electron transfer between the LUMO of the reduced radical and the slightly less energetic LUMO of the oxidized radical (A). In this case only a small amount of energy (\textasciitilde 0.2 eV) needs to be dissipated in mechanical modes, this satisfies the Frank-Condon principle and leads to the formation of an excited state product, which emits light on relaxation, forming the stable ground state products.\textsuperscript{146}

The requirements for reactions leading to ECL have also been explained within the framework of the Marcus theory of electron transfer which predicts that for an electron transfer reaction, the rate constant \( k_{\text{et}} \) depends on the standard free energy of reaction \( \Delta G^\circ \), according to expression (6);

\[
RT \frac{d \ln(k_{\text{et}})}{d(-\Delta G^\circ)} = \frac{1}{2} \ln\left[ 1 + \frac{\Delta G^\circ}{\lambda} \right]
\]  

(6)

where \( \lambda \) is the re-organisation energy. Thus for low to moderate \( -\Delta G^\circ \) values an increase in \( \ln(k_{\text{et}}) \) with increasing \( \Delta G^\circ \) is expected. A maximum value of \( k_{\text{et}} \) can be obtained for \( \Delta G^\circ = -\lambda \), and for reactions in which \( |\Delta G^\circ| > \lambda \), an inverse behaviour is observed in which the rate decreases with increasing driving force. Thus, the lack of significant direct reaction to the ground state for homogeneous reactions in ECL systems is rationalised as an example of slow electron transfers to be expected for highly exergonic reactions in the inverted region of the Marcus theory.\textsuperscript{13} Therefore the kinetic electron transfer path for the excited state is preferred rather than the thermodynamically favoured ground state.
Figure 1.12 Molecular orbital diagram showing two alternative pathways for electron transfer between oxidised and reduced precursors $R^-$ and $R^+$. (A) Formation of an excited state and (B) direct production of ground state products. (Adapted from reference 146).
An ECL annihilation reaction (see reaction 3 below on page 40) between oxidised [Ru(bpy)$_3$]$^{3+}$ and reduced [Ru(bpy)$_3$]$^+$ species requires a high free energy of reaction. This driving force constitutes the energy available for electronically exciting the product to its excited state. The free energy available from the annihilation reaction is given by equation 7.

$$-\Delta G = E^\circ(Ru^{2+}/Ru^{3+}) - E^\circ(Ru^{2+}/Ru^+)$$  \hspace{1cm} (7)

These values can be calculated from the peak potentials of Ru$^{2+}/Ru^{3+}$ and Ru$^{2+}/(Ru)^+$ couples in the CV used to generate the emission. If the $-\Delta G$ from the redox potentials (in eV) is larger than the energy calculated from the luminescence emission energy (converted from nm to eV) then it is said that the energy requirement for population of the excited state is satisfied.$^{174}$

For the majority of ECL systems the light emission intensity is considered by three main factors. (1) The rate of the annihilation reaction, N (mol s$^{-1}$); (2) the efficiency production of the excited state ($\Phi_{ES}$); (3) efficiency of light emission from the excited state ($\Phi_p$). The expression is:

$$I_{ECL} = \Phi_p\Phi_{ES}N$$  \hspace{1cm} (8)

where $I_{ECL}$ is intensity in einsteins s$^{-1}$. The product of $\Phi_p$ and $\Phi_{ES}$ is termed the overall ECL efficiency ($\Phi_{ECL}$) and is defined as the number of photons emitted per redox event. The expression below gives the ECL efficiency ($\Phi_{ECL}$)

$$\Phi_{ECL} = \frac{\int_0^\infty Idt}{\int_{i_c}^\infty i_{c,a}dt} = \frac{\int_0^\infty Idt}{\int_{i_c}^\infty i_{c,a}dt}$$  \hspace{1cm} (9)

In equation 9, $I$ represents emission intensity in einsteins per second intergrated
over a period of time 0 to t’, and \( i_{c,a} \) represents the current integrated over the same period from either the total cathodic or anodic charge. The direct measurement of this value is often difficult, so the ECL efficiencies are often determined by comparison with the annihilation ECL emission, (see annihilation ECL, section 1.42), of a known standard, usually \([Ru(bpy)_3]^{2+}\) which is known to have a 5% efficiency.\(^{149}\) The efficiency is calculated using the equation below:

\[
\Phi_{ECL} = \Phi_{ECL}^* \frac{I}{Q} \frac{Q^o}{\Phi_{ECL}}
\]

In equation 10, \( I \) and \( I^o \) are the integrated light responses for the sample complex and standard respectively, and \( Q_f \) and \( Q^o_f \) are the faradaic charges passed for the sample and standard. Furthermore, \( \Phi_{ECL} \) strictly approaches the luminescence efficiency \( \Phi_p \), but it is generally found to be considerably lower. This can be attributed to at least two reasons\(^9\); (i) The instability of the oxidation and/or reduction products which participate in the reaction leading to the excited state. (ii) The competition between the reaction leading to the excited state product and that leading to the ground state product.

The measurement of \( \Phi_{ECL} \) in co-reactant systems is nearly impossible due to the complexity of co-reactant mechanisms caused by irreversibility and the high concentration of co-reactants in solution compared to luminophore. However, if the same conditions are used for the luminophore of interest and for the standard \(([Ru(bpy)_3]^{2+})\), relative efficiencies can be inferred.
1.5 Conclusion

Overall, a range of modified electrode systems and techniques have been examined to demonstrate the complexity and challenges faced in the design and improvement in sensors for today’s technological demand on high throughput, simplicity, low cost and sensitivity. Thus, the aim of this study is to utilize and reflect on recent improvements in the field of modern electrochemistry and organometallic synthesis to develop immobilized luminescent sensors utilizing electrochemiluminescence.
References

Chapter 1 Modified Electrodes and Theoretical Principals

Chapter 2 Synthesis of polypyridyl ligands and organometallic complexes

2.0 Introduction

Since the first synthesis of 2,2′-bipyridine 110 years ago by Fritz Blau\(^1\) there have been dramatic improvements in the synthesis of the compound and its analogues. The area has also been the subject of numerous reviews since the mid 1980s.\(^2\) Figure 2.0 summarises the main synthetic strategies used to form 2,2′-bipyridine.

![Synthetic strategies for formation of 2,2′-bipyridine](image)

**Figure 2.0** Synthetic strategies for formation of 2,2′-bipyridine. (Adapted from reference 2).

The synthesis of symmetrical, unsymmetrical (mono- / di-substituted), functionalized bipyridines and bis-bipyridines is relatively facile. The most
widely used method is the metal-catalysed (Ni and Pd/C) coupling of pyridine, substituted pyridines and 2-halo-pyridines to form the desired 2,2′-bipyridine. Directed cross coupling procedures such as Stille-type\textsuperscript{3,4} and Neigishi-type\textsuperscript{5,6} have been described which provide high yielding syntheses of symmetrically as well as unsymmetrically substituted and functionalised bipyridines. The Kröhnk procedure is useful and has been used to synthesis 4-substituted bipyridines formed from simpler entities.\textsuperscript{7-12} Condensation between aldehydes and amines by a ring-assembly method has also given rise to bipyridines.\textsuperscript{13} Alternatively, 4,4′-dimethyl-2,2′-bipyridine has been used to introduce side chains to 2,2′-bipyrene.\textsuperscript{14-18} The advances in this field have had a bearing on other, structurally similar classes of ligand, such as 1,10-phenanthrolines,\textsuperscript{19-22} terpyridines,\textsuperscript{10,11,23} tetrazolates\textsuperscript{24} bipyrazines,\textsuperscript{25} phenyl pyridines\textsuperscript{26} and many others (Figure 2.1). The importance of these ligands will be described later.
Figure 2.1 Ligands which have been used in metal complexes employed in various applications. bpy: 2,2′-bipyridine; mab-bpy: 4-methyl-4′-aminobutyl-2,2′-bipyridine; bpz: bipyrazine; dm-bpy: 4,4′-dimethyl-2,2′-bipyridine; dp-bpy: 4,4′-diphenyl-2,2′-bipyridine; dppz: dipyrdo[3,2-a:2′,3′-c]phenazine; dtdp: 1,3-dihydro-1,1,1,3,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthre-2-one; dc-bpy: 4,4′-dicarboxy-2,2′-bipyridine; dpp: 4,7-diphenyl-1,10-phenanthrone; phen: 1,10-phenanthroline; ppy: 2-phenylpyridine; terpy: 2,2′,2″-terpyridine Bphb: 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)benzene; Aza-bpy: 4-(N-aza-18-crown-6-methyl-2,2′-bipyridine.
Luminescent coordination complexes have been an area of active research for many decades. Complexes of ruthenium have perhaps received the most attention due to their sometimes exceptional properties. More recently there has been growing interest in metal complexes based on Iridium and osmium.

Coordination complexes of ruthenium(II) with ligands based on bipyridine and its derivatives (Figure 2.1), as well as structurally related ligands, have found applications in diverse areas. They have been utilized as building blocks in supramolecular and macromolecular chemistry and in the development of solid state light emitting devices, nanowires and dye sensitized solar cells. Applications in the area of analytical chemistry such as photoluminescence (PL), chemiluminescence (CL) and electrochemiluminescence (ECL) based sensing, have proved very useful for the sensitive detection of a wide range of analytes. For example, ruthenium complexes have been of particular interest in analytical biochemistry for DNA probe analyses and immunoassays. Other sensing strategies based on ruthenium complexes include oxygen and pH sensors, typically based on changes to the luminescent properties of the complex on interaction with the analyte.

The main goal in this chapter is to synthesize a series of homoleptic and heteroleptic ruthenium(II) polypyridyl complexes that would enable the investigation of various modes of attachment of such materials to electrode surfaces. Thus, the interest lies in the development of luminescent materials suitable for solution and solid state ECL-based sensing strategies. The desired features for such applications include high quantum yields, chemical attachment functionality, stability and favourable electrochemical properties (both thermodynamic and kinetic). The study involves to investigate the use of both novel and known polypyridine based ligands for electroactive luminescent material synthesis. This chapter describes the use of cyclisation reactions such as the Kröhnke ring assembly, for the synthesis of new bipyridine molecules. The selective conversions of the methyl groups on 4,4'-dimethyl-bipyridine for mono-substituted, di-substituted and functionalized
bipyridines is also described.

### 2.1 Experimental

#### General

All commercial reagents (Sigma-Aldrich) were of reagent grade or higher and were used without further purification except where stated. CH₂Cl₂, CH₃CN and Et₂O were distilled from CaH₂ in a recycling still. THF was dried with LiAlH₄ then distilled from potassium metal in a recycling still. Methanol and ethanol were dried from the reaction with magnesium and iodine and distilled under a N₂ atmosphere then stored with 3 Å molecular sieves. Ruthenium(II) bis-(2,2ʹ-bipyridine) dichloride Ru(II)(bpy)₂Cl₂, and potassium aquapentachlororuthanate(III) K₃[Ru(III)(H₂O)Cl₅], were purchased from Sigma-Aldrich and used as received. Aqueous solutions were prepared using deionised water (18 MΩ cm⁻¹). Moisture-sensitive reactions were performed under argon or nitrogen.

Reaction progress was monitored via thin layer chromatography using Merck kieselgel 60 F₂₅₄ plates or Merck aluminium oxide 60 F₂₅₄ neutral (Type T) plates as the stationary phase and ethyl acetate/hexane mixtures as the mobile phase unless otherwise indicated. These were visualised using a 254 nm UV lamp and/or permanganate stain consisting of KMnO₄ (3.0 g), K₂CO₃ (20 g) and 5% w/v aqueous NaOH (5 ml) in H₂O (300 mL) or aqueous solution of NH₄Fe(II)SO₄·(H₂O)₆. Purification by flash column chromatography was performed using silica gel (silica gel 60, 230-400 mesh) or alumina gel (aluminium oxide, activated, Brockmann 1, standard grade, ~150 mesh, 58 Å) as the stationary phase and ethanol / methanol or ethyl acetate / hexane mixtures as the mobile phase unless otherwise indicated. Other column chromatography techniques included the use of Sephadex as the stationary phase and ethanol, methanol, ethyl acetate and acetonitrile mixtures were used as the mobile phase. Typically, these columns were 20 mm in diameter and used 5-7 cm of Sephadex. Nuclear Magnetic Resonance (NMR) spectra
were obtained on a Bruker AV-300 spectrometer (\(^1\)H at 300.13 MHz and \(^{13}\)C at 75.47 MHz, respectively). These spectra were obtained in chloroform-d, DMSO-d6, acetone-d6 or acetonitrile-d3. Proton and carbon chemical shifts reported as \(\delta\) values in parts per million (ppm) are relative to the residual solvent signal and coupling constants (\(J\)) are in Hz. Infrared (IR) spectra were recorded on a Bruker Vector 22 fourier-transform spectrometer. Oils were analysed using sodium chloride plates. Solids were analysed using KBr discs or a diffuse reflectance (DRIFT) accessory. All melting points were uncorrected and performed on a Reichert “Thermopan” microscope hot-stage apparatus. Mass spectra were obtained using Electro-Spray Ionisation with an Ion trap on a Bruker Esquire 6000 Mass Spectrometer, or a Kratos Concept ISQ mass spectrometer at an ionisation energy of 70 eV; \(m/z\) values reported include the parent ion peak.
2.1.1 Synthesis of 2,2’-bipyridyl derivatives

Scheme I Synthesis of substituted 4,6-diphenyl-2,2’-bipyridine derivatives.

(step 1) synthesis of the enone (A7-A11). Pathways A: 100 Watts, 10 mol%, EtOH; pathway B: grinding of aldehyde with A5; pathway C: 0.5 M NaOH, EtOH / H2O. (step 1b) Isolation of the 1,5-diketone involves (A12), grinding of A8 with A5; (step 2) Kröhnk synthesis of substituted 4,6-diphenyl-2,2’-bipyridine ligands (A13-A17) from the reaction of the enone and pyridinium salt in the presence of NH4OAc to yield the 1,5-diketone intermediate, which cyclises.
2-acetylpyridine pyridinium bromide. Compound A6

Phenacyl bromide (20 g) (caution: lacrimator) was dissolved in dry pyridine (400 mL) and the mixture was allowed to stir at room temperature under nitrogen for 3h. During this time, a yellow precipitate formed which was collected by filtration, washed with ether (2 x 10 mL). The salt was obtained as white crystals (24 g, 80%) and used without further purification; m.p (lit. 201-202 °C) m.p (observed): 202 °C.

3-phenyl-1-(2-pyridinyl)-2-propen-1-one. Compound A7

Compound A7 from scheme I was synthesised using a literature procedure\(^9,\)\(^103\) and was obtained as a white powder in 75% yield. M.p 74.5–75.3 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.47 (m, 4H), 7.71 (m, 2H), 7.84 (t, 1H, \(J = 1.54\) Hz), 7.92 (d, 1H, \(J = 16.06\) Hz), 8.18 (d, 1H, \(J = 7.85\) Hz), 8.30 (d, 1H, \(J = 16.06\) Hz), 8.72 (d, 1H, \(J = 4.19\) Hz).
1,3-diphenyl-2-propen-1-one (benzalacetophenone). Compound A8

Compound A8 was prepared by a modified literature procedure. Benzaldehyde (A1) (1.04 g, 9.75 mmol) and acetophenone (1.17 g, 9.75 mmol) were combined using a mortar and pestle, and the oily yellow mixture was manipulated until a white powder had formed (5 min). The tacky solid coated on the walls of the mortar were scraped off and then re-combined with the bulk of the powder formed, to aid reaction completion. A 1:1 mixture ethanol:water (10 mL) was added to the mortar and the powder was further grounded (2 min). The supernatant was then removed via filtration and the resulting fine white solid was collected washed with a portion of 1:1 ethanol:water (10 mL). The product was obtained as a white solid (1.6 g, 79%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.40-7.6 (m, 10H), 7.77 (d, 1H, $J$ = 15.72 Hz), 8.02 (d, 2H, $J$ = 7.34 Hz).

2.1.2 General procedure of alternative microwave synthesis of compounds in scheme I Step 1a:

Into a round bottom flask (100 mL) with an extended neck equipped with a reflux condenser and stirrer bean were introduced 2-acetyl pyridine (8.25 mmol), substituted benzaldehyde (8.25 mmol), a catalytic quantity of powdered NaOH (10 mol%) and dry ethanol (10 mL). The mixture was thoroughly mixed before entering the microwave and rapid cooling was activated on the instrument. Irradiation began at 100 watts and was ramped for 20-30 sec at 30 °C with a range of 3-6 cycles. All reactions were monitored via TLC. It was important to maintain constant stirring during irradiation. Most products precipitated out of solution once the solution was cooled on ice; otherwise water was added to induce precipitation.
3-(4-nitrophenyl)-1-(2-pyridinyl)-2-propen-1-one. Compound A9

Compound A9 was prepared with the generalised procedure 2.1.2 using 4-nitrobenzaldehyde (A2) (1.25 g, 8.25 mmol), 2-acetyl pyridine (0.93 mL, 8.25 mmol), NaOH (33 mg) and ethanol (20 mL). A yellow solid was obtained (1.68 g, 80%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.56 (m, 1H), 7.88 (m, 5H), 8.24 (m, 3H), 8.43 (d, 1H, $J = 16.01$ Hz), 8.77 (d, 1H, $J = 4.28$ Hz); LRP +LSIMS 255.1 m/z

3-(4-chlorophenyl)-1-(2-pyridinyl)-2-propen-1-one. Compound A10

Compound A10 was prepared with the generalised procedure 2.1.2 using 4-chlorobenzaldehyde (A3) (1.17 g, 8.25 mmol), 2-acetyl pyridine (0.93 mL, 8.25 mmol), NaOH (33 mg) and ethanol (10 mL). A white solid was obtained (1.1 g, 53%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.38 (d, 2H, $J = 8.47$ Hz), 7.48 (m, 1H), 7.62 (d, 2H, $J = 8.47$ Hz), 7.86 (m, 2H), 8.15 (d, 1H, $J = 7.83$ Hz), 8.23 (d, 1H, $J = 16.05$ Hz), 8.73 (d, 1H, $J = 4.18$ Hz); LRP +LSIMS 244.1 m/z

1,4-bis[3-(2-pyridyl)-3-oxoprop-2-enyl]benzene. Compound A11

Compound A11 was prepared using the generalised procedure 2.1.2 with terethaldehyde (A4) (1.61 g, 2 mmol), 2-acetyl pyridine (2.7 mL, 24 mmol), NaOH (96 mg) and ethanol (35 mL). The yellow solid was obtained (2.5 g, 73%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 (m, 2H), 7.76 (s, 4H), 7.76 (s, 4H), 7.89 (ddd, 2H, $J = 13.24, 6.07, 1.69$ Hz), 7.95 (s, 2H), 8.20 (d, 2H, $J = 7.8$ Hz), 8.37 (d, 2H, $J = 16.01$ Hz), 8.75 (d, 2H, $J = 4.11$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 121.53, 122.6, 126.62, 128.89, 136.70, 136.81, 143.21, 148.51, 153.73, 188.96; HRMS: 341.12861 (dev -1.14 ppm).
1,3-diphenyl-5-pyridin-2-ylpentane-1,5-dione. Compound A12

Compound A12 was synthesised as described in the literature.\textsuperscript{9} The white solid was recrystallised from ethanol to yield a white crystalline solid (0.88 g, 55%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): $\delta = 8.55$ (m, 1H), 7.88 (m, 1H), 7.83 (m, 2H), 7.69 (dt, $J = 7.65$, $J = 1.73$ Hz, 1H), 7.44 (m, 1H), 7.32 (m, 3H), 7.25 (m, 2H), 7.20 (t, $J = 7.48$ Hz, 2H), 7.06 (m, 1H), 4.05 (m, 1H), 3.63 (m, 2H), 3.33 (m, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): $\delta = 200.2$, 198.7, 153.6, 149.0, 144.5, 137.3, 137.0, 133.1, 128.7, 128.5, 128.3, 127.8, 127.3, 126.7, 122.0, 45.4, 44.1, 36.8. HR-MS: 330.14951 (dev 0.33 ppm)
4,6-diphenyl-2,2′-bipyridine. Compound A13

Compound A13 was prepared using either Step 2a or 2b shown in Scheme I. This compound was synthesised as described in the literature\(^9\) via Step 2b which gave a white powder (0.32 g, 40%). Alternatively, using method 2a of (Scheme 2.1), a suspension of 3-phenyl-1-(2-pyridinyl)-2-propen-1-one (1.0 g, 4.8 mmol), 2-acetylpypyridine pyridinium bromide (1.32 g, 4.7 mmol), ammonium acetate (1.8 g, 24 mmol) in ethanol (20 mL) was heated under reflux for 7 h. A red colour change was observed within a few minutes under refluxing conditions. After this time the reaction solution was cooled removed and left to stand at 5 °C overnight. Some of the crude product had precipitated out of solution and water (20 mL) was added to induce further precipitation. The solid was then collected by filtration and washed with water (2 x 20 mL) and recrystallised from ethanol to give fine white crystals (0.7 g, 56%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.32\) (1H, ddd, \(J = 7.5, 4.8, 1.2\) Hz), \(\delta 7.50\) (m, 6H), \(\delta 7.84\) (m, 3H), \(\delta 7.98\) (d, 1H, \(J = 1.5\) Hz), \(\delta 8.19\) (m, 2H), \(\delta 8.64\) (d, 1H, \(J = 1.5\) Hz), \(\delta 8.70\) (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 157.2, 156.4, 156.3, 150.3, 149.1, 139.5, 138.8, 136.9, 129.1, 129.0, 128.9, 128.7, 127.3, 127.1, 123.8, 121.6, 118.5, 117.6.
4-(4-nitrophenyl)-6-phenyl-2,2′-bipyridine. Compound A14

Compound A14 was prepared by a modified literature procedure. A suspension of 3-(4-nitrophenyl)-1-(2-pyridinyl)-2-propen-1-one (0.80 g, 3.1 mmol), phenacylpyridinium bromide (0.87 g, 3.1 mmol), ammonium acetate (1.2 g, 15.6 mmol) in ethanol (20 mL) was heated at reflux for 4 h. After 1 h at reflux a precipitate began to form. The reaction was cooled and then the solid was collected by filtration and washed with water (2 x 10 mL) followed by ethanol (10 mL). The product was obtained as yellow solid (0.87 g, 79%). R_f = 0.45 in 15 % EtOAc/Hex on silica plate. 1H NMR (300 MHz, CDCl_3) δ 7.38 (1H, ddd, J = 7.4, 4.8, 1.1 Hz), δ 7.54 (m, 3H), δ 7.89 (ddd, 1H, J = 7.8, 1.7 Hz), δ 7.96 (m, 3H), δ 8.20 (d, 2H, J = 8.4 Hz), δ 8.36 (dd, 2H, J = 7.0, 1.5 Hz), δ 8.72 (m, 3H); 13C NMR (75 MHz, CDCl_3) δ 117.83, 118.52, 122.04, 123.96, 124.16, 126.72, 127.95, 128.54, 129.25, 138.29, 144.36, 147.25, 147.75, 147.91, 154.39, 157.54; LRP +LSIMS 354.2 m/z
4-(4-aminophenyl)-6-phenyl-2,2′-bipyridine. Compound A15

To a 3-necked flask fitted with a stopper, hydrogen balloon and vacuum tap was added ethyl acetate (50 mL), 10% Pd/C (0.3 g) and 4-(4-nitrophenyl)-6-phenyl-2,2′-bipyridine. The flask was purged with H₂ and stirred at RT under a H₂ atmosphere. TLC was used to monitor the reaction and after completion (approx 3.5 h), the reaction mixture was filtered through a plug of celite and the plug was further washed with ethyl acetate (2 x 20 mL). The fractions were pooled and the solvent was removed under reduced pressure to give a white solid. Recrystallisation from ethanol afforded compound A15 as a fine microcrystalline white solid (0.18 g, 80%). Rᵣ = 0 versus nitro derivative in 15 % EtOAc / Hex on silica plate. $^{1}$H NMR (300 MHz, CDCl₃) δ 5.53 (s, 2H), 6.72 (d, 2H, $J = 8.52$ Hz), 7.51 (m, 4H), 7.71 (d, 2H, $J = 8.52$ Hz), 7.96 (t, 1H, $J = 6.24$ Hz), 8.12 (s, 1H), 8.29 (d, 2H, $J = 7.12$ Hz), 8.5 (s, 1H), 8.58 (d, 1H, $J = 7.93$ Hz), 8.7 (d, 1H, $J = 3.98$ Hz); $^{13}$C NMR (75 MHz, CDCl₃) δ 114.22, 144.82, 116.28, 120.86, 123.98, 124.28, 126.96, 127.89, 128.78, 129.17, 137.39, 138.99, 149.29, 149.70, 150.49, 155.47, 155.68, 156.25; HRMS: 324.14975 (dev -0.99).
Chapter 2 Synthesis of polypyridyl ligands and organometallic complexes

4-(4-chlorophenyl)-6-phenyl-2,2’-bipyridine. Compound A16

Compound A16 was synthesised using a modified literature procedure. To prepare this compound a suspension of 3-(4-chlorophenyl)-1-(2-pyridinyl)-2-propen-1-one (0.80 g, 3.2 mmol), phenacyl pyridinium bromide (0.91 g, 3.2 mmol), ammonium acetate (1.26 g, 16.3 mmol) in ethanol (20 mL) was heated at reflux for 6 h. The reaction was cooled and an off-white crystalline solid precipitated. The white solid was collected and washed with water (2 x 10 mL) and ethanol (10 mL) (0.36 g, 79%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.32 (1H, ddd, $J = 7.5$, 4.8, 1.2 Hz), $\delta$ 7.50 (m, 6H), $\delta$ 7.84 (m, 3H), $\delta$ 7.98 (d, 1H, $J = 1.5$ Hz), $\delta$ 8.19 (m, 2H), $\delta$ 8.64 (d, 1H, $J = 1.5$ Hz), $\delta$ 8.70 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 116.89, 117.80, 118.32, 121.25, 123.57, 126.71, 128.15, 128.41, 128.86, 131.45, 134.85, 136.70, 136.76, 138.89, 148.52, 148.59, 155.67, 155.84, 156.93; HRMS: 343.10097 (dev 2.23 ppm)
4-phenyl-6-(4-chlorophenyl)-2,2ʹ-bipyridine. Compound A17

Compound A17 was synthesised using a modified literature procedure. A suspension of 3-phenyl-1-(2-pyridinyl)-2-propen-1-one (1.0 g, 4.7 mmol), phenacyl pyridinium bromide (1.31 g, 4.7 mmol), ammonium acetate (1.83 g, 24 mmol) in ethanol (20 mL) was heated under reflux for 7 h. During the course of the reaction the solution turned from bright yellow to dark green. The mixture was then cooled and a green solid precipitated. The green solid was collected by filtration and washed with water (2 x 10 mL) and ethanol (1 x 10 mL) to yield green crystals (0.86 g, 47%). 

1H NMR (300 MHz, CDCl₃) δ 7.35 (1H, ddd, J = 7.4, 4.9, 1.1 Hz), δ 7.54 (m, 3H), δ 7.65 (dd, 2H, J = 4.3, 2.4 Hz), δ 7.81 (dd, 2H, J = 3.6, 1.6 Hz), δ 7.87 (ddd, 1H, J = 7.7, 1.8 Hz), δ 7.93 (d, 1H, J = 1.5 Hz), δ 8.06 (dd, 2H, J = 4.3, 2.4 Hz), δ 8.63 (s, 1H), δ 8.67 (m, 1H), δ 8.70 (m, 1H) δ 118.12, 118.33, 121.92, 123.35, 123.90, 126.94, 128.28, 128.76, 128.93, 131.55, 137.69, 137.77, 138.24, 147.21, 150.40, 154.67, 155.88 HRMS: 387.04956 (dev -0.33 ppm).
Scheme II Synthesis of 4-monosubstituted-2,2′-bipyridines.

B20 was synthesised from 4-nitrobenzaldehyde (B18) and sodium pyruvate (CH₃OCOCO⁻Na⁺), in 0.5 M NaOH / H₂O / EtOH; B21 synthesised from B20 and B19 in the presence of ammonium acetate / H₂O; the nitro derivative B21 was reduced to the amine (B22) from 55% hydrazine / EtOH / Pd / C. All steps were performed under an N₂ atmosphere.

Pyridacyl pyridinium iodide (PPI). Compound B19

Compound B19 was synthesised using a literature procedure and was obtained as a dark yellow microcrystalline solid (40%); ESMS: m/z [C₁₂H₁₁N₂O]⁺ 199.0 (Calculated: 199.23).
4-(4-nitrophenyl)-2-oxo-3-butenoic acid. Compound B20

Compound B20 was synthesised using a literature procedure\(^\text{11}\) and was obtained as a white solid (70%). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 7.2 (d, 1H, \(J = 16.4\) Hz) 7.66 (d, 1H, \(J = 16.4\) Hz) 7.98 (d, 2H, \(J = 8.44\) Hz), 8.18 (d, 2H, \(J = 8.44\) Hz).

4-(4-nitrophenyl)-2,2\('\)'-bipyridine. Compound B21

Compound B21 was synthesised using a literature procedure\(^\text{11}\) and was obtained as a white solid (58%). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 7.47 (t, 1H, \(J = 6.4\) Hz), 7.85 (d, 1H, \(J = 3.3\) Hz), 7.96 (t, 1H, \(J = 7.8\) Hz), 8.12 (d, 2H, \(J = 7.2\) Hz), 8.33 (d, 2H, \(J = 7.2\) Hz), 8.42 (d, 1H, \(J = 4.9\) Hz), 8.8 (d, 1H, \(J = 5.1\) Hz).

4-(4-nitrophenyl)-2,2\('\)'-bipyridine. Compound B22

Compound B22 was synthesised using a literature procedure\(^\text{11}\) and was obtained as white crystalline solid (54%). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 5.52 (s, 2H, Ar-NH2), 6.67 (d, 2H, \(J = 8.4\) Hz), 7.42 (m, 1H), 7.58 (m, 3H), 7.90 (t, 1H, \(J = 6.41\) Hz), 8.37 (d, 1H, \(J = 7.88\) Hz), 8.55 (m, 2H), 8.67 (d, 1H, \(J = 4.56\) Hz); \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 114.26, 115.89, 119.89, 119.89, 120.63, 123.65, 124.19, 127.61, 137.33, 148.44, 149.29, 149.79, 150.48, 155.60, 155.70; ESI-MS: \(m/z\) [C\(_{16}\)H\(_{13}\)N\(_3\)H\(^+\)] 248.0 (Calculated: 247.32).
Scheme III Synthesis of carboxylic acid functionalised 4 monosubstituted 2,2′-bipyridines and 4,4′-disubstituted-2,2′-bipyridines.

C24 was prepared from 2-(2-Bromoethyl)-1,3-dioxolane and n-butyllithium (LDA) (in stoichiometric amounts) in THF at -78 °C. Compound C25 was prepared in same way except LDA was used in excess. Compounds C26 and C27 were obtained via hydrolysis of the acetal in 1 M HCl at 55 °C. Compounds C28 and C29 were obtained from a mixture containing NaCO$_3$ / H$_2$O$_2$ / NaH$_2$PO$_4$ in CH$_3$CN and H$_2$O. All steps were performed under an N$_2$ atmosphere.
4-methyl-4’-(3-propyl-1,3-dioxolane)-2,2’-bipyridine. Compound C24

Compound C24 was synthesised using a literature procedure and was obtained as a colourless oil (2.0 g, 54%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.73 (m, 2H), 1.83 (m, 2H), 2.42 (s, 3H), 2.74 (t, 2H, $J = 9.5$ Hz), 3.8-3.97 (m, 4H), 4.87 (t, 1H, $J = 5.5$ Hz), 7.10-7.14 (m, 2H), 8.20-8.22 (m, 2H), 8.51-8.55 (m, 2H).

4,4’-di(3-propyl-1,3-dioxolane)-2,2’-bipyridine. Compound C25

Compound C25 was synthesised using a literature procedure and was obtained as a white solid (2.49 g, 60%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.52-1.71 (m, 8H), 2.56 (t, 4H, $J = 7.7$ Hz), 3.60-3.77 (m, 8H), 4.68 (t, 2H, $J = 4.5$ Hz), 6.95 (d, 2H, $J = 4.2$ Hz), 8.09 (s, 2H), 8.38 (d, 2H, $J = 4.8$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 24.1, 32.8, 34.7, 64.3, 120.8, 123.4, 148.5, 151.6, 155.6.

4-methyl-4’-butanal-2,2’-bipyridine. Compound C26

Compound C26 was synthesised using a literature procedure from C24. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.02 (m, 2H), 2.45 (s, 3H), 2.50 (t, 2H, $J = 6.7$ Hz), 2.74 (t, 2H, $J = 7.5$ Hz), 7.12-7.14 (m, 2H), 8.16-8.21 (m, 2H), 8.52-8.58 (m, 2H).
4,4′-dibutanal-2,2′-bipyridine. Compound C27

Compound C27 was synthesised using a literature procedure from C25. Spectroscopic data for compound C27 were compared to literature values and was obtained as an amber oil (227 mg, 89%).

\[ \text{H NMR (300 MHz, CDCl}_3\] \delta 1.97-2.07 (pentet, 4H, \( J = 7.4 \) Hz), 2.25 (dt, 4H, \( J = 7.2 \) Hz, \( J = 1.1 \) Hz), 2.49 (t, 4H, \( J = 7.4 \) Hz), 6.91 (dd, 2H, \( J = 5.0 \) Hz and 1.6 Hz), 8.03 (s, 2H), 8.34 (d, 2H, \( J = 5.0 \) Hz), 9.52 (t, 2H, \( J = 1.2 \) Hz).

4-methyl-4′-butoxy-2,2′-bipyridine. Compound C28

Compound C28 was synthesised based on literature procedures from C26. The aldehyde C26 (13.0 mmol, 3.13 g) was dissolved in MeCN (15 mL) and added to a 100 mL round bottomed flask containing a magnetic stirring bar, along with \( \text{H}_2\text{O}_2 \) (19.5 mmol, 2.0 ml of a 30% v/v solution in \( \text{H}_2\text{O} \)) and an aqueous solution of \( \text{NaH}_2\text{PO}_4 \) (0.65 M, 7.5 mL). The flask was fitted with a 100 mL pressure compensating dropping funnel connected to a gas bubbler filled with paraffin oil, and then stirred and cooled to 10°C in an ice bath filled with cold water. A solution of \( \text{NaClO}_2 \) (0.61 M, 30 mL) was added to the reaction mixture drop wise over a period of 1 h. The reaction was monitored via TLC and the evolution of \( \text{O}_2 \). The reaction was deemed complete via TLC and when the evolution of \( \text{O}_2 \) had ceased. After 2 h, the reaction mixture was extracted with \( \text{CH}_2\text{Cl}_2 \) (3 x 30 mL). The organic extracts were pooled, washed with \( \text{H}_2\text{O} \) (20 mL), sat. \( \text{NaCl} \) solution (15 mL), dried with sodium sulfate, filtered and concentrated under reduced pressure. The resultant amber coloured oil crystallised to provide a pale pink solid. The crude solid was recrystallised using ethyl acetate/hexane to provide C28 as a white solid (2.87 g, 86%). IR (KBr, cm\(^{-1}\)) approx 2500 (br, OH), 1700 (C=O). \[ \text{H NMR (300 MHz, CDCl}_3\] \delta 2.10 (m, 2H), 2.42-2.49 (m, 5H), 2.74 (t, 2H, \( J = 7.3 \) Hz), 7.12-7.14 (m, 2H), 8.19-8.21 (m, 2H), 8.52-8.58 (m, 2H).
Compound C29 was synthesised based on literature procedures from aldehyde C27.\(^{105-107}\) The dialdehyde C27 (300 mg, 1.06 mmol) was dissolved in CH\(_3\)CN (1.2 mL) and added to a 50 mL round bottomed flask containing a magnetic stirring bar, along with H\(_2\)O\(_2\) (3.19 mmol, 328 \(\mu\)L of a 30% v/v solution in H\(_2\)O) and a aqueous solution of NaH\(_2\)PO\(_4\) (6.67 M, 1.2 mL). The flask was fitted with a gas bubbler filled with paraffin oil, and then stirred and cooled to 10°C in an ice bath filled with cold water. A solution of NaClO\(_2\) (0.31 M, 4.8 mL) was added to the reaction mixture via Pasteur pipette over a period of 1 h. The mixture was then allowed to warm to RT and monitored via TLC and was deemed to be complete via TLC and when the evolution of O\(_2\) had ceased. After 2 h, a thick white precipitate had formed. The precipitate was filtered, rinsed with deionised H\(_2\)O and allowed to air dry to provide C29 as a white solid (377 mg, 99%). IR (KBr, cm\(^{-1}\)): 3410 (OH), 1702 (C=O), 1631 (Ar), 1595 (Ar), 1184. \(^1\)H NMR (D\(_2\)O, 300 MHz): \(\delta\) 8.59 (d, \(J = 5.7\) Hz, 2 H), 8.14 (br s, 2H), 7.65 (d, \(J = 5.7\) Hz, 2H), 2.83 (t, \(J = 7.2\) Hz, 4H), 2.36 (t, \(J = 7.2\) Hz, 4H), 1.69 (quint, \(J = 7.5\) Hz, 8H), 1.57 (quint, \(J = 7.5\) Hz, 4H). \(^{13}\)C NMR (D\(_2\)O, 75 MHz) \(\delta\) 178.6, 160.9, 146.4, 145.2, 127.3, 124.0, 34.9, 33.5, 28.6, 23.8.
Scheme IV Synthesis of functionalised 4-monosubstituted-2,2’-bipyridines.

Lithiation of compound C23 followed by reaction with 1,3-dibromopropane in THF at -78 °C gave C30. Compound C30 was then reacted with potassium phthalate in DMF to form C31. Compound C32 with a free amine group was generated by treatment of C31 with 55% hydrazine in ethanol. All steps were performed under an N₂ atmosphere.

4-methyl-4’-(4-bromobutyl)-2,2’-bipyridine. Compound C30

Compound C30 was synthesised using a literature procedure from C23.¹⁶ ¹H NMR (300 MHz, DMSO-d₆) δ 1.70-1.80 (m, 4H), 2.29 (s, 3H), 2.58 (t, 2H, J = 6.87 Hz), 3.28 (t, 2H, J = 6.29 Hz), 7.01 (d, 2H, J = 4.67 Hz), 8.13 (s, 2H), 8.41-8.45 (m, 2H); ¹³C NMR (75 MHz, DMSO-d₆) δ 20.74, 28.30, 31.73, 32.80, 34.06, 120.71, 121.56, 123.34, 124.18, 124.25, 147.62, 148.48, 148.67, 151.25, 155.50, 155.58, 155.82.
4-(4-phthalimidobutyl)-4′-methyl-2,2′-bipyridine. Compound C31

Compound C31 was synthesised using a literature procedure from C30.\textsuperscript{15} 1H NMR (300 MHz, DMSO-d\textsubscript{6}) δ 1.67-172 (m, 4H), 2.36 (s, 3H), 2.69 (t, 2H, $J = 6.8$ Hz), 3.67 (t, 2H, $J = 6.48$ Hz), 7.05-7.08 (m, 2H), 7.61-7.65 (m, 2H), 7.737.77 (m, 2H), 8.15 (s, 2H), 8.45-8.5 (m, 2H); 13C NMR (75 MHz, DMSO-d\textsubscript{6}) δ 20.77, 27.23, 27.82, 34.54, 37.19, 120.86, 121.61, 122.79, 123.48, 124.22, 131.7, 133.48, 147.66, 148.51, 148.69, 151.52, 155.6, 155.82, 167.96. HR-MS (+ESI): m/z [C\textsubscript{23}H\textsubscript{22}N\textsubscript{3}O\textsubscript{2}]\textsuperscript{+} 372.1714 (Calculated: 372.1712).

2.1.3 General procedure for metathesis of Cl\textsuperscript{-} to PF\textsubscript{6}\textsuperscript{-} ruthenium 2,2′-bipyrine and 1,10-phenanthroline complexes

To a solution of the chosen complex dissolved in Milli Q water (10 mL) a saturated solution of potassium hexafluorophosphate was added drop wise with stirring. The resulting precipitate was collected by vacuum filtration. The freshly prepared salt was dried under vacuum and stored over P\textsubscript{2}O\textsubscript{5} in screw top vials shielded from light.

Metathesis of [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2}.xH\textsubscript{2}O $\rightarrow$ [Ru(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2}

[Ru(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2} was prepared using the general metathesis procedure 2.1.3 and yielded orange needles (95%). 1H NMR (300 MHz, CD\textsubscript{3}CN) δ 7.35-7.39 (m, 6H), 7.7 (d, 6H, $J = 5.3$ Hz), 8.03 (t, 6H, $J = 7.9$ Hz), 8.48 (d, 6H, $J = 8.2$); UV-Vis: $\nu^\text{max}$ MLCT band 455 nm, $\epsilon^\text{max}$ 1.33 x 10\textsuperscript{4} M$^{-1}$cm$^{-1}$ at 452 nm; $\nu^\text{max}$ (Emission) 620 nm; ESMS: m/z [\textsuperscript{102}Ru-2PF\textsubscript{6}]\textsuperscript{2+} 285.3 (calculated: 284.8).
Metathesis of $[\text{Ru(phen)}_3]\text{Cl}_2 \rightarrow [\text{Ru(phen)}_3](\text{PF}_6)_2$. (Complex 10)

Complex 10 was prepared using the general metathesis procedure 2.1.3 and yielded a dark orange solid (0.18 g, 90%). $^1$H NMR (300 MHz, CD$_3$CN) δ 7.57-7.62 (m, 6H), 7.99-8.01 (dd, 6H, $J = 1.04$ Hz), 8.23 (s, 6H), 8.55-8.59 (dd, 6H, $J = 3.0$ Hz); UV-Vis: $\nu_{\text{max}}$ MLCT band 447 nm, $\varepsilon_{\text{max}}$ 1.820 x 10$^4$M$^{-1}$cm$^{-1}$ at 446 nm; $\nu_{\text{max}}$ (Emission) 600 nm; ESMS: $m/z$ [102Ru -2PF$_6$]$^{2+}$ 321.7 (calculated: 321).

2.1.4 Synthesis of 2, 2ʹ-bipyridine and 1,10-phenanthroline based ruthenium(II) complexes.

**tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) bis(hexafluorophosphate), [Ru(dpp)$_3$](PF$_6$)$_2$. (Complex 8)**

To a solution of RuCl$_3$·3H$_2$O (113 mg, 0.5 mmol) in a mixture of (4:1) ethylene glycol : water (2.5 mL) heated to 120 °C was added 4,7-diphenyl-1,10-phenanthroline (431 mg, 1.3 mmol). The solution was then refluxed for 1 h at 165 °C and the mixture turned from a black slurry to a deep red solution. After cooling, the solution was diluted with acetone (25 mL) filtered and a saturated aqueous solution of potassium hexafluorophosphate (KPF$_6$) was added precipitating the crude ruthenium complex as an orange solid. The solid was collected by vacuum filtration and washed with distilled water (10 mL) and ether (10 mL). Recrystallisation from (4:1) acetone : water mixture and drying under vacuum yielded an orange powder (0.5 g, 83 %). IR (KBr) $\nu_{\text{max}}$ 3095 (aromatic); $^1$H NMR (300 MHz,
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CDCl₃) δ 7.52-7.59 (m, 10H), 7.79 (d, 2H, J = 4.96 Hz), 8.21 (s, 2H), 8.37 (d, 2H, J = 5.01 Hz); ESMS: m/z [¹⁰²Ru-2PF₆]²⁺ 549.5 (Calculated: 549.2).

tris(3,4,7,8-tetramethyl-1,10-phenanthroline)ruthenium(II) bis(hexafluorophosphate), [Ru(tmphen)₃](PF₆)₂. (Complex 9)

Complex 9 was synthesized using a previously published procedure using K₃[Ru(III)(H₂O)Cl₅].¹⁰⁸ Yield (50 %). The complex as its chloride salt was converted to the hexafluorophosphate salt by dissolving it in distilled methanol and adding a saturated solution of KPF₆ while stirring to precipitate the salt as a dark orange powder (95 %). ¹H NMR (300 MHz, CD₃CN) δ 1.93 (s, 18H), 2.75 (s, 18H), 7.64 (s, 6H), 8.34 (s, 6H); ESMS: m/z [¹⁰²Ru-2PF₆]²⁺ 405.6 (Calculated: 406); EA: C₄₈H₄₈N₆RuP₂F₁₂ calc. %C 52.41, %H 4.40, %N 7.64, obs. %C 52.60, %H 4.49, %N 7.75.

bis-(2,2′-bipyridine)(4,6-diphenyl-2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate), [Ru(bpy)₂(dpdb)](PF₆)₂. (Complex 11)

A solution of ruthenium bis-(2,2′-bipyridine) dichloride (0.16 g, 0.32 mmol) and 4,6-diphenyl-2,2′-bipridine (0.10 g, 0.33 mmol) in a mixture of (3:1) ethanol and water (20 mL), were refluxed for 2 h under a nitrogen atmosphere. Once a deep red solution had formed the solvent was removed under reduced pressure and the residue was redissolved in Milli Q water (10 mL). The resulting red solution was filtered, and the filtrate was treated with saturated aqueous KPF₆ to precipitate the Ru(II) complex as the hexafluorophosphate salt. The resulting orange precipitate was then collected by filtration and washed with water (2 x 10 mL) and ether (2 x 10 mL). Recrystallisation from an (2:1) acetone : water mixture gave an orange
powder which was collected by filtration and washed with diethyl ether (10 mL) and dried under vacuum to yield a red powder (0.13 g, 79%). IR (KBr, cm⁻¹) ν_max (aromatic C=C) 3087, 1612, 1486, 1466, 1424, 1414, 1400; ¹H NMR (300 MHz, DMSO-d₆) δ 6.01 (brd s, 1H), 6.65 (brd s, 1H), 6.86-6.94 (m, 4H), 7.33 (d, 3H, J = 4.16 Hz), 7.44 (t, 1H J = 6.35 Hz) 7.51-7.67 (m, 7H), 7.73 (s, 1H), 7.81 (d, 1H, J = 5.3 Hz), 8.01 (q, 1H J = 4.7 Hz), 8.15-8.28 (m, 7H), 8.61-8.72 (m, 3H), 9.2 (m, 2H). ¹³C NMR (75 MHz, DMSO-d₆) δ 120.47, 123.3, 124.35, 124.50, 126.01, 126.51, 127.32, 127.50, 127.80, 128.10, 128.95, 129.40, 130.92, 134.56, 135.98, 137.86, 138.04, 138.11, 138.71, 148.31, 150.56, 151.14, 151.34, 155.93, 156.69, 156.74, 157.59, 157.78, 157.85, 166.31; ESI-MS: m/z [¹⁰²Ru-PF₆]⁺ 867.2 (Calculated: 866.78); EA: C₄₂H₃₂N₆RuP₂F₁₂.CH₃CN.(H₂O)₂ calc. %C 48.49, %H 3.61, %N 9.00, obs. %C 48.79, %H 3.35, %N 9.26

bis(2,2′-bipyridine)(4′-aminophenyl-2,2′bipyridine)ruthenium(II) bis(hexafluorophosphate) 

[Ru(bpy)₂(apb)](PF₆)₂. (Complex 12)

A solution of ruthenium bis-(2,2′-bipyridine) dichloride (100 mg, 0.38 mmol) and 4′-aminophenyl-2,2′-bipyridine (94 mg, 0.4 mmol) in a mixture of (1:1) ethanol : water (20 mL), were heated at reflux for 5 h under a nitrogen atmosphere. Once a deep red solution had formed the solvent was removed under reduced pressure. The solid was redissolved in Milli-Q water (20 mL) and the solution was then filtered. The filtrate was treated with a saturated aqueous solution of KPF₆, which gave an orange precipitate. The resulting solid was collected by filtration and washed with Milli Q water (2 x 5 mL) and diethyl ether (2 x 5 mL). The red precipitate was recrystallised from acetone-water mixture and then dried under vacuum
at 50 °C to afford an orange powder (0.150 g, 42 %). ¹H NMR (300 MHz, DMSO-d₆) δ 5.81 (s, 2H), 6.64-6.68 (m, 3H), 7.43-7.61 (m, 8H), 7.68-7.82 (m, 7H), 8.13 (t, 4H, J = 7.8 Hz), 8.81 (d, 3H, J = 8.4 Hz), 8.91 (s, 1H), 9.1 (d, 1H, J = 8.10 Hz); ¹³C NMR (125 MHz, CD₃CN) δ 114.59, 114.67, 116.70, 119.98, 120.23, 120.81, 122.93, 123.0, 124.02, 124.21, 127.41, 127.55, 127.85, 128.50, 137.11, 137.62, 137.67, 149.03, 149.18, 149.45, 149.54, 149.65, 151.02, 151.62, 151.67, 155.83, 156.02, 156.83, 157.01, 157.05, 157.36 ESI-MS: m/z [¹⁰²Ru-PF₆⁺H⁺]⁺ 806.0 (Calculated: 805.7), [¹⁰²Ru-2PF₆⁺2H⁺]⁺ 663.1 (Calculated: 660.74), [Ru-2PF₆]²⁺ 330.6 (Calculated: 330.37).

bis(2,2’-bipyridine)(4’-methyl-2,2’-bipyridine-4-butanoic acid)ruthenium(II)

bis(hexafluorophosphate), [Ru(bpy)₂(mbpyb)](PF₆)₂. (Complex 6)

A solution of ruthenium bis-(2,2'-bipyridine) dichloride (0.19 g, 0.39 mmol) and 4’-methyl-2,2'-bipyridine-4-butanoic acid (0.11 g, 0.41 mmol) in a mixture of ethanol and water (20 mL, 1:1) was heated at reflux for 5 h under a N₂ atmosphere. After cooling, the solvents were removed under reduced pressure and the residue was dissolved in water (10 mL), and filtered. The filtrate was treated with a saturated aqueous KPF₆ solution, and an orange precipitate formed. The mixture was cooled on ice 2 h and the fluffy precipitate was then collected by filtration and washed with Milli-Q water (2 x 5 mL). The orange solid was purified by column chromatography using lipophilic sephadex. An orange band was eluted with 1:1 mixture of acetonitrile : ethanol to yield a bright orange powder after solvent evaporation (0.25 g, 67%). IR (KBr, cm⁻¹) νmax (-C₃H₆COOH) 3440.10, (Aromatic C=C) 3086.16,1619, (Saturated C-H) 2929.92; ¹H NMR (300 MHz, DMSO-d₆) δ 1.51-1.61 (q, 2H, J = 7.35 Hz), 1.90 (t, 2H, J = 6.5 Hz), 2.15 (s, 3H), 2.43 (t,
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2H, $J = 7.3$ Hz), 6.83 (t, 2H, $J = 5.7$ Hz), 7.04 (m, 5H), 7.22 (m, 5H), 7.6 (t, 4H, $J = 7.99$ Hz), 8.1 (d, 2H, $J = 8.9$ Hz), 8.21 (d, 4H, $J = 8.12$ Hz); $^{13}$C NMR (75 MHz, DMSO-d$_6$) δ 20.53, 24.27, 32.61, 33.66, 123.94, 124.03, 124.91, 127.32, 127.39, 128.19, 128.39, 149.35, 149.61, 149.97, 150.28, 151.19, 153.46, 155.55, 155.80, 156.08, 156.18, 173.71 (C=O); HR-MS (+ESI): $m/z$ [$_{102}$Ru-2PF$_6$]$^{2+}$ 335.0814 (Calculated: 335.0815); EA: C$_{35}$H$_{32}$N$_6$O$_2$RuP$_2$F$_{12}$ calc. %C 43.80, %H 3.36, %N 8.76, obs. %C 42.56, %H 3.55, %N 8.24.

bis(2,2’-bipyridine)-[4-(4-Phthalimidobutyl)-4’-methyl-2,2’-bipyridine) ruthenium(II)bis(hexafluorophosphate)

[Ru(bpy)$_2$(pht-bpy)](PF$_6$)$_2$. (Complex 13)

Ruthenium bis-(2,2’-bipyridine) dichloride (0.20 g, 0.41 mmol) and 4-(4-phthalimidobutyl)-4’-methyl-2,2’-bipyridine (0.16 g, 0.43 mmol), was suspended in a mixture of (1:1) ethanol : water (20 mL). The mixture was heated at reflux for 7 h under a N$_2$ atmosphere. The solvent was removed under reduced pressure and the cherry red solid was redissolved in water (10 mL). The solution was filtered and treated with a saturated solution of KPF$_6$. The mixture was cooled 2 h and then the bright orange precipitate was collected by filtration, washed with water (2 x 5 mL) and dried. The orange precipitate was purified by column chromatography with lipophilic sephadex. An orange band was eluted with acetonitrile and the solvent was removed under reduced pressure to yield an orange powder (0.32 g, 73%). $^1$H NMR (300 MHz, CD$_3$CN) δ 1.70 (m, 4H), 2.5 (s, 3H), 2.82 (t, 2H, $J = 8.07$ Hz), 3.64 (t, 2H, $J = 6.21$ Hz), 7.22 (d, 2H, $J = 5.76$ Hz), 7.40 (m, 4H), 7.52 (m, 2H), 7.75 (m, 8H), 8.02 (m, 4H), 8.33 (s, 2H), 8.46 (d, 4H, $J = 8.19$ Hz); $^{13}$C NMR (75 MHz, CD$_3$CN) δ 19.90, 26.64, 27.01, 33.64, 36.80, 122.42, 123.91, 124.59, 127.13, 127.13, 26, 127.91, 131.81, 133.79, 137.8, 150.05, 150.35, 150.59, 151.15, 151.31, 153.85, 156.11,
156.26, 156.69, 168.10; ESI-MS: \( m/z \ [^{102}\text{Ru-PF}_6]^+ \) 930.0 (Calculated: 929.84), \( [^{102}\text{Ru-2PF}_6]^{2+} \) 392.4 (Calculated: 392.6); HR-MS (+ESI): \( m/z \ [^{102}\text{Ru-2PF}_6]^{2+} \) 392.6028 (Calculated: 392.6026); EA: \( \text{C}_{43}\text{H}_{37}\text{N}_7\text{O}_2\text{RuP}_2\text{F}_{12} \) calc. %C 48.05, %H 3.47, %N 9.12, obs. %C 47.58, %H 3.57, %N 8.91.

\textbf{bis(2,2’-bipyridine)-[4-(4’-methyl-2,2’-bipyridine)aminobutyl]ruthenium(II)bis(hexafluorophosphate)}

\[ [\text{Ru(bpy)}_2(\text{mab-bpy})](\text{PF}_6)_2 \]. (Complex 7)

A solution of complex 13 (71 mg, 0.066 mmol) in ethanol (10 mL) was stirred under \( \text{N}_2 \) for 1 h. Hydrazine monohydrate (0.02 g, 20 \( \mu \)L) was added and the mixture was heated to 50 °C for 24 h. After cooling, the mixture was filtered and the solvents were removed under reduced pressure.

The sticky red solid was redissolved in water (5 mL) and treated with saturated KPF\(_6\) and an orange precipitate formed. The orange solid was collected by filtration and washed with water (2 x 5 mL) and dried under vacuum (50 mg, 72%). IR (KBr, \( \text{cm}^{-1} \)) \( \nu_{\text{max}} (-\text{NH}_2) \) 3301, 3272; \( ^1\text{H} \) NMR (300 MHz, CD\(_3\)CN) \( \delta \) 1.65-1.69 (m, 4H), 2.52 (s, 3H), 2.796 (t, 2H, \( J = 7.8 \) Hz), 2.928 (t, 2H, \( J = 6.9 \) Hz), 7.22 (d, 2H, \( J = 3.9 \) Hz) 7.38 (quintet, 4H, \( J = 6.3 \) Hz) 7.53 (m, 2H), 7.70 (m, 4H), 8.01 (t, 4H, \( J = 6.3 \) Hz), 8.34 (d, 2H, \( J = 10.5 \) Hz), 8.46 (d, 4H, \( J = 8.10 \) Hz); \( ^{13}\text{C} \) NMR (75 MHz, CD\(_3\)CN) \( \delta \); ESI-MS: \( m/z \ [^{102}\text{Ru+2PF}_6+\text{H}^+]^+ \) 946.0 (Calculated: 945.7), \( [\text{Ru}+\text{PF}_6]^+ \) 800.1 (Calculated: 799.74), \( [^{102}\text{Ru+2PF}_6-\text{NH}_2]^+ \) 928.1 (Calculated: 928.7); HR-MS (+ESI): \( m/z \ [^{102}\text{Ru-2PF}_6]^{2+} \) 327.5999 (Calculated: 327.5998); EA: \( \text{C}_{35}\text{H}_{36}\text{N}_7\text{RuP}_2\text{F}_{12} \) calc. %C 38.54, %H 3.33, %N 8.99, obs. %C 40.72, %H 3.69, %N 9.04.
Chapter 2 Synthesis of polypyridyl ligands and organometallic complexes

2.2 Results and Discussion

The objective of the work described in this chapter was to produce a range of polypyridyl ligands suitable for the formation of ECL active ruthenium complexes with favourable properties and tailored functionality to facilitate their attachment to electrode surfaces.

2.2.1 Ligand Synthesis

Our first approach for the preparation of appropriate ligands involved the synthesis of non-symmetrical substituted 4,6-diphenyl-2,2′-bipyridines (scheme I). Polypyridine molecules substituted in this way have been prepared previously using a variety of methods and procedures. Traditionally, these compounds have been synthesised through the reaction of N-phenacylpyridinium salts with α,β-unsaturated ketones in the presence of ammonium acetate. The drawback of this method is the pyridinium salts and unsaturated ketone precursor molecules have to be synthesised, resulting in a relatively time consuming and expensive protocol. Based on more recent work published in this area, a straightforward synthetic pathway was applied for the preparation of the 4,6-diphenyl-2,2′-bipyridine derivatives by utilizing the Kröhnke ring assembly. In general, the procedure shown in scheme I involves the preliminary synthesis of the enone through an aldol condensation (step 1) of a para-substituted benzaldehyde and ortho-substituted 2-acetylpyridine in the presence of NaOH and typically an alcohol solvent. A generic bromomethyl ketone, typically aromatic, reacts with anhydrous pyridine to yield the corresponding pyridinium salt. From there, (Step 2 of Scheme I), the desired pyridinium salt is treated with the unsaturated ketone and by a Michael addition, a 1,5-diketone intermediate is formed. Furthermore, as shown in Step 1a the 1,5-diketone can be isolated and the pyridinium salt is not required in this instance. Thus, the 1,5-diketone cyclises in the presence of ammonium acetate to result in the 4,6-disubstituted-2,2′-bipyridine ligand.
The enone based precursor compounds (A7-A12) were prepared under ‘Green Chemistry’, microwave and conventional conditions to identify the best method to introduce the desired functionality. The best yields of enones were obtained with short bursts of 100 W microwave energy with 3-6 cycles, lasting 20-30 seconds each time (Pathway A, step 1, Scheme I). The enones A9-A11 were prepared in this way. The crude enone product would typically precipitate upon cooling in an ice bath, but due to the slight solubility of these enones in ethanol, a small amount of water was added to induce precipitation. In most cases $^1$H NMR indicated the unsaturated enones prepared in this way were sufficiently pure to proceed to the next synthetic step without further purification. Non-derivatised benzaldehyde was also used; however the reaction was complicated by charring of the reaction mixture.

An alternative method for the formation of enones A7-A8 is shown in pathway B, Step 1(Scheme I) and diketone A12, step 1b (Scheme I). It involved a solventless synthesis, where the reactants were ground together adopting the principles of ‘Green Chemistry’ and quantitative reaction yields were obtained. As stated in the literature$^9$ this route worked best for benzaldehyde and terethaldehyde when reacted with acetylpyridine derivatives. This simple preparation led to the synthesis of the desired unsaturated enone, which could either undergo the Kröhnke ring assembly via the addition of the pyridinium salt. Or, the unsaturated enone could be reacted with another single equivalence of base and a second enolisable methyl ketone under solventless conditions to generate the 1,5-diketone intermediate (i.e. compound A12) via a Michael addition. This 1,5-diketone could then be used for the subsequent pyridine ring formation using the Kröhnke synthesis without the pyridinium salt. The more common route to the enone, shown in pathway C, Step 1, Scheme I, was routinely high yielding. However, it was less attractive due to longer reaction times and higher amounts of reagents used compared to pathways A and B but was used to primarily synthesis A7. Thus, pathway A and B were used to synthesise the various unsaturated enones of interest. Once the enone precursors were prepared, the bipyridine derivatives A13-A14 and A16-A17 were formed by reaction with ammonium acetate giving solids which precipitated out rapidly during the reaction. By
using compound \textit{A12} in a similar manner (Step 2, Scheme I) the product (\textit{A13}) was synthesised with a yield of 65\%. Thus, either pathways to the final 2,2′-bipyridine derivative were comparable with respect to the final yield. The nitro group of compound \textit{A14} was reduced to an amine (\textit{A15}) with 80\% conversion using 10\% Pd / C in ethyl acetate under a H$_2$ atmosphere.

With the goal of simplifying and improving methods for the functionalisation of electrodes, alternative synthetic schemes were derived for the synthesis of known mono / di substituted 4,4′-functionalised 2,2′-bipyridine derivatives. The goal was to use these ligands to covalently attach the electro-active luminophore to the electrode substrate.

Using the approach similar to Scheme I, mono-phenyl substituted 2,2′-bipyridines can be synthesised as shown in Scheme II. Sodium pyruvate is reacted with para-nitro benzaldehyde to generate 4-(4-nitrophenyl)-2-oxo-3-butenoic acid, (\textit{B20}). Compound \textit{B20} is then reacted with the pyridinium salt in an aqueous solution of excess ammonium acetate to 4-(4-Aminophenyl)-2,2′-bipyridine (\textit{B22}). Scheme II is based on the synthetic scheme published by Baba et al.\textsuperscript{12} and others,\textsuperscript{11,43} using a variation of the Kröhnke pyridine synthesis. The reduction of the nitro group of \textit{B21} yielded \textit{B22} as the aromatic amine. This external amine group is of particular interest as a potential site for means of binding the luminescent metal complexes to solid surfaces for sensor development.

The synthetic scheme shown in Scheme III is a very flexible way of introducing a functionalized alkyl side chain onto the 2,2′-bipyridine structure and involves the reaction of lithiated 4,4′-dimethyl-2,2′-bipyridine (dm-bpy) with 2-(2-bromoethyl)-1,3-dioxolane. In order to minimize the amount of symmetrical bipyridines produced, which were difficult to separate from the desired unsymmetrical bipyridine, it was necessary to use just under 1 equivalent (0.9-0.98) of n-butyllithium in the lithiation of 4,4′dimethyl-2,2′-bipryridine. The product, 4-[3-(1,3-dioxolan-2-yl)propyl]-4′-methyl-2,2′-bipyridine (\textit{C24}) was obtained in 56\% yield, was efficiently de-protected (90\%)
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by acid hydrolysis to the aldehyde $C26$. The symmetrically substituted derivative of 2,2'-bipyridine was also of interest in this project, and was synthesized in a similar way as the mono analogue except 2-equivalences of n-butyllithium was used. The product, 4,4'-di(3-propyl-1,3-dioxolane)-2,2'-bipyridine, ($C25$) was obtained in 60% yield and was also deprotected in high yield (89%) by acid hydrolysis to the di-aldehyde $C27$. The aldehyde functional group, with its intermediate oxidation level, could then be easily subjected to a range of transformations under mild conditions. Additionally, the aldehydes were easily oxidised to the corresponding carboxylic acids ($A28$, $A29$) with sodium chlorite and hydrogen peroxide were collectively quantitative with 98-99% yields obtained.

In Scheme, IV, the lithiation of 4,4'-dimehtyl-2,2'-bipyridine (dm-bpy, $C23$) is shown followed by the reaction of this compound with 1,3-dibromopropane to form the bipyridine linked alkyl bromide ($C30$). The bromide could then be used to synthesis the phthalate intermediate ($C31$). The standard Gabriel synthesis was not carried out on $C31$ to the amine ($C32$). Although the deprotection of $C31$ has been demonstrated to be quantitative$^{15}$ it was not necessary to obtain the free amine at this stage, as a better yield was obtained by first synthesising the ruthenium(II) complex, [Ru(bpy)$_2$(pht-bpy)](PF$_6$)$_2$ ($C31$), followed by conversion of the phthalate of $C31$ to the amine group by treatment with hydrazine.

2.2.2 Synthesis of ruthenium(II) polypyridyl complexes

The series of luminescent ruthenium(II) polypyridyl complexes [Ru(phen'')$_3$]$^{2+}$ and [Ru(bpy)$_2$(bpy'')]$^{2+}$, (where phen' is a 1,10-phenanthroline derivative and bpy' is a 2,2'-bipyridine derivative) synthesised in this project represent a series of compounds that posses chemical functionality for electrode modification which will be useful for electrochemical and ECL studies. All complexes were characterised via mass spectrometry, NMR ($^{13}$C, $^1$H), IR, and CHN elemental analysis. The mass spectrometry results of each complex
showed an isotopic pattern for ruthenium. The abundant isotope $^{102}\text{Ru}$ was used to determine the main ion peak for each complex synthesised.

In generalised procedure 2.1.3 the chloride salts of $[\text{Ru(bpy)}_3]\text{Cl}_2\cdot x\text{H}_2\text{O}$ and $[\text{Ru(phen)}_3]\text{Cl}_2$ were metathesised to their respective $\text{PF}_6^-$ salts in quantitative yields. The Ru(II) complexes containing 1,10-phenanthroline based ligands $[\text{Ru(dpp)}]([\text{PF}_6])_2$ (complex 8) and $[\text{Ru(tmphen)}_3]([\text{PF}_6])_2$ (complex 9), dpp$^\prime = 4,7$-diphenyl-1,10-phenanthroline, and tmphen $= 3,4,7,8$-tetramethyl-1,10-phenanthroline, were obtained in different conditions. The sequential reaction of $\text{RuCl}_3.3\text{H}_2\text{O}$ with (dpp) in ethylene glycol / H$_2$O generated complex 8; Complex 9 was first obtained as the chloride salt via the reaction of $\text{K}_3[\text{Ru(III)(H}_2\text{O})\text{Cl}_5]$ with tmphen in HCl / H$_2$O and was then metathesised to the $\text{PF}_6$ salt using generalised procedure 2.1.3. In most cases, we adopted $[\text{Ru(bpy)}_2\text{Cl}_2]$ as the starting complex because of its stability, ready availability and versatile nature for the introduction of a third functionalised bipyridine ligand into the coordination sphere. Introduction of the new ligand will change the electronic properties of the resulting complex and ultimately provide new chemical approaches to electrode modification. Thus, we have synthesised a series of Ru(II) complexes from $[\text{Ru(bpy)}_2\text{Cl}_2$ with bpy$^\prime$ in EtOH / H$_2$O to form $[\text{Ru(bpy)}_2\text{(bpy)}]([\text{PF}_6])_2$ complexes where bpy$^\prime$ is 4,6-diphenyl-2,2$^\prime$-bipyridine, (dpb, complex 11); 4$^\prime$-aminophenyl-2,2$^\prime$bipyridine, (apb), (complex 12); 4$^\prime$-methyl-2,2$^\prime$-bipyridine-4-butoanoic acid, (mbpyb, complex 6); 4-(4-Phthalimidobutyl)-4$^\prime$-methyl-2,2$^\prime$-bipyridine, (pht-bpy, complex 13); 4-(4$^\prime$-methyl-2,2$^\prime$-bipyridine)aminobutyl, (mab-bpy, complex 7). These heteroleptic ruthenium(II) complexes were isolated as $\text{PF}_6^-$ salts with yields ranging from 40-80%, which depended on the ligand used to chelate with $[\text{Ru(bpy)}_2\text{Cl}_2]$. 

2.3 Conclusion

A series of 2,2′-bipyridyl ligands were synthesised using Kröhnke ring assembly or chemical functionalisation of 4,4′-dimethyl-2,2′-bipyridine. In the case of the former, the precursors were easily prepared using conventional methods, a microwave method and in some cases under solventless conditions. The pyridine ring assembly of 4,6-disubstituted-2,2′-bipyridine ligands were synthesised through the reaction of N-phenacylpypyridinium salts with α,β-unsaturated ketones in the presence of ammonium acetate. Furthermore, 4-phenyl substituted 2,2′-bipyridine derivatives were synthesised using a modified version of the Kröhnke synthesis. These bipyridines were used to prepare [Ru(bpy)₂(bpy′)](PF₆)₂ complexes. The chemical functionalisation of 4,4′-dimethyl-2,2′-bipyridine was used as the starting material to generate species with alkyl carboxylic acid or amine functionality. We also utilised 1,10-phenanthroline derivatives to synthesis homoleptic complexes of [Ru(phen′)₃](PF₆)₂ which adhere to electrode surfaces simply by virtue of their hydrophobicity, (see chapter 4).
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References

Chapter 3 Solution phase properties of ECL active tris(2,2′-bipyridine)ruthenium(II) derivatives.

3.0 Introduction

Amongst their many important applications,\textsuperscript{1-3} ruthenium polypyrine complexes have been widely used for photoluminescence, chemiluminescence (CL) and electrochemiluminescence (ECL) analysis.\textsuperscript{4-6} Although the majority of these studies have focussed on tris(2,2′-bipyridine)ruthenium(II) \([\text{Ru(bpy)}_3]^{2+}\) (see Figure 3.0 for ligand structures), a wide range of analogues and derivatives have been explored\textsuperscript{5-7} to modify the chemical or spectroscopic properties, immobilise the complex, or to bind it to specific functionality to create new avenues for chemical measurement, such as the synthesis of ECL labels for immunoassay or luminescent hosts for anion sensing.
Figure 3.0 Ligands selected for comparison (within heteroleptic [Ru(bpy)$_2$(L)]$^{2+}$ complexes denoted by the number below each ligand): 2,2′-bipyridine (bpy); 4,4′-dimethyl-2,2′-bipyridine (dm-bpy); 2,2′-bipyridine-4,4′-dicarboxylic acid (dc-bpy); dimethyl 2,2′-bipyridine-4,4′-dicarboxylate (dm-bpy-dc); bis((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) 2,2′-bipyridine-4,4′-dicarboxylate (men-bpy-dc); $N^4,N^4$-bis((2S)-1-methoxy-1-oxopropan-2-yl) 2,2′-bipyridyl-4,4′-dicarboxamide (Me-ALA-bpy-dca); 4′-methyl-2,2′-bipyridine-4-butanoic acid (mba-bpy); 4-methyl-4′-aminobutyl-2,2′-bipyridine (mab-bpy) and [4-(4-phthalimidobutyl)-4′-methyl-2,2′-bipyridine (pht-bpy).
The characteristic orange photoluminescence from $[\text{Ru(bpy)}_3]^{2+}$ follows the excitation of an electron from the metal-based d ($\pi^*$) orbitals to the ligand-based $\pi^*$ antibonding orbitals – a metal-to-ligand charge-transfer (MLCT) – followed by intersystem crossing to the lowest triplet state, from where the emission occurs. The same MLCT state may be attained in CL or ECL reactions if an electron is transferred from a powerful reductant derived from the analyte/co-reactant to the $\pi^*$ orbital of a bipyridine ligand of $[\text{Ru(bpy)}_3]^{3+}$. The addition of electron withdrawing groups on the ligands of $[\text{Ru(bpy)}_3]^{2+}$ causes a red-shift in the emission spectrum by lowering the $\pi^*$ (LUMO) energy levels. Ligands that have electron-donating substituents (such as methyl groups) can also lower the energy of the radiative transition, because the extra electron density destabilises the $d\pi$ (HOMO) orbital in the ground state species, reducing the energy gap to the $\pi^*$ level of the charge-acceptor bipyridine ligands. However, a clear understanding of the extent that different functional groups influence the spectral distribution has been hampered by the disparity of conditions (solvent, reference electrode, concentration of the complex, number of derivatised ligands on each complex) between studies, and the frequent use of uncorrected emission spectra, which is particularly problematic for species that emit above 600 nm, where there is significant changes in the relative response of many photomultiplier tubes.

The work presented here was motivated by our interest in developing ECL based sensing materials with varying emission wavelengths for potential applications in multiplexed sensing, as well as the ability to be coupled to target analytes or electrode surfaces. Such applications require careful control over often opposing redox, spectroscopic and physical properties. Because the ECL process is typically complex, spectroscopic or electrochemical information cannot be used in isolation to predict ECL intensity. For example, tris(2-phenylpyridine)iridium(III), which has a photoluminescence quantum yield of 97% in oxygen-free solvent, was investigated as a promising ECL emitter. However, its favourable photophysical properties did not translate into analytically useful ECL because the oxidation potential (~0.55 V vs. Fc/Fc+).
ferrocene)\textsuperscript{17} is too low to give efficient co-reactant ECL. On the other hand if
the oxidation potential of a complex is too high, parasitic side reactions may
degrade the sensitivity or selectivity of the ECL assay.\textsuperscript{18}

In this study, we compare the spectroscopy, electrochemistry and ECL of
tris(2,2'-bipyridine)ruthenium(II) derivatives containing one ligand with
chemical functionality that has commonly been used to either modify the
characteristics of the parent complex or link it with other species. One such
ligand is 4,4'-dimethyl-2,2'-bipyridine (dm-bpy). Numerous researchers have
examined the influence of simple electron-donating substituents on the
fundamental properties (such as electron localisation, photoluminescence
quantum yields, and ECL intensities) of ruthenium polypyridine
complexes.\textsuperscript{9,10,19,20} Longer alkyl groups have been used to provide space
between the ruthenium complex and functionality used for labelling or
immobilisation\textsuperscript{21,22} or link multiple ruthenium complexes.\textsuperscript{23} We have therefore
included 4-methyl-4'-aminobutyl-2,2'-bipyridine (mab-bpy) and 4'-methyl-2,2'
bipyridine-4-butanoic acid (mba-bpy), which have previously been utilised as
ECL labels\textsuperscript{24} and in the synthesis of ECL dendrimers.\textsuperscript{25,26}

The influence of electron-withdrawing substituents on the physical and
photophysical properties of ruthenium complexes containing 2,2'-bipyridine-
4,4'-dicarboxylic acid (dc-bpy) has also been explored by numerous
researchers.\textsuperscript{9,11,27-29} Moreover, there has been considerable interest in
ruthenium complexes containing this ligand as components of dye-sensitised
solar cells, because the carboxylate groups provide a convenient point of
attachment to TiO\textsubscript{2} semiconductors.\textsuperscript{30,31} The esterification of 2,2'-bipyridine-4,
4'-dicarboxylic acid has been used to develop ligands that further modify the
properties of the complex,\textsuperscript{14,32} introduce new structures (such as labelling
groups,\textsuperscript{33} hydrophobic alkyl chains\textsuperscript{34} and chiral functionality\textsuperscript{35,36}) and form
electrochemiluminescent metallo dendrimers.\textsuperscript{37} Ruthenium complexes
incorporating the dimethyl ester of 2,2'-bipyridine-4,4'-dicarboxylic acid (dm-
bpy-dc) have been used in solid-state light-emitting devices because the
esterified ligands result in a more "technologically useful" red luminescence
(λ_{max} = 690 nm) compared to the red-orange emission of [Ru(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2}.\textsuperscript{38} For the current investigation, we have prepared the dimethyl ester (dm-bpy-dc), and di-(1R,2S,5R)-menthyl ester (men-bpy-dc) derivatives of 2,2′-bipyridine.

The formation of amides by combining 2,2′-bipyridine-4, 4′-dicarboxylic acid with derivatised amino acids is another convenient approach to manipulate the exterior structure of ruthenium polypyridine complexes, which has been exploited for the development of photoinduced electron transfer agents.\textsuperscript{39,40} More generally, ligands with an amide group adjacent to the bipyridine ring have been incorporated into ruthenium complexes for the development of ECL dendrimers,\textsuperscript{26} immobilised CL and ECL reagents\textsuperscript{41,42} and anion sensors,\textsuperscript{43} and to introduce chiral functionality\textsuperscript{44} or other groups that modify the properties of the complex.\textsuperscript{31} We have included a complex containing a 2,2′-bipyridyl-4, 4′-dicarboxamide ligand (Me-ALA-bpy-dc) prepared using the methyl ester of L-alanine, to examine the influence of amide functionality. Furthermore, we have included complex 13 containing a [4-(4-phthalimidobutyl)-4′-methyl-2,2′-bipyridine ligand (bpypht) for comparison with the free amine complex 7.

I would like to acknowledge that ruthenium polypyridyl complexes (1-5) were synthesised by Naomi A. Lewcenko (Deakin University, Geelong, Australia). The photoluminescence data were collected by Dr Paul Francis (Deakin University) and the computational studies were performed by Dr David Wilson (La Trobe University, Bundoora, Australia).
3.1 Materials, Apparatus and Methods

General

All commercial reagents (Sigma-Aldrich) were of analytical grade or higher were used without further purification unless otherwise stated. Acetonitrile was distilled from CaH₂ in a recycling still. Aqueous solutions were prepared using deionised water (18 MΩ cm⁻¹) and were kept refrigerated at 5 °C for no longer than 1 week. Deionised water (18 MΩ cm⁻¹) and/or acetonitrile were used for rinsing the electrochemical glass cell throughout these experiments. Ruthenium complexes (1-5) described in this chapter were supplied by Deakin University, Geelong, Victoria, Australia.

General instrumentation

Absorption and emission spectra

UV-visible absorbance spectra were collected using a Cary 300 Bio UV-Vis spectrophotometer (Varian Australia, Mulgrave, VIC, Australia) with 1 cm path length quartz cells. Photoluminescence spectra were collected with a Cary Eclipse Spectrofluorimeter (Varian Australia, Mulgrave, VIC, Australia) with a R928 photomultiplier tube (Hamamatsu, Iwata-gun, Shizuoka-ken, Japan), using a 1 cm quartz cuvette (5 nm band pass, 1 nm data interval, PMT voltage: 800 V). Emission spectra correction factors were established using an Optronic Laboratories spectral irradiance standard (model OL 245M) with constant current source (model OL 65A). ECL spectra were obtained using a Ocean Optics CCD, model QE6500, UV/VIS fibre optic (length 1.00 metre) and the trigger was a HR 4000 Break-Out box in conjunction with the P.G stat 12 AUTOLAB. All ECL intensities recorded were baseline corrected to eliminate scattered light in the custom built faraday cage.

Photoluminescence quantum yields (Φₚ) were measured with reference to the following equation:

\[
\Phi_x = \Phi_{\text{ref}} \left( \frac{\text{Grad}_x}{\text{Grad}_{\text{ref}}} \right) \left( \frac{\eta^2_x}{\eta^2_{\text{ref}}} \right) \]  

(1)
where $\Phi_{\text{ref}}$ is the quantum yield of the reference complex, $[\text{Ru(bpy)}_3\text{(PF}_6\text{)}_2]^{2+}$ (0.062 in CH$_3$CN)$^{45}$; $x$ denotes sample and ref is the reference; $\text{Grad}$ is the gradient of the absorbance vs. integrated emission intensity graph, using at least five different concentrations with absorbance below 0.1 and achieving $R^2$ close to 1; $\eta$ is the refractive index of the solvent used. Quantum yield determinations were conducted at room temperature (21±3°C). All solutions were thoroughly degassed with nitrogen in septum sealed quartz cells prior to measurements.

**Cyclic voltammetry and ECL**

Electrochemical experiments were performed using µAUTOLAB type II electrochemical station potentiostat (MEP Instruments, North Ryde, NSW, Australia) with General Purpose Electrochemical Systems (GPES) software (version 4.9). The electrochemical cell consisted of a glass cell with a quartz window base and Teflon cover with spill tray. The cell was encased in a custom-built light-tight faraday cage (see Figure 3.1). A conventional three-electrode configuration, consisting of a glassy carbon 3 mm diameter working electrode shrouded in Teflon (CH Instruments, Austin, TX, USA), a 1 cm$^2$ platinum gauze auxiliary electrode and a silver wire quasi reference electrode. Potentials were referenced to the ferrocene/ferrocenium couple measured in situ (1 mM) in each case.

Solution phase ECL efficiencies ($\Phi_{\text{ECL}}$) were evaluated using the equation:

$$\Phi_{\text{ECL}} = \Phi^\circ_{\text{ECL}} \left( \frac{I}{Q_f} \right) \left( \frac{I^\circ}{Q^\circ_f} \right)$$

(2)

where $\Phi^\circ_{\text{ECL}}$ is the ECL efficiency of the standard, (1 mM $[\text{Ru(bpy)}_3]^{2+}$ and 0.1 M $[\text{Bu}_4\text{N}]\text{[PF}_6\text{]}$ in acetonitrile) taken as 5.0% $^{46}$, I and $I^\circ$ are the integrated PMT responses for the sample and the standard respectively, and $Q_f$ and $Q^\circ_f$ are the faradaic charges passed for the sample and standard respectively.

The potentials used to generate the 3+ and 1+ forms of the ruthenium complex in the annihilation reaction were obtained from the cyclic voltammograms. The cathodic and anodic potentials were stepped for 1.0 s
and the ECL chronoamperometry experiments underwent 10 cycles. $\Phi_{\text{ECL}}$ values measured using the CCD and PMT were identical within experimental error.

The ruthenium complexes were prepared at a concentration of 1 mM in freshly distilled acetonitrile, with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte. Prior to each experiment, the working electrode was polished using 0.3 µm and then 0.05 µm alumina with water on a felt pad, sonicated in Milli-Q water (1 min), rinsed in freshly distilled acetonitrile and dried with a stream of nitrogen. The working electrode was then positioned at an appropriate distance (~2 mm) from the bottom of the cell for detection of the ECL signal, and the solution was purged with nitrogen for 10-15 min. See Figure 3.1 for electrochemical cell set up for ECL experiments. All solutions were scanned between 1.6 V and -2.5 V with an initial potential of 0 V. Scan rates ranging from 0.01 to 0.5 V s$^{-1}$ were used in cyclic voltammetry to evaluate diffusion coefficients (D) using the Randles Sevcik equation.
Chapter 3 Solution phase properties of ECL active tris(2,2'′-bipyridine)ruthenium(II) derivatives.

Figure 3.1 This is the cell used to perform all electrochemical and ECL experiments which is enclosed in a light tight Faraday cage.

Computational Methods

Density functional theory (DFT) calculations were carried out by Dr. David Wilson, La Trobe University, within the Gaussian 09 suite of programs.\(^{47}\) Geometries were optimised in the absence of solvent with the B3LYP \(^{48-50}\) and mPW1PW91 \(^{51,52}\) functionals, with both yielding similar structures. Only mPW1PW91 results are presented, since it has been shown previously that this functional yields reliable results.\(^{53}\) Symmetry of the optimised structures was D$_3$ (0), C$_2$ (1-3) and C1 (4-7). Three metal effective-core potential (ECP) basis sets were considered for geometry optimizations and molecular orbital
Chapter 3 Solution phase properties of ECL active tris(2,2′-bipyridine)ruthenium(II) derivatives.

(MO) calculations: LANL2MB,$^{54-56}$ LANL2DZ,$^{56,57}$ and SDD.$^{57,58}$ In each case the 6-31+G(d) basis set$^{59-61}$ was used for all non-metal atoms. Final single-point energy calculations were carried out at the SDD/6-31+G(d) optimised geometries using the SDD basis for Ru and the TZVP basis set$^{62,63}$ for all other atoms. The polarisable continuum model (PCM)$^{64}$ was used to model solvent effects at the gas-phase optimised geometries with a solvent of acetonitrile. Calculations with water solvent produced almost identical results and so only results including solvation by acetonitrile are presented here. HOMO and LUMO energies were calculated using DFT MOs, as well as with time-dependent DFT (TD-DFT)$^{65}$ using the SDD/TZVP basis sets, which may be expected to yield more accurate and reliable LUMO energies. SCF convergence criteria of $10^{-8}$ a.u. was employed throughout. Molecular orbital analysis was carried out with the AOMix program.$^{66}$
3.2 Results and Discussion

3.2.1 Spectroscopic Properties of [Ru(bpy)$_2$(L)](PF$_6$)$_2$

The UV-VIS spectra of compounds 0 – 7 on page 96 are typical of ruthenium polypyridyl complexes. The UV region is dominated by spin allowed $\pi$-$\pi^*$ ligand-centered (LC) transitions while a broad lower intensity band appears at longer wavelengths assigned to a metal to ligand charge transfer (MLCT) (i.e. $d \rightarrow \pi^*$ transition). The position of the MLCT band for the complexes in acetonitrile varies between 450 nm and 480 nm depending on the identity of the ligands (Table 3.0). Following optical excitation, the initially produced $^1$MLCT rapidly decays through intersystem crossing to the corresponding triplet state ($^3$MLCT) with close to unit efficiency.

<table>
<thead>
<tr>
<th>Complex number</th>
<th>Ligand</th>
<th>Functionality</th>
<th>Abs. $\lambda_{\text{max}}$ / nm</th>
<th>Photoluminescence $\lambda_{\text{max}}$ / nm (corrected)</th>
<th>$\Phi_p^a$</th>
<th>ECL $l_{\text{max}}$ / nm</th>
<th>$\Phi_{ECL}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>bpy</td>
<td>-</td>
<td>451</td>
<td>618</td>
<td>0.062</td>
<td>620</td>
<td>0.050</td>
</tr>
<tr>
<td>7</td>
<td>mab-bpy</td>
<td>alkyl</td>
<td>448</td>
<td>625</td>
<td>0.055</td>
<td>625</td>
<td>0.001</td>
</tr>
<tr>
<td>6</td>
<td>mba-bpy</td>
<td>alkyl</td>
<td>454</td>
<td>629</td>
<td>0.074</td>
<td>630</td>
<td>0.040</td>
</tr>
<tr>
<td>4</td>
<td>Me-ALA-bpy-</td>
<td>amide</td>
<td>469</td>
<td>668</td>
<td>0.085</td>
<td>666</td>
<td>0.065</td>
</tr>
<tr>
<td>3</td>
<td>dm-bpy-dc</td>
<td>ester</td>
<td>478</td>
<td>686</td>
<td>0.061</td>
<td>685</td>
<td>0.049</td>
</tr>
<tr>
<td>5</td>
<td>men-bpy-dc</td>
<td>Ester</td>
<td>478</td>
<td>686</td>
<td>0.072</td>
<td>685</td>
<td>0.055</td>
</tr>
<tr>
<td>13</td>
<td>pht-bpy</td>
<td>alkyl-phthalate</td>
<td>450</td>
<td>625</td>
<td>0.047</td>
<td>625</td>
<td>0.074</td>
</tr>
</tbody>
</table>

Table 3.0 Spectroscopic data for the [Ru(bpy)$_2$(L)]$^{3+}$ complexes in acetonitrile.

$^a$Relative quantum yield (tris(2,2′-bipyridine)ruthenium(II) = 0.062) (acetonitrile, room temperature, degassed).

For each of the complexes, intense luminescence results from the decay of this excited state. Figure 3.2a shows the corrected photoluminescence spectra for [Ru(bpy)$_3$]$^{2+}$ and the derivatives containing attachment functionality (in deaerated CH$_3$CN at room temperature). The emission colour varies significantly depending on the nature of the substituents. The data presented...
in Table 3.0 show that there is a range of approximately 70 nm between the unsubstituted \([\text{Ru(bpy)}_3]^{2+}\) standard and the longest wavelength emitting ester derivatised complex. The y-axis has been normalised in Figure 3.2a for the absorbance of each solution in order to emphasize the relative photoluminescence efficiencies \((\Phi_p)\) of the complexes. The values of \(\Phi_p\), using \([\text{Ru(bpy)}_3]^{2+}\) as a standard, varied between approximately 6% and 8% (Table 3.0).

![Figure 3.2 Photoluminescence (a) and ECL spectra (b) of \([\text{Ru(bpy)}_2(L)]^{2+}\) complexes in acetonitrile. The ECL was generated using a glassy carbon electrode in a 1 mM solution of the complex containing 0.1 M TBAPF$_6$ supporting electrolyte. The y-axis in (a) is normalised for the photons absorbed while the y-axis in (b) is normalised for the electrons passed during the generation of the luminescence.](image-url)
3.2.2 Solution phase electrochemistry of [Ru(bpy)$_2$(L)]($PF_6$)$_2$ complexes in organic media

The electrochemical data are summarised in Table 3.1, while Figure 3.3 shows representative cyclic voltammetric responses for three complexes; the butanoic acid (6), methyl (1), and ester (5) derivatives. All of the complexes exhibit voltammetric behaviour typical of ruthenium polypyridyl complexes. A single redox process corresponding to the Ru$^{2+}$/Ru$^{3+}$ redox couple occurs at high positive potentials, while three or more stepwise ligand reductions are observed in the negative region of the voltammogram. Electrochemical reversible solution phase behaviour was observed for most processes. However, when the potential was swept further negative for complex 2 irreversible peaks were observed in the cathodic region for the 2,2ʹ-bipyridyl reductions. Values of the diffusion coefficient (D) (see Table 3.1) in each case were evaluated from the slopes of plots of peak current versus square root of scan rate for the metal based redox couple.

<table>
<thead>
<tr>
<th>Complex number</th>
<th>Ligand</th>
<th>$E^0$ / V (vs Fc)</th>
<th>$10^8$ D / cm$^2$s$^{-1}$</th>
<th>$\Delta E^0$ (II - I)$^a$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>bpy</td>
<td>0.892</td>
<td>-1.754 -1.937 -2.178</td>
<td>5.8 -2.65</td>
</tr>
<tr>
<td>1</td>
<td>dm-bpy</td>
<td>0.833</td>
<td>-1.759 -1.961 -2.211</td>
<td>7.3 -2.59</td>
</tr>
<tr>
<td>7</td>
<td>mab-bpy</td>
<td>0.833</td>
<td>-1.755 -1.954 -2.217</td>
<td>2.1 -2.59</td>
</tr>
<tr>
<td>13</td>
<td>pht-bpy</td>
<td>0.91</td>
<td>-1.677 -1.783 -1.882</td>
<td>2.4 -2.59</td>
</tr>
<tr>
<td>6</td>
<td>mba-bpy</td>
<td>0.836</td>
<td>-1.756 -1.972 -2.233</td>
<td>4.3 -2.59</td>
</tr>
<tr>
<td>2</td>
<td>dc-bpy</td>
<td>0.996 (-1.494)</td>
<td>- - -</td>
<td>6.4 -2.49</td>
</tr>
<tr>
<td>4</td>
<td>Me-ALA-bpy-dc</td>
<td>0.967</td>
<td>-1.467 -1.861 -2.077</td>
<td>4.4 -2.43</td>
</tr>
<tr>
<td>3</td>
<td>dm-bpy-dc</td>
<td>0.983</td>
<td>-1.396 -1.857 -2.058</td>
<td>4.9 -2.38</td>
</tr>
<tr>
<td>5</td>
<td>men-bpy-dc</td>
<td>0.996</td>
<td>-1.385 -1.837 -2.036</td>
<td>4.9 -2.38</td>
</tr>
</tbody>
</table>

Table 3.1 Electrochemical data for the [Ru(bpy)$_2$(L)]$^{3+}$ complexes in acetonitrile. $^a$$\Delta E^0$ (II - I) represents the HOMO - LUMO gap or the free energy ($\Delta G$) for the reaction between the oxidised, [Ru(bpy)$_2$(L)]$^{3+}$ and reduced [Ru(bpy)$_2$(L)]$^{2+}$ forms of the complex.
Adding an electron withdrawing ester functionality has a significant effect on the voltammetric response, resulting in a large positive shift of 0.36 V in the first reduction potential. This is illustrated in Figure 3.3 for complex 5, which shows that the reduction process associated with the derivatised ligand is significantly displaced from the two subsequent bipyridine reductions. There is also a small positive shift of 0.1 V in the formal potential of the Ru$^{2+/3+}$ couple. By contrast, the ligand reductions remain evenly spaced and virtually unaffected by the methyl substitution in the case of complex 6 (Figure 3.3), though there is a small negative shift of 0.06 V in the metal oxidation potential. Figure 3.4(a) and the data in Table 3.1 show that these trends also apply to the other complexes studied. The carboxylate functionality on 2, 3, 4 and 5 significantly lowers the reduction potential relative to the unsubstituted
complex 0 but only moderately increases the oxidation potential, with the ester producing a larger shift than the amide. In the case of 1, and 6, the ligand based reductions are unaffected by the electron donating alkyl substituent, but the complexes are slightly more easily oxidised. Moreover, neither the alkyl chain length nor its end group have any effect on the redox potentials.
Figure 3.4 Effect of substituents on the (a) electrochemical properties and (b) MO energies of $[\text{Ru(bpy)}_2(L)]^{2+}$, where L is the ligand indicated by the number of the complex on the x-axis. Experimental conditions as in Figure 3.3. The open circle represents an irreversible wave. Calculated MO energies at the mPW1PW91/SDD level of theory with acetonitrile solvent.

Electrochemical characteristics are often found to be a good predictor of spectroscopic properties,\textsuperscript{12,67} in particular the HOMO - LUMO gap is closely related to the difference in ground state redox potentials, $\Delta E^\circ (= E^\circ(I) - E^\circ(II))$, see Table 3.1). These values may be compared with the excited state energies from the photoluminescence data. Although the spectroscopic
energy is more accurately estimated from the $E_{0-0}$ band from the low temperature emission spectrum, it has been shown that for a series of related transition metal complexes the difference is constant.$^{12}$ Figure 3.5 shows that there is excellent correlation between $\Delta E^0$ and the energy corresponding to absorption or emission maxima. This implies that the orbitals involved in the electrochemical reactions are identical to those implicated in the MLCT absorption and $\pi^*$-d emission processes. The slope of the linear fit (0.85) also supports this. The intercept of -130 mV arises for two reasons. Firstly, as a consequence of the use of room temperature spectroscopic data, and secondly from coulombic factors because of the different electronic configuration of the state produced by electrochemical reduction of the [Ru(bpy)$_2$(L)]$^{2+}$ complex, i.e. $(t_2g)^6(\pi^*)^1$, and the spectroscopic excited state $(t_2g)^5(\pi^*)^1$.

![Figure 3.5](image)

**Figure 3.5** Correlation of electrochemical with spectroscopic data. $\Delta^0$ is the difference between the first oxidation and first reductions potentials. $E_{em}$ (circles) and $E_{abs}$ (squares) are the energies of the emission and absorption bands respectively. The DFT HOMO-LUMO gap is calculated from mPW1PW91/SDD orbital energies, including effect of acetonitrile solvent.
As the spectroscopic and redox orbitals are equivalent, this allows interpretation of the trends in emission wavelength with reference to the electrochemical data. Clearly, alkyl substitution has the smallest impact on the spectroscopic properties with the emission from 6 and 7 red shifted by no more than 11 nm with respect to the unsubstituted standard, 0. On the basis of the electrochemical data in Figure 3.4, we can surmise that these groups have a small destabilising effect on the HOMO but scarcely impact on the energy of the LUMO at all. This is related to the low percentage contribution to the LUMO for the substituted ligands (L) for these particular complexes as shown in the next section.

On the other hand, amide or ester groups red shift the emission by 50 to 70 nm. The electrochemical trends in Figure 3.4 reveal that this occurs as a result of a significant stabilisation of the LUMO accompanied by a minor decrease in the energy of the HOMO. These data show that the colour of the luminescence can be tuned in these species without significantly altering the energy of the HOMO. This is an important conclusion because, to give efficient, analytically useful ECL, a luminophore also needs to be a strong oxidant, generally with a formal potential $\approx 1$ V vs. Ag/AgCl or greater. These experiments show that ECL active sensing materials could be designed to exhibit significantly different coloured emission for multiplexed detection while maintaining relatively constant redox ability.

### 3.2.3 Theoretical Calculations

Initial calculations of HOMO-LUMO energies in the gas phase produced results with little correlation to experimental trends. In this work the effect of solvation on MO energies, and in particular the HOMO-LUMO gap, was very significant. Inclusion of solvent effects yielded trends in much better agreement with experimental data. For this reason, only theoretical results including solvation effects are presented. The minimal LANL2MB basis set produced apparently spurious results, while the LANL2DZ and SDD results
followed similar trends. Single-point energies with the TZVP basis (with SDD for Ru) yielded similar results to the 6-31+G(d) basis (SDD for Ru), with the TZVP calculated HOMO-LUMO gap consistently smaller by 0.02 eV. For the purpose of comparison with experimental data, only SDD/TZVP calculated results have been considered, although the SDD/6-31+G(d) results may equally have been used.

Plots of MO energies in Figure 3.4 illustrate the similarity of trends between the calculated energies and the observed electrochemical properties. That is, two groups are formed with LUMOs of ca. -3.1 eV (2-5), and ca. -2.6 eV (0, 1, 6, 7). The HOMO energy is reasonably consistent for all compounds. This grouping in LUMO energy is responsible for the significant increase in HOMO-LUMO gap that occurs between 4 and 0, which is consistent with the experimental observation of a change in redox and spectroscopic properties between the same compounds. The actual values of the HOMO-LUMO gaps calculated by DFT and time dependant (TD) DFT are presented in supporting information where they are compared with the corresponding spectroscopic and electrochemical data.

Mulliken population analysis of the frontier MOs (summarised in Figure 3.6) serves to illustrate how the nature of the HOMO and LUMO explains the observed trends in spectroscopic and electrochemical properties. The population analyses are included in the appendix (Appendix Figure 3.0 - 3.8). For compounds 0, 1, 6, and 7, the LUMO is predominantly bpy in character, however for compounds 2-5, the LUMO is dominated by contributions from the modified ligand (L). In each case the HOMO contributions are reasonably consistent (about 80% Ru metal contribution). This analysis goes some way to confirming that we can ‘tune’ electrochemical and photophysical properties by ‘tuning’ the LUMO energy, as was our goal in this work.
Figure 3.6 Percentage contribution to HOMO and LUMO of metal centre (Ru), bipyridine ligands (bpy) and substituted ligand (L) in \( [\text{Ru(bpy)}_2(L)]^{2+} \) complexes.

3.2.4 Solution phase electrochemiluminescence

The ECL properties of ruthenium diimine complexes are well known. One pathway by which the emission can be produced is via potential step annihilation ECL experiments, where the electrode potential is alternated between values sufficiently positive to generate the 3+ form and sufficiently
negative to generate the 1+ forms of the complex. This results in generation of
the excited complex according to reactions (1-5):

1. \[ [\text{Ru}(\text{bpy})_2(L)]^{2+} \rightarrow [\text{Ru}(\text{bpy})_2(L)]^{3+} + e^- \]
2. \[ [\text{Ru}(\text{bpy})_2(L)]^{2+} + e^- \rightarrow [\text{Ru}(\text{bpy})_2(L)]^+ \]
3. \[ [\text{Ru}(\text{bpy})_2(L)]^{3+} + [\text{Ru}(\text{bpy})_2(L)]^+ \rightarrow [\text{Ru}(\text{bpy})_2(L)]^{2+} + [\text{Ru}(\text{bpy})_2(L)]^{2+} \]
4. \[ [\text{Ru}(\text{bpy})_2(L)]^{3+} + [\text{Ru}(\text{bpy})_2(L)]^+ \rightarrow 2 [\text{Ru}(\text{bpy})_2(L)]^{2+} \]
5. \[ [\text{Ru}(\text{bpy})_2(L)]^{2+} \rightarrow [\text{Ru}(\text{bpy})_2(L)]^{2+} + h\nu \]

Although this annihilation mode of ECL is not typically used in sensing, it
serves as a useful means to characterise the fundamental aspects of the ECL
properties of luminophores because of the relative complexity of mechanisms
involved in the co-reactant mode of ECL. For each of the complexes studied
here, such annihilation experiments resulted in intense emission from the
electrode surface that was easily visible with the naked eye. ECL efficiencies
(\(\Phi_{\text{ECL}}\)), defined as the number of photons emitted per electron transferred in
reaction 5 and 6 above, were determined by comparing charge passed in the
forward step to the integrated light intensity from the ECL spectrum collected
during the reverse step, using Equation 2, with \([\text{Ru}(\text{bpy})_3]^{2+}\) as a reference
(\(\Phi_{\text{ECL}} = 0.05\)).

Figure 3.2b shows the ECL spectrum for each of the ruthenium complexes.
The y-axis is normalised for the charge passed during the forward potential
step of the experiment used to generate the emission. The relative heights of
the peaks in this figure therefore reflect the relative ECL efficiencies of the
complexes in an analogous manner to the absorbance normalised spectra in
Figure 3.2a. This figure and the data in Table 3.0 show that with the exception
of complex 7 (\(\Phi_{\text{ECL}} = 0.001\)), the ECL efficiency \(\Phi_{\text{ECL}}\) varies over quite a
limited range (0.040 to 0.065) and each of the complexes have similar or
slightly higher efficiencies than the parent complex, \([\text{Ru}(\text{bpy})_3]^{2+}\).
In general, the efficiency of ECL emission is determined by a number of (sometimes competing) factors including the quantum yield of emission $\Phi_p$ according to:

$$\Phi_{ECL} = \Phi_{ex} \Phi_p$$  \hspace{1cm} (7)

where $\Phi_{ex}$ is the efficiency associated with the production of the excited state. Thus $\Phi_{ECL}$ also depends on the competition between reactions leading to excited state and ground state and on the stability of the redox partners in 0 above. Finally, $\Phi_{ECL}$ also depends on the free energy change associated with the annihilation reactions (5) and (6) above. Reaction (5), which produces an excited state (es), competes with the much more exergonic reaction (6) to ground state (gs). According to the Marcus theory of electron transfer, photons are produced because the rate of (6) is kinetically inhibited depending on the extent of its exergonicity.

The values of $\Delta G_{gs}$ for reaction (6) are calculated from the redox potentials of the species involved and are numerically equal to the $\Delta E^o$ (HOMO - LUMO gap) values given in Table 3.1. The values of $\Delta G_{es}$ for reaction 0 may be estimated using equation (8):

$$\Delta G_{es} = \Delta E^o + E_{MLCT}$$  \hspace{1cm} (8)

where $E_{MLCT}$ is the spectroscopic energy of the excited state, which is best taken from the low temperature emission spectrum, but may be obtained from room temperature data to a first approximation. Table 3.1 shows that the values of $\Delta G_{gs}$ ($=\Delta E^o$) vary between -2.38 and -2.66 eV. As these values exceed the excited state energies in each case, which vary between 1.81 eV for 5 and 2.01 eV for 0, all of the ECL reactions are energy sufficient systems. Substituting this data into equation 8 shows that values of $\Delta G_{es}$ vary over quite a narrow range between -0.59 eV and -0.65 eV. That no correlation is observed between $\Phi_{ECL}$ or $\Phi_{ex}$ and $\Delta G_{gs}$ or $\Delta G_{es}$, is perhaps not surprising given the narrow range of exergonicities, however it is also clear that other factors apart from energetics come into play in determining the ECL intensity.
In agreement with eqn 7, the value of $\Phi_{\text{ECL}}$ tracks $\Phi_{\text{p}}$ quite well in most cases; the efficiency of excited state production $\Phi_{\text{ex}}$ is $78 \pm 3\%$ for each compound excluding 6 and 7. The butanoic acid functionalised complex 6 has the highest photoluminescence efficiency yet the lowest ECL efficiency, which we attribute to side reactions with the carboxylic acid that compete with reaction 5. Similarly, complex 7 has a pendant amine group, which may be directly oxidised at the electrode. In addition to degrading the overall efficiency of reaction 5, this is likely to interfere with ECL in other ways such as electrode passivation or quenching of the excited state.

### 3.3 Conclusions

The luminescence of tris(2,2'-bipyridine)ruthenium(II) derivatives (with functionality enabling coupling to other molecules or surfaces) can be spectrally tuned over a range of wavelengths by varying the substituents at the 4 and 4' positions of one of the bipyridine ligands. Alkyl groups tend to moderately destabilise the HOMO without affecting the LUMO. Amide or ester groups on the other hand moderately stabilise the HOMO but significantly stabilise the LUMO. The ability to tune the luminescence without significantly altering the energy of the HOMO (i.e. maintaining relatively constant redox ability) is important as it allows for the design of ECL probes with different coloured emission for applications such as multiplexed detection. DFT calculations showed that the LUMO is dominated by the substituted ligand for the complexes containing electron withdrawing substituents and by the unsubstituted bpy ligand for the complexes containing electron donating groups. Therefore, in addition to offering insights into their fundamental properties, DFT may be used to predict trends in redox and spectroscopic properties within a related set of complexes such as this. It is thus a potentially useful tool in the discovery of new ECL and CL active luminophores.

The electrochemical HOMO-LUMO gap is a good predictor of the spectroscopic properties. Excellent correlation was observed between the
difference in ground state redox potentials, $\Delta E^o$, ($\Delta E^o = II - I$), and the energy corresponding to absorption or emission maxima. ECL intensity in general depends on a number of competing factors; if some of these can be held constant, ECL efficiency can be more easily predicted. The relationship between the exergonicity of the annihilation reaction leading to photon emission and $\Phi_{ECL}$ is well known. $^{68}$ Because the same factors that dictate $\Delta G$ for the annihilation reaction (i.e. the relative energies of the HOMO and LUMO) have a corresponding effect on the energy of the excited state product, the value of $\Delta G_{es}$ is relatively constant (0.61 ± 0.03 eV) for this series of complexes. Most of the complexes populate the excited state with an efficiency ($\Phi_{ex}$) of close to 80% under the conditions used in this study, suggesting that the stability of the redox partners and the competition between reactions leading to excited state and ground state is about the same for most of the complexes. However, in the case of 6, $\Phi_{ex}$ is only 54%, with the result that it has the second lowest ECL efficiency despite having the highest PL quantum yield. The low $\Phi_{ex}$ may be because the acid functionality introduces the possibility of competing side reactions. The ECL of the alkylamine complex 7, which has a $\Phi_{ex}$ of only 2%, is even more dramatically affected because in addition to other possible side reactions the amine moiety may react with the carbon electrode itself resulting in passivation. Clearly, potentially reactive groups should be avoided in the design of ECL based sensing materials because of the possibility of side reactions occurring during or after the electrochemical step. It should be noted however that the effect of the reactive group is negated when it is used for labelling purposes, as demonstrated by the strong ECL observed for 4 where the carboxylic moiety has been used to couple the complex to an amino acid. Complexes 6 and 7 have served the purpose of illustrating a point in this study but it is acknowledged that their properties will be altered when used in a labelling or bioconjugation context. Despite the range of factors that may degrade the efficiency of population of the excited state, in general, the photoluminescence quantum yield ($\Phi_p$), is a reasonable predictor of the ECL yield ($\Phi_{ECL}$), within related sets of compounds such as this.
Chapter 3 Solution phase properties of ECL active tris(2,2'-bipyridine)ruthenium(II) derivatives.

References:

Chapter 3 Solution phase properties of ECL active tris(2,2'-bipyridine)ruthenium(II) derivatives.

Chapter 3 Solution phase properties of ECL active tris(2,2′-bipyridine)ruthenium(II) derivatives.


(66) Gorelsky, S. I.; University of Ottawa.


Chapter 4 Solid-state electrochemical properties of ruthenium polypyridyl complexes

4.0 Introduction

A rich array of applications has sprung from studies of ECL-producing systems both in solution and solid-state formats. The growing interest in ECL is driven primarily by their use in analysis.1-3 Another motivation for the study of electrochemiluminescent systems is the development of organic light-emitting devices (OLEDs) and the investigation of their principles of operation, since a similar mechanism to ECL is proposed for such solid-state systems. This is especially the case for the relatively new type of OLED known as a light emitting electrochemical cell (LEEC), which makes use of metal electrodes and ionic charge carriers.4 Indeed, high quantum efficiency and high radiant output have been achieved for OLEDs based on ruthenium and osmium bipyridyl complexes.5

The majority of ECL systems that have been investigated have involved freely diffusing species, with emission originating from a reaction layer near the electrode surface. However, ECL has also been generated in films constrained to the surface of an electrode, which usually involves attachment to or entrapment within a passive matrix.6 Examples include electrostatic binding to ionomers such as Nafion, covalent attachment to polymeric species such as polyvinyl pyridine7 and dispersion within sol-gels and sol-gel composites. Modification of electrode surfaces with films of the luminescent moiety alone has also been demonstrated in the form of Langmuir-Blodgett films, self-assembled monolayers8 and electropolymerization of vinyl-containing luminescent monomers.9 However, apart from studies involving two-electrode solid-state devices,10 where cathodic and anodic processes cannot be studied separately, the ECL properties of a neat luminescent complex in solid form has scarcely been investigated.11,12
From an electrochemical point of view, direct immobilization of insoluble micro-crystalline material on electrode surfaces represents a powerful approach to the investigation of charge transfer and related processes in solids. This so-called voltammetry of micro-particles methodology, developed by Scholz, Bond and others\textsuperscript{13-15} allows switching of the oxidation state of solid deposits in contact with an electrolyte phase, in which the material is insoluble, with charge neutrality maintained by permeation of ions into the solid. A range of solid-state phenomena have been probed using this approach. For example, nucleation and growth\textsuperscript{13,14} electrocrystallization, protonation\textsuperscript{15} charge transport\textsuperscript{16,17} and isomerisation\textsuperscript{18} have been investigated within solid particles adhered to electrode surfaces in this way. In applications relating to analytical, electrochromic and light emitting device alike, a short response time for switching from one oxidation state of a solid to another is crucial\textsuperscript{13,14,19}. Therefore, an important objective is to determine the rate at which mobile species, i.e., ions and electrons, can shuttle through these materials. The electrochemistry of micro-particles approach allows this as well as kinetic and thermodynamic aspects of such materials to be studied with relative ease.

The use of optically transparent electrodes (OTEs) for \textit{in situ} spectral monitoring of electrochemical processes represents a powerful combination of techniques. Spectroelectrochemistry has been used not only for the identification of electrogenerated products, but has been successfully applied to the delineation of both homogeneous and heterogeneous kinetics and the evaluation of thermodynamic parameters. While the majority of such investigations have focused on solution phase systems, spectroelectrochemical approaches have also been used successfully in the characterization of modified electrodes. For example, in the field of bioelectrochemistry the technique known as derivative cyclic voltabsorptometry (DCVA), where the derivative of the optical signal is monitored with respect to an applied triangular potential waveform, has been used for the study of redox proteins immobilized on electrode surfaces\textsuperscript{19,20}. DCVA is particularly useful in this area because the signal is morphologically identical to a background-free cyclic voltammogram. \textit{In situ} combinations of
spectroscopic techniques such as UV-VIS absorbance,\textsuperscript{21} X-ray diffraction\textsuperscript{22} and diffuse reflectance\textsuperscript{23,24} with the voltammetry of micro-particles methodology, significantly augment and enhance the efficacy of the approach in the characterization of solid-state processes. \textit{In situ} UV-VIS absorbance solid-state spectro electrochemistry is particularly relevant to the characterization of materials for electrochromic applications.

We have used the solid-state approach to investigate the solid-state electrochemical, spectro electrochemical and ECL properties of the ruthenium tris-phenanthroline derivatives \([\text{Ru(dpp)}_3](\text{PF}_6)_2\) and \([\text{Ru(tmp)}_3](\text{PF}_6)_2\), where dpp is 4,7-diphenyl-1,10-phenanthroline and tmp is 3,4,7,8-tetramethyl-1,10-phenanthroline. The properties of \([\text{Ru(phen)}_3](\text{PF}_6)_2\) and \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) (where phen is 1,10-phenanthroline and bpy is 2,2′-bipyridine) were also obtained for comparison. The ability to study ECL in the solid-state is valuable as it may provide valuable fundamental insights into radiative charge recombination in solids. Moreover, the ability to easily screen the solid-state properties of such materials will aid the design and optimisation of new light emitting devices.

A noteworthy aspect of this chapter is the application of DCVA and chronospectrometry (CS) to the characterization of complexes in the solid-state. We have singled out two of the complexes for special attention in this regard; tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)bis-hexafluorophosphate, \([\text{Ru(dpp)}_3](\text{PF}_6)_2\), and a novel complex, bis-(2,2′-bipridine)(4,6-diphenyl-2,2′-bipyridine)ruthenium(II)bis-hexafluorophosphate, \([\text{Ru(bpy)}_2(dpb)](\text{PF}_6)_2\) which is similar in structure to \([\text{Ru(bpy)}_3]^{2+}\), but made hydrophobic by the substitution of phenyl groups on one of the ligands.

Ruthenium (N)\textsubscript{6} species generally have high oxidation potentials. The motivation for using DCVA and CS was driven in part by the difficulty, under some circumstances, of obtaining a clear voltammetric signals for these materials due to the proximity of their peaks to the solvent limit. We
demonstrate also the possibility of obtaining peak height as well as peak potential data from appropriately corrected responses and the equivalent of a “pure” CV in which the signal is solely due to the redox reaction under study. We also demonstrate a facile method for the simulation of Spectro electrochemical responses (CS or DCVA) using commercially available electrochemical simulation software such as DigiElch or DigiSim.

4.1 Experimental

Materials, Apparatus and Methods

General

All Commercial reagents (Sigma-Aldrich) were of analytical grade or higher were used without further purification unless otherwise stated. All electrolyte solutions used in this study were freshly prepared in deionised water (18 MΩ cm\(^{-1}\)) and kept for no longer than 1 week in a refrigerator at 5 °C. Deionised water (18 MΩ cm\(^{-1}\)) and/or reagent grade ethanol were used for rinsing the electrochemical glass cell throughout these experiments.

General instrumentation

Solid-state electrochemical measurements were carried out using µAUTOLAB type (II) (Eco Chemie) electrochemical station potentiostat (MEP Instruments, North Ryde, NSW, Australia) with General Purpose Electrochemical Systems GPES 3.9 software or CH instruments (Austin, TX, USA) model 660B, 620C electrochemical workstation potentiostat on a personal computer. Solid-state and solution phase Ultraviolet-visible spectra were recorded using an Ocean Optics USB2000 USB-ISS-UV/VIS spectrometer with OOIBase32 software; or on a Varian Cary UV/Vis spectrometer with Eclipse software. Fluorescence spectra were recorded on Varian Cary Eclipse Fluorescence spectrometer
with a solid sampling accessory used to determine the solid-state emission of the phenanthroline based ruthenium complexes.

Cyclic Voltammetry and ECL

For ECL experiments refer to Chapter 3 (pg 8-12) for ECL experimental details. Solid-state electrochemical experiments were performed in a conventional three-electrode cell where the working electrode was either a 3 mm glassy carbon (GC) electrode (CH Instruments) or Boron Doped Diamond (BDD). These were fitted with a rubber O-ring for a secure placement in the electrode holder. These GC and BDD electrodes were cleaned in the same way previously stated in Chapter 3 of the experimental. A Ag/AgCl (3 M KCl) reference electrode was employed for solid-state electrochemistry in aqueous media. In all aqueous solid state electrochemical experiments, the potentials were referenced to the formal potential of the ferrocene / ferrocenium couple measured \textit{in situ}. A platinum wire or gauze (1 cm$^2$) served as the counter electrode in each case. GC disks (15 mm diameter) (Sigradur-G) were used for the \textit{in situ} and \textit{ex situ} AFM studies. Imaging was done on an NT-MDT Ntegra AFM platform (http://www.ntmdt.com) capable of \textit{in situ} electrochemistry, with µMasch NSC36B uncoated probes, using intermittent contact (aka tapping) mode. Spectroelectrochemical measurements were made using a 1 cm$^2$ quarts cuvette as the electrochemical cell. This consisted of a transparent 5 cm x 0.9 cm Indium tin oxide (ITO) coated glass slide (Aldrich) as the working electrode (8-12 $\Omega$.cm$^{-2}$) with the active area defined by masking part of the conductive surface with Teflon® tape (see electrode modification chapter 4 for details). ITO electrodes were sonicated for 5 min in Milli Q water and then left to dry prior to solid-state deposition for electrochemical experiments. A modified ITO electrode was held flush against the inner face of the cuvette, with the conductive side facing the solution, such that it was maintained perpendicular to the beam. The working electrodes, excluding ITO substrates, were polished in the same fashion with BUEHLER Microcloth® Polishing Cloth in aqueous slurries of 0.3 $\mu$m and 0.05 $\mu$m alumina as described in Chapter 3. The BDD electrode was subject to a cathodic pre-
treatment in 1 M HNO₃ once at the beginning of the study. All solutions were deoxygenated using grade 5 nitrogen for 10-15 min prior electrochemical experiments measurements and were carried out at ambient temperature (20 ± 2 °C).

Numerical smoothing and differentiation were carried out using a fifteen or seventeen-point Savitsky–Golay algorithm. Simulation of transient electrochemical (and absorbance) data was performed using the electrochemical simulation software, DigiElch (version 4, build 2.704).

4.1.1 Electrode Modification

For solid-state voltammetric measurements on all conventional and GC disc electrodes, the ruthenium polypyridyl hexafluorophosphate salt complexes dissolved in analytical grade acetone were typically immobilised on the working electrode by drop coating 1 to 2 µL of a cold (4 °C) 1.0 mM solution. Upon evaporation of the solvent, a thin film is seen on the pre-polished electrode surface. The modified layer was then further left to stand and dry on the electrode surface in an enclosed container for 4 - 6 minutes prior to electrochemical measurements.

For electrochemical and spectroscopic measurements on ITO electrodes, the complexes were deposited in the same manner and dried as described above, except the area covered by deposition solution (0.2 to 0.5 cm²) was defined by drop coating over a Teflon tape mask.
4.2 Results and Discussion

4.2.1 Solution phase electrochemical and spectroscopic properties of the Ru(II) polypyridyl complexes

The solution phase electrochemical and spectroscopic properties were measured in order to benchmark the solid-state studies we performed. The solution phase cyclic voltammetric responses for [Ru(dpp)_3]^{2+}, [Ru(tmp)_3]^{2+} and [Ru(bpy)_3]^{2+} are shown in Figure 4.0 and the data are summarized in Table 4.0. The corresponding data for, [Ru(phen)_3]^{2+} and [Ru(bpy)_2(dpz)]^{2+} under the same conditions are also given in Table 4.0 for comparison. The solution phase CVs, shown in Figure 4.0, are typical for ruthenium diimine complexes of this type. When freely diffusing, all of the ruthenium complexes exhibit archetypal reversible solution phase behaviour for the Ru^{2+}/Ru^{3+} redox couple. Values of the diffusion coefficient (D) for the Ru^{2+} species in each case were evaluated from the slopes of plots of peak current versus square root of scan rate. The formal potential (E°) for the Ru^{2+}/Ru^{3+} couple increases in the order tmp < dpp < dpb < bpy < phen, consistent with the relative donor abilities of bipyridine and phenanthroline and the relative electron donating abilities of the substituents on the phenanthroline and bipyridine ligands. When the electrode potential was negatively scanned, in the case of [Ru(tmp)_3]^{2+}, three closely spaced redox couples are observed in the region of -2.0 V vs. ferrocene. These are assigned to three successive one electron reductions associated with the ligands. In the case of [Ru(dpp)_3]^{2+}, only a typical diffusional response was obtained in this negative range when the potential was reversed immediately following the first ligand reduction. If the potential was scanned to values favouring the formation of an uncharged complex, the response was strongly perturbed by adsorption effects.

Table 4.0 also lists the solution phase ECL efficiencies (Φ_{ECL}) and photoluminescent quantum yields (Φ_{em}). Because Φ_{ECL} is a function of Φ_{em}, as expected the photoluminescent quantum yields follow a similar trend to the
ECL efficiencies for the complexes used in this study. The photoluminescence in these complexes originates from a triplet state populated by efficient intersystem crossing from the singlet. The good agreement between the ECL and photoluminescence maxima in each case suggests that the same excited state is reached regardless of the mode of excitation. The solution phase $\Phi_{ECL}$ and $\Phi_{em}$ yields are not displayed for $[\text{Ru(bpy)}_2(\text{dpb})]^2^+$, as this complex showed poor luminescence properties. Although, it was used in the solid-state spectro electrochemistry study which will be discussed later in this chapter.
Figure 4.0 Solution phase cyclic voltammograms of (top to bottom), [Ru(tmp)$_3$]$^{2+}$, [Ru(dpp)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ at 0.1 Vs$^{-1}$ using a 3 mm GC electrode. 1 mM solutions in acetonitrile containing 0.1 M [Bu$_4$N][PF$_6$] as supporting electrolyte.

The absorbance properties of each complex are also summarized in Table 4.0. The UV / VIS spectra each show a characteristic d-$\pi^*$ metal to ligand charge transfer (MLCT) band in the region of 450 nm. Other peaks are observed in the UV region which are chiefly associated with ligand centred (LC) $\pi$-$\pi^*$ states. Figure 4.1 shows the solution phase spectro
electrochemistry of $[\text{Ru}(\text{dpp})_3](\text{PF}_6)_2$. Electrolysis at a sufficiently positive potential of solutions of any of these complexes in acetonitrile results in the loss of the MLCT band, and the appearance of a shoulder at $<400$ nm, (assigned to a metal centred transition). When the electrolysis potential is returned to a value more negative than the formal potential for the Ru$^{2+}$/Ru$^{3+}$ couple, the MLCT band reappears and the shoulder disappears signifying the restoration of the original 2+ oxidation state of the complex. This demonstrates that oxidation/reduction of these complexes is chemically reversible.

**Figure 4.1** Solution phase UV-VIS spectro electrochemistry of $[\text{Ru}(\text{dpp})_3](\text{PF}_6)_2$ in contact with a Pt gauze electrode in CH$_2$CN / 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte. The electrode was biased at a potential of 1.3 V vs. Ag wire for 5 mins.
Chapter 4 Solid-state electrochemical properties of ruthenium polypyridyl complexes

<table>
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<th>Solution Phase</th>
<th>Solid-State</th>
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<tr>
<td>$E^o / V$ (vs Fc)</td>
<td>$E_{1/2} V$ (vs Ag/AgCl)</td>
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<tr>
<td>I</td>
<td>II</td>
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<tr>
<td>[Ru(dppe)$_3$]$^{2+}$</td>
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</tr>
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<td>[Ru(bpy)$_2$(dpb)]$^{2+}$</td>
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<th>Table 4.0</th>
<th>Solution phase and solid-state electrochemical, spectroscopic and ECL properties of ruthenium diimine complexes.</th>
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<td>$^a$Ref.27  $^b$Ref.28  $^c$Values of $\lambda_{max}$ are corrected for variation in photomultiplier tube (PMT) response with wavelength.</td>
<td></td>
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4.2.2 Solid-state electrochemistry of Ru(II) polypyridyl complexes

Figure 4.2 illustrates the repetitive cyclic voltammetry for a layer of micro-particles of [Ru(dpp)₃](PF₆)₂ immobilized on a GCE in the presence of 0.1 M perchlorate at a scan rate of 0.1 V s⁻¹. The voltammetric response evolves during the initial scans, with the peak current increasing by approximately 30% over the first 50 cycles (~20 min). Also, the anodic and cathodic peak potentials, $E_{p,a}$ and $E_{p,c}$, shifted in a negative potential direction by approximately 25 mV during this period. After this initial “break-in” period, a relatively stable voltammetric response is obtained. The magnitude of the voltammetric peaks gradually decrease in magnitude, typically decreasing by less than 20% with constant cycling (at 0.1 V s⁻¹) for 1 hour.
Figure 4.2 Solid-state cyclic voltammogram of micro-particles of \([\text{Ru(dpp)}_3](\text{PF}_6)_2\) on a 3-mm GCE in contact with 0.1 M LiClO₄ electrolyte at 0.1 V s⁻¹ showing break-in effect. The first 15 cycles are solid lines while the 50th cycle is shown as a dotted line. The inset shows the variation in the oxidation peak current \((i_{p,\text{ox}})\) with cycle number.

With less frequent cycling (2 cycles / h) the peaks take approximately 8 h to decrease by a similar proportion. The voltammetry of the solid deposits is similar in some respects to the solution phase response shown in Figure 4.0; the reversible potential, \(E_{1/2}\), of 1.14 V (defined as the average of \(E_{p,a}\) and \(E_{p,c}\)), is similar to 0.85 V obtained for the complex in the solution phase experiment and the anodic to cathodic peak current ratio of 0.95 is close to unity. The peaks show distinct tailing, reminiscent of a diffusional response and the peak currents \((i_{p,\text{ox,red}})\) vary linearly with the square root of scan...
rate at moderate to high scan rates (as shown in Figure 4.3B). The peak to peak separation ($\Delta E_p$) is larger in the CV for the immobilised material compared to its solution phase response seen in Figure 4.0. This is likely due to ohmic effects associated with the solid deposit, although slow interfacial kinetics may also contribute. At slower scan rates ($<5 \text{ mV s}^{-1}$) the cyclic voltammogram shows little or no peak tailing, and the peak current varies linearly with scan rate which is shown in Figure 4.3A. This behaviour is consistent with the onset of finite diffusional behaviour where the immobilised material is exhaustively oxidised during the voltammetric scan. The transition between the two types of peak shape is best observed in the cyclic voltabsorptommetric response which represents the pure faradaic response without the distorting effects of the solvent electrolysis limit. The finite / semi infinite interpretation is confirmed by such spectro electrochemical experiments conducted on the solid deposits which will be illustrated later in this chapter.
Layers of the [Ru(tmp)_3](PF_6)_2 show a similar break-in effect to [Ru(dpp)_3](PF_6)_2 and similar overall voltammetric response with the exception that the magnitude of the peaks decreases over a shorter period of time. In this case, by about half in the first 60 minutes of constant cycling. The lesser stability of immobilized layers of this material is not unexpected given the relatively lower hydrophobicity of the tetramethyl phenanthroline ligands. By contrast with the substituted phenanthroline complexes, layers composed of [Ru(phen)_3](PF_6)_2 or [Ru(bpy)_3](PF_6)_2 prepared in the same way, dissolved entirely from the electrode surface within 2-3 cycles.
Morphological studies

The results of *in situ* electrochemical AFM studies are shown in Figure 4.4. Images were taken in 0.1 M perchlorate electrolyte solution. The electrode surface was largely featureless prior to deposition, with a few visible scratches from polishing, as shown in Figure 4.4 (top left). Immobilization of [Ru(dpp)$_3$](PF$_6$)$_2$ as described in the experimental section, results in a surface layer of sub-micron size particles that cover the surface relatively homogeneously; the electrode surface is exposed in gaps between the particles (Figure 4.4, top right).

**Figure 4.4** Atomic force microscopy (AFM) and *in situ* electrochemical AFM of immobilized micro-particles on a glassy carbon substrate. The upper two frames show the substrate before and after deposition, while the four lower frames show the particles after 1, 10, 50 and 70 voltammetric cycles. Initial and final potentials used were 0 V and 1.3 V respectively. A composite movie, available as online supplementary material to ref, makes finding the changes easier.
Cyclic voltammetry results in structural changes, noticeable as appearance and disappearance of small particles around the larger ones (Figure 4.4, bottom panel, circles). While at first AFM tip artefacts might be suspected, particles appear on different frames in different parts of the picture: 1) in frames 2 and 3; 2) in frames 1-3; 3) in frames 1, 4; and 4) in frame 4. Thus, the effect is real. Simultaneously, the size of the larger (original) particles also undergoes subtle changes, in a few cases suggesting that smaller particles fuse into larger ones in what may be an Ostwald ripening type phenomenon. Note however that the voltammetric current increased during the time over which these changes were observed. Therefore, it would seem that electrocrystallization of smaller particles at the expense of larger ones is the dominant process, at least during these early scans. A composite movie, available online makes finding the changes easier. See: 

**Ion pairing Effects** Changes in reversible potential ($E_{1/2}$) reflect variations in the relative stabilities of reduced and oxidized forms and may be used to probe ionic interactions within the solid. Figure 4.5 shows that the reversible potential of the immobilized $[\text{Ru(dpp)}_3](\text{PF}_6)_2$ complex is sensitive to the concentration of supporting electrolyte. Consistent with ion pairing, $E_{1/2}$ shifts in a negative direction as $[\text{ClO}_4^-]$ increases, indicating that it becomes progressively easier to oxidize the solid with increasing perchlorate ion concentration. In solid-state systems of this type, the reversible potential as defined, characterizes both an electron and an ion transfer equilibrium

$$[\text{Ru(dpp)}_3]^{2+}[\text{A}^-]_{2(s)} - e^- + [\text{A}^-]_{(aq)} \rightleftharpoons [\text{Ru(dpp)}_3]^{3+}[\text{A}^-]_{3(s)} \quad (1)$$

where $\text{A}^-$ is the $\text{ClO}_4^-$ or $\text{PF}_6^-$ anion which is incorporated into or expelled from the particle in order to maintain electroneutrality. Assuming electrochemical reversibility, the Nernst equation predicts a slope of 56 mV
per decade change in [ClO$_4$] at 20°C. Our observed slope of 61 mV dec$^{-1}$ for [Ru(dpp)$_3$](PF$_6$)$_2$ is consistent with electroneutrality being maintained by means of a single anion entering the solid and becoming paired with the redox centre, when Ru$^{2+}$ is oxidized to Ru$^{3+}$. Immobilized particles of [Ru(tmp)$_3$](PF$_6$)$_2$ displayed a similar sensitivity to electrolyte concentration with the $E_{1/2}$ of the Ru$^{2+/3+}$ redox couple decreasing by 70 mV per decade change in perchlorate ion concentration. The solid-state electrochemical properties of [Ru(dpp)$_3$]$^{2+}$ and [Ru(tmp)$_3$]$^{2+}$ are summarized in Table 4.0

![Dependence of the solid-state reversible potential ($E_{1/2}$) on log [LiClO$_4$] between 0.1 M and 1.0 M electrolyte concentration for micro-crystals of [Ru(dpp)$_3$](PF$_6$)$_2$ immobilised on a GCE.](image)
The electrochemical response was also dependent on the identity of the anion of the supporting electrolyte. For example, in the presence of KCl, KF, Na$_2$SO$_4$ and NaNO$_3$, no Faradaic current at all was detectable. This is due to the hydrophobic nature of the thin layer of the ruthenium complex on the electrode surface which would not allow hydrophilic charge compensating counterions to perform charge neutrality during a voltammetric scan. Only in the presence of ClO$_4^-$, PF$_6^-$ or BF$_4^-$ based electrolytes, was a wave similar to that in Figure 4.2 observed. Within this set of anions a small dependence of reversible potential on anion was also noted with ClO$_4^-$ < PF$_6^-$ < BF$_4^-$ . The $E_{1/2}$ values obtained were 1.14, 1.17 and 1.20 V for ClO$_4^-$, PF$_6^-$ and BF$_4^-$ respectively. Similar ion dependences have been noted in previous studies involving solid-state electrochemical transitions. Such observations highlight the importance of the ion transfer step in solid-solid transitions of this type. Anions of low charge density (such as the latter three mentioned) will tend to be weakly solvated and thus more hydrophobic, allowing for more facile transport across the solution-solid interface with these hydrophobic ruthenium complexes.

**Homogeneous charge transport**

The response time of electrochromic or light emitting devices is related to the rate at which an electrochemical reaction can spread through the solid material of which it is composed. In solid-state electrochemical systems such as these, the charge transfer reaction is assumed to start at the electrode-particle-solution triple interface followed by growth of the depletion zone into the particle following semi-infinite linear diffusion. The rate of this charge percolation may be characterized by the apparent charge transport diffusion coefficient ($D_{CT}$). Since physical diffusion of the redox centres is not possible within a rigid solid matrix, $D_{CT}$ may be limited by either electron hopping (self-exchange) or by the movement of charge compensating counter ions. When ion transport is the rate limiting step, $D_{CT}$ may exhibit sensitivity to electrolyte concentration. It
is important to investigate the dynamics of the charge transport as it gives an insight to the rate and mechanism of charge propagation in solid-state devices based on materials of this type. We have used a combination of electrochemical and spectro electrochemical techniques to gain insight into the rate and mechanism of homogeneous charge transport through \([\text{Ru}(\text{dpp})_3](\text{PF}_6)_2\) and \([\text{Ru}(\text{tmp})_3](\text{PF}_6)_2\) solid deposits.

As noted\(^{32}\), the voltammetric response of these deposits is well described by a semi-infinite diffusional model of charge transport at sufficiently short experimental timescales. For example, between \(0.08 \text{ V s}^{-1} < n < 0.500 \text{ V s}^{-1}\) the peak current scales linearly with the square root of scan rate. The slope of such a plot may be used to obtain information regarding the charge transport characteristics of the deposit using the Randles-Sevcik equation, given below.

\[
i_p = 2.69 \times 10^5 n^{3/2} A D_{\text{CT}}^{1/2} C_o \nu^{1/2}
\]

Where \(i_p\) is the peak current (A), \(n\) is the electron stoichiometry, \(A\) is the electrode area (cm\(^2\)), \(D_{\text{CT}}\) is the apparent charge transport diffusion coefficient (cm\(^2\) s\(^{-1}\)), \(\nu\) is the scan rate (V s\(^{-1}\)) and \(C_o\) is the effective fixed site concentration (mol cm\(^{-3}\)). The concentration of Ru sites within the solid particles of the diphenyl phenanthroline complex was estimated as 0.95 M based on a crystallographic volume of 7013 Å\(^3\) (unit cell, \(z = 4\))\(^{33}\). In the case of the tetramethyl phenanthroline complex, a concentration of 1.36 M was used based on the crystallographic data for the dimethyl phenanthroline complex, 2442 Å\(^3\) (unit cell, \(z = 2\))\(^{34}\). These values are of a similar magnitude to experimentally determined concentrations used in previous solid-state electrochemical investigations of structurally similar systems\(^{35,36}\).

Randles-Sevcik plots constructed from data obtained in 0.1 M LiClO\(_4\) at scan rates between 0.08 and 0.5 V s\(^{-1}\) indicate that the \(D_{\text{CT}}\) values are \(2.8(\pm1.0) \times 10^{-11}\) and \(3.5(\pm1.0) \times 10^{-11}\) for \([\text{Ru}(\text{dpp})_3](\text{PF}_6)_2\) and \([\text{Ru}(\text{tmp})_3](\text{PF}_6)_2\) respectively in 0.1 M LiClO\(_4\).

Charge transport rates may also be conveniently assessed using chronoamperometry. One advantage of using potential step techniques is that the experimental time scale can be straightforwardly controlled such that the
depletion zone remains within the individual micro-particles. It can easily be shown that this is the case for timescales below 40 ms when $D_{CT} < 10^{-10} \text{ cm}^2\text{s}^{-1}$, even for particles as small as 0.04 $\mu\text{m}$. This conclusion is justified based on the AFM results presented in Figure 4.4 which show that the smallest particles are approximately 0.3 $\mu\text{m}$. Therefore, $D_{CT}$ for the each of the deposits was evaluated as a function of electrolyte ion concentration at short timescales, using the Cottrell equation:

$$i(t) = nFAD_{CT}^{1/2} C_o/(\pi t)^{1/2}$$

(3)

where $n$ is the number of electrons transferred, $F$ is the Faraday constant, $A$ is the area of the electrode, $D_{CT}$ is the apparent charge transport diffusion coefficient, $C_o$ is the effective fixed site concentration, $t$ is time (s).

Linear Cottrell plots ($i$ vs. $t^{1/2}$) with zero intercepts were obtained and the slopes were used to evaluate $D_{CT}$ for immobilized deposits of both complexes in contact with concentrations of perchlorate electrolyte ranging from 0.1 M to 1.0 M. As illustrated in Figure 4.6, for $[\text{Ru(tmp)}_3](\text{PF}_6)_2$, $D_{CT}$ depends only weakly on perchlorate ion concentration in this range, increasing from 4.0 to $6.3 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$ as the electrolyte concentration is increased. However, for $[\text{Ru(dpp)}_3](\text{PF}_6)_2$, $D_{CT}$ increases substantially from values similar to that of $[\text{Ru(tmp)}_3]^{2+}$ at low electrolyte concentration, to values of the order of $1 \times 10^{-10} \text{ cm}^2\text{s}^{-1}$ at electrolyte concentrations above 0.6 M.
Figure 4.6 Dependence of the homogenous charge transport diffusion coefficient ($D_{CT}$) of (upper graph) [Ru(dpp)$_3$](PF$_6$)$_2$ and (lower graph) [Ru(tmp)$_3$](PF$_6$)$_2$ on LiClO$_4$ between 0.1 and 1.0 M electrolyte concentrations. Data obtained using chronoamperometry.
Chronospectrometry was used to confirm the charge transport characteristics of the solid material immobilized on transparent ITO electrodes which will be discussed in more detail later in this chapter. The spectro electrochemical approach is a useful verification because the absorbance signal is not affected by charge consuming background processes which could result in errors in the interpretation of Cottrell plots. In all cases the absorbance varied linearly with the square root of time at short timescales demonstrating that semi-infinite diffusional type behaviour is adhered to in this regime. While acknowledging that $D_{\text{CT}}$ is found to vary with the thickness of the deposit, values calculated from such chronospectrometry plots for similar surface coverages were in good agreement with the values obtained here from Cottrell plots using glassy carbon electrodes.

The data in Figure 4.6 may reflect differing rate limiting steps between the two materials. If electron self-exchange is rate determining in either case, the second order self-exchange rate constant ($k_{\text{SE}}$) may be estimated using the Dahms-Ruff expression:

$$D_{\text{CT}} = D_{\text{phys}} + \frac{k_{\text{SE}} \delta^2 C}{6}$$

where $\delta$ is the electron transfer distance, i.e. the separation between adjacent ruthenium atoms and $C$ is the concentration of ruthenium in the solid deposits. $D_{\text{phys}}$, which represents physical diffusion, is zero in this solid-state system. Taking the crystallographic values for $C$ as before and a value of about 9 Å for $\delta$ (also from crystallographic data), the maximum value of $D_{\text{CT}}$ observed for either system yields an apparent self-exchange rate constant of no more than $8.6 \times 10^4$ M$^{-1}$s$^{-1}$. Given that this value is several orders of magnitude lower than the published data for structurally similar ruthenium complexes in solution phase or within self assembled monolayers, it seems reasonable to assume that charge propagation is not limited by self-exchange for either complex.

The weaker dependence of $D_{\text{CT}}$ on electrolyte concentration for the tetramethyl complex may be understood in light of the smaller cell volume (corrected for $z$) associated with the latter (see above). Steric interactions
between phenyl moieties in \([Ru(dpp)_3](PF_6)_2\) result in a structure which is more open and thus more favourably disposed towards ion insertion. Indeed, the existence of a solvent channel parallel to the \(a\) axis was confirmed in the crystal structure of this complex.\(^{33}\) It would appear that the smaller electron transfer distance (\(\delta\)) between ruthenium centres in the denser solid is less important than the impediment to ion flux in determining the rate of charge transport.

4.2.3 Electrochemiluminescent properties of micro-crystals of Ru(II) complexes deposited onto glassy carbon electrodes

### Solution phase ECL

The solution phase electrochemiluminescence of ruthenium diimine complexes is well known. One of the pathways by which the emission can be produced is via potential step chronoamperometric annihilation ECL experiments, where the electrode potential is alternated between values sufficiently positive to generate the 3+ form and sufficiently negative to generate the 1+ forms of the complex. For each of the complexes in Table 4.0 such solution phase annihilation experiments resulted in intense emission from the electrode surface, which was easily visible with the naked eye. ECL efficiencies (\(\Phi_{ECL}\)) were determined by comparing charge passed in the forward step to the integrated light intensity during the reverse step, using equation 1, with \([Ru(bpy)_3]^{2+}\) as a reference (\(\Phi_{ECL} = 0.05\)).\(^{37,38}\) As shown in Table 4.0, \(\Phi_{ECL}\) decreases in the order \([Ru(dpp)_3]^{2+} > [Ru(bpy)_3]^{2+} > [Ru(phen)_3]^{2+} > [Ru(tmp)_3]^{2+} > [Ru(bpy)_2(dpby)]^{2+}\). The ECL of ruthenium complexes may also be generated by application of a single potential in the presence of a suitable co-reactant. For example, when 1 mM solutions of any of the above complexes are oxidized in the presence of sodium oxalate or a suitable amine, an intense emission is visible from the vicinity of the electrode surface.
Solid-state co-reactant ECL

Solid-state ECL was also achieved using immobilized micro-particles of the insoluble phenanthroline complexes. Figure 4.7 shows the results of coreactant ECL experiments conducted with [Ru(dpp)$_3$](PF$_6$)$_2$ immobilized on a GCE. The responses to codeine and oxalate are presented to exemplify the responses for the two main classes of ECL coreactant, (amines and organic acids). Similar responses were observed for tripropylamine, streptomycin and tetracycline.
Figure 4.7 Solid-state ECL from [Ru(dpp)₃](PF₆)₂ using co-reactants in 0.1 M LiClO₄ electrolyte at 0.1 Vs⁻¹. (b) and (f) are blank voltammetric responses in the absence of co-reactant; (a) is the voltammetric response in the presence of 10 mM codeine phosphate; (e) the voltammetric response in the presence of 10 mM sodium oxalate; (c) the ECL emission from 10 mM codeine phosphate; (g) ECL emission from 10 mM sodium oxalate. (d) and (h) are the blank responses representing the PMT signal in the absence of co-reactant.
Solid-state ECL intensities were lower by an order of magnitude in these experiments compared to the solution phase coreactant ECL of [Ru(bpy)_3]^{2+} at a concentration of 5 mM in aqueous solution. It is reasonable to assume that the solid-state ECL follows a similar mechanism to the mechanism of solution phase ECL when the concentration of the emitter is greater than that of the coreactant.\textsuperscript{39-41} i.e.

1. \[ \text{[Ru(dpp)_3]^{2+} \rightarrow [Ru(dpp)_3]^{3+} + e^-} \]
2. \[ \text{[Ru(dpp)_3]^{3+} + A \rightarrow A^{+} + [Ru(dpp)_3]^{2+}} \]
3. \[ \text{A^{+} \rightarrow A^{+} + H^+} \]
4. \[ \text{[Ru(dpp)_3]^{3+} + A^{+} \rightarrow [Ru(dpp)_3]^{2+} + P} \]
5. \[ \text{[Ru(dpp)_3]^{2+*} \rightarrow [Ru(dpp)_3]^{2+} + h\nu} \]

where A is an amine coreactant and P is a product.

Curves (a) and (b) in Figure 4.7 show the solid-state voltammetric response of the immobilized particles, in the presence and absence of 10 mM codeine phosphate respectively. The significant enhancement in oxidative current, observed at the potential at which the Ru^{3+} species is generated, is consistent with an electrocatalytic (EC') mechanism in which Ru^{3+} is recycled electrochemically following its reduction by reactions 2 and 4 above. Curves (c) and (d) show that the oxidation of ruthenium in the presence of the co-reactant is accompanied by emission of light from the layer of immobilised particles, indicating that the Ru^{3+} centres are reduced to the excited state, [Ru(L)_3]^{2+*}, which then relaxes back to the ground state by emission a photon. As little or no direct oxidation of the co-reactant at the electrode is evident in the CV (the amine would be oxidised at \(~0.9\ V\)), the highly reducing intermediate (A^+) necessary to generate the excited state is assumed to be produced predominantly through mediated oxidation, i.e. via reaction 2 above rather than via direct oxidation at the electrode.

The two graphs to the right hand side of Figure 4.7 show the results of the same experiment using oxalate as the co-reactant. The mechanism is similar to that involving amine co-reactants except that in this case the energetic
species produced on reaction with Ru$^{3+}$ is assumed to be CO$_2^-$ and of course reaction 3 above is omitted.$^{40}$ Although the solid-state ECL responses to oxalate and the amine are similar, both current and light emission signals are significantly smaller with the latter. This may be the result of a less favourable interaction of the more polar oxalate ion with the hydrophobic solid or differences in the rate of the cross reaction with Ru$^{3+}$.

The ECL response was found to vary linearly with concentration of co-reactant between 1 mM and 20 mM. This is demonstrated in Figure 4.8, which shows $I_{ECL}$ intensity vs. concentration (mM). At the high concentration end of the graph, the intensity for sodium oxalate detection begins to level off. This is possibly due to the saturation of available [Ru(dpp)$_3$]$^{3+}$ ECL sites at the electrode interface in the presence of an excess concentration of sodium oxalate for ECL analyte detection.
Figure 4.8 Calibration curve ($I_{ECL}$ intensity vs. concentration) for solid-state ECL from $[\text{Ru(dpp)}_3]^{2+}$ micro-crystals deposited on a 3 mm GC electrode in the presence of a solution of sodium oxalate in 0.1 M LiClO$_4$ supporting electrolyte. ECL was generated using chronoamperometry; potential bias 1.3 V. $R^2 = .997$

**Solid-state annihilation ECL**

It is also of interest to explore the ECL which may be produced in these solid deposits in the absence of a co-reactant, via annihilation between the sequentially generated oxidized and reduced forms of the ruthenium complex. Because of the relatively large negative potentials associated with the generation of the +1 form of the ruthenium complexes, electro-reduction of the solid in contact with aqueous electrolyte is complicated by the limited potential window available using conventional electrodes. To address this issue we immobilized the micro-particles on boron doped diamond (BDD) electrodes, which exhibits a significantly enhanced potential window compared to glassy carbon. The solid-state voltammetry associated with the Ru$^{2+}$/Ru$^{3+}$ couple on
BDD is similar to that obtained on glassy carbon, however the response associated with 2+/1+ couple, obtained at about -1.4 V vs. Ag/AgCl, is quasi reversible in nature and becomes irreversible on continuous scanning. This is not surprising, as ruthenium diimine complexes are well known to have relatively poor stability in the reduced form. Similar instability in the reduced form has been reported for solid layers of a hydrophobic tris-bipyridyl ruthenium derivative immobilized in ITO. Figure 4.9 shows the ECL response observed from the solid layer during repetitive pulsing between the oxidized and reduced forms of the material (-1.7 and +1.4 V). No emission was observed when the potential of cathodic step was less negative than that of the reduction peak for the complex. Similar to the solution phase experiment, the emission occurs as a result of the following sequence of reactions:

$$\begin{align*}
6. & \quad [\text{Ru}(L)_3]^{2+} \quad \longrightarrow \quad [\text{Ru}(L)_3]^{3+} + e^- \\
7. & \quad [\text{Ru}(L)_3]^{2+} + e^- \quad \longrightarrow \quad [\text{Ru}(L)_3]^+ \\
8. & \quad [\text{Ru}(L)_3]^{3+} + [\text{Ru}(L)_3]^+ \quad \longrightarrow \quad [\text{Ru}(L)_3]^{2+} + [\text{Ru}(L)_3]^{2+} \\
9. & \quad [\text{Ru}(L)_3]^{2+} \quad \longrightarrow \quad [\text{Ru}(L)_3]^{2+} + h\nu
\end{align*}$$

where L is dpp or tmp. A co-reactant ECL experiment is also shown in Figure 4.9 for comparison, where the potential is pulsed only between 0 V and 1.4 V in the presence of 10 mM sodium oxalate. In this case light emission is only observed during the positive step. The annihilation ECL emission is notably more intense than that produced using the co-reactant pathway. The solid-state ECL intensity was two orders of magnitude higher when produced by annihilation compared to the most intense emission observed using any of the co-reactants tested. However, unlike the co-reactant experiment, the intensity diminishes steadily with time, decreasing by ~70% within 5 double potential steps and reaching background levels after 1-2 minutes of pulsing. The decrease in signal is almost certainly due to the instability of the reduced form of the complex as suggested by the irreversible nature of the voltammetry in the negative region. The pattern observed in the annihilation experiment in Figure 4.9 where the anodic ECL emission peaks are
consistently lower in intensity and shorter lived than each of the alternate cathodic ECL peaks. The higher light intensity during annihilation ECL compared to the co-reactant experiment can be understood if it is considered that the reaction between the reduced and oxidized forms of the complex takes place in a three-dimensional reaction zone within the solid. The difference in undesirable polarity and large molecular size of the analytes compared to the electrolytes used makes them less accessible within the solid layer. Thus, the amine or oxalate molecules are unlikely to penetrate the solid easily. Therefore, the co-reactant ECL emission most likely originates from a two-dimensional interface between the particles and the contacting solution.
Figure 4.9 Solid-state ECL of [Ru(dpp)₃](PF₆)₂ micro-particles on a borondoped diamond (BDD) electrode. Annihilation ECL emission (upper graph) produced by alternating the electrode potential between 1.4 V and -1.7 V using chronoamperometry; co-reactant ECL emission (lower graph) produced by stepping the potential between 1.4 V and open circuit, in the presence of 10 mM sodium oxalate. The first pulse (t = 0) is to the positive limit in both cases and 0.1 M LiClO₄ electrolyte was used.

Figure 4.10 (left hand side) compares the solid-state ECL spectrum for [Ru(dpp)₃](PF₆)₂ with the solution phase spectrum for the complex dissolved in acetonitrile. Similar ECL spectra are produced regardless of whether the co-reactant or annihilation pathway is employed. The corresponding solid and solution phase photoluminescence responses are compared in the right hand
side of Figure 4.10, where an excitation wavelength of 460 nm was used to produce the emission. Significantly, while the emission is identical regardless of whether it is photo-induced or electrochemically derived, the emission maxima for both solid-state spectra occur at ~15 nm longer wavelength with respect to the corresponding solution phase experiments. Similar observations of shifts in spectral distribution have previously been observed on immobilization\textsuperscript{43,44} and may be attributed to the different dielectric environment experienced by the emitter in the solid matrix or to reabsorption\textsuperscript{45} since there is some overlap between absorption and emission of the compound. The spectra in Figure 4.9 indicate that the states involved in the ECL and photo-induced emission processes whether in solution phase or solid-state are indistinguishable.
4.2.4 Solid-state spectro electrochemistry of ruthenium (II) complexes on Indium Tin Oxide electrodes

Solid-state electrochemistry

Figure 4.11 illustrates the cyclic voltammetric responses at various scan rates, for layers of micro-particles of [Ru(dpp)₃](PF₆)₂ (upper graph) and
[Ru(bpy)$_2$(dpb)$_3$](PF$_6$)$_2$, where dpb 4,6-diphenyl-2,2′-bipyridine (lower graph), immobilized on ITO electrodes where the supporting electrolyte is 0.1 M LiClO$_4$. The solid-state response for [Ru(dpp)$_3$](PF$_6$)$_2$ is similar to that observed on glassy carbon substrate as described in section 4.2.2. Furthermore, it should be noted that a bipyridine type Ru(II) complex was also used in this study. Thus, [Ru(bpy)$_2$(dpb)$_3$](PF$_6$)$_2$ demonstrated a reversible electrochemical response for the Ru$^{2+/3+}$ redox couple. The solid-state redox process in both cases is assumed to involve the transfer of both electrons and ions as described later under ion pairing affects.
Figure 4.11 Scan rate dependences of the solid-state cyclic voltammetric responses for deposits of micro-particles of (a) \([\text{Ru(dpp)}_3](\text{PF}_6)_2\) and (b) \([\text{Ru(bpy)}_2(\text{dpb})](\text{PF}_6)_2\) immobilized on ITO. The scan rates are 0.01, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 V s\(^{-1}\) for both plots, the electrode area was 0.25 cm\(^2\) for (a) and 0.27 cm\(^2\) for (b) and the supporting electrolyte was 0.1 M LiClO\(_4\) in both cases. The inset shows the dependence of peak current \((i_p)\) on square root of scan rate between 0.1 V s\(^{-1}\) and 0.5 V s\(^{-1}\) in each case.
In the case of [Ru(bpy)$_2$(dpb)$_3$](PF$_6$)$_2$ the introduction of disubstituted ligand (dpb) in the structure of the complex increases the hydrophobicity of the complex compared with [Ru(bpy)$_3$](PF$_6$)$_2$ which does not adhere sufficiently well to the electrode. The solution phase electrochemical properties of this complex were also examined. Figure 4.12 shows the solution phase cyclic voltammetric response for [Ru(bpy)$_2$(dpb)$_3$]$^{2+}$ dissolved in acetonitrile containing 0.1 M [Bu$_4$N][PF$_6$] as supporting electrolyte. The voltammetric and spectroscopic data for this novel complex are summarized in Table 4.0 and compared to [Ru(bpy)$_3$]$^{2+}$. The voltammogram for [Ru(bpy)$_2$(dpb)$_3$]$^{2+}$ in Figure 4.12 is typical for ruthenium (N)$_6$ complexes. The peaks centred at 0.85 V (vs. Fc) (process I), are due to the oxidation / reduction of the metal between the 2+ and the 3+ state, while the three processes (II, III and IV), at more negative potentials are attributed to the successive reductions of the ligands. On the basis of comparison with [Ru(bpy)$_3$]$^{2+}$ and its relatively large displacement from the preceding ligand reductions, the third reduction process (IV), is assigned to the phenyl substituted ligand. This is consistent with the electron donating ability of the substituents. Furthermore, other Ru(II) complexes similar to this, described in chapter 3 where one unsubstituted bipyridine ligand was replaced with a 4-substituted-2,2′-bipyrene ligand show similar electrochemical behaviour. The spectroscopic properties for [Ru(bpy)$_2$(dpb)$_3$]$^{2+}$ presented in Table 4.0 are also characteristic of ruthenium(tris)diimine complexes.
Chapter 4 Solid-state electrochemical properties of ruthenium polypyridyl complexes

Figure 4.12 Solution phase cyclic voltammetry of 1 mM \([\text{Ru(bpy)}_2(\text{dpb})]^2+\) dissolved in acetonitrile containing 0.1 M TBAPF_6 as supporting electrolyte. The scan rate was 0.1 V s\(^{-1}\) and the working electrode a 3 mm diameter glassy carbon electrode. The potential scale is referenced to the formal potential of the ferrocene / ferrocinium couple measured \textit{in situ}.

The solid-state voltammetry of both complexes exhibited a pronounced “break-in” effect, similar to that found when using glassy carbon where the peak current gradually increased in magnitude during continuous cycling, before reaching a steady state, typically after 20 – 50 cycles. The voltammograms in Figure 4.10 represent the response after the solid deposits had been repeatedly cycled until an unchanging response was obtained. After the break-in period the layers showed excellent stability typically with < 10% decrease in peak currents after 100 voltammetric cycles at 0.1 V s\(^{-1}\). The insets in Figure 4.11 show that at moderately fast scan rates (0.1 V s\(^{-1}\) –
0.5 V s\(^{-1}\)) the magnitude of the peak currents for both complexes scales linearly with the square root of scan rate. At these scan rates also, the peaks exhibit tailing, reminiscent of a diffusional response, such as that obtained for the freely diffusing complex in Figure 4.12. At slower scan rates (0.005 V s\(^{-1}\) – 0.05 V s\(^{-1}\)) the peak heights scale linearly with scan rate and are more symmetrical in shape. These observations suggest that, as with the layers studied in the previous section, charge percolation through these deposits can be treated as a diffusion-like process and that they may exhibit semi-infinite or finite diffusional type behaviour depending on experimental timescale.

**Solid-state spectro electrochemistry**

Figure 4.13 shows the changes in the visible absorption spectrum of a low surface coverage (\(\Gamma = 1.5 \times 10^{-9}\) mol cm\(^{-2}\)) layer of immobilized particles of [Ru(dpp)_3](PF\(_6\))\(_2\), during a slow (10 mV s\(^{-1}\)) linear scan voltammetric experiment between 0.5 V and 1.5 V vs. Ag/AgCl. Oxidation of Ru\(^{2+}\) to Ru\(^{3+}\) within the solid deposit is signalled by a gradual decrease in the intensity of the MLCT band at 464 nm and the growth of a shoulder at 380 nm, which is due to a Metal Centred (MC) transition.\(^{46}\) The clear isospestic point observed at 400 nm indicates that no other products are generated during the electrolysis. Experiments where the potential was maintained at 1.5 V, at the conclusion of the scan, for up to 60 s resulted in no further changes to the spectrum. This implies that after electrolysis the complex resorts back to its spectroscopic ground state conditions.
Chapter 4 Solid-state electrochemical properties of ruthenium polypyridyl complexes

Figure 4.13 Changes in solid-state UV-Vis absorbance spectrum of a layer of 
[Ru(dpp)_3](PF_6)_2 micro-particles immobilised on ITO in contact with 0.1 M LiClO_4, during slow voltammetric scan between 0.5 V and 1.5 V vs. Ag/AgCl. The inset shows the absorbance signal monitored at 460 nm during repetitive pulsing of the applied potential between 0.5 and 1.5 V.

As described earlier, when a 1 mM solution of the complex dissolved in acetonitrile was oxidized in a thin-layer cell using a Pt gauze working electrode, a very similar pattern to that observed in the solid-state experiment
is seen. The inset in Figure 4.13, which shows the absorbance monitored at 460 nm with respect to time during repetitive potential pulsing demonstrates that, the spectral changes due to oxidation of the solid material are reversible over many cycles. That the MLCT band is lost completely at the end of the scan indicates that the layer is exhaustively oxidized on the time scale of the experiment and further supports the interpretation of the electrochemical behaviour of these deposits in the context of a finite diffusional / thin layer model. Analogous spectro electrochemical behaviour to that described above was observed for solid deposits of \([\text{Ru(bpy)}_2(\text{dpb})_3](\text{PF}_6)_2\) and \([\text{Ru(tmp)}_3](\text{PF}_6)_2\) (Appendix Figure 4.0) immobilised on ITO.

Another aspect of the spectro electrochemical approach is the monitoring of the absorbance signal at a single wavelength as a function of time or applied potential.\(^1\) The total absorbance \(A(t, \lambda)\) is given by the integration of the concentration profile \(c(x, t)\) of the coloured species as the beam passes through the layer perpendicular to the surface,\(^47\) i.e.

\[
A(t, \lambda) = \varepsilon(\lambda) \int_0^\infty c(x, t) \, dx
\]  

(4)

Since the integral in this equation is equal to the number of moles per unit area (\(\Gamma\)), the absorbance \(A(t, \lambda)\) (or \(D \ A(t, \lambda)\) if the depleted species is being monitored) can be equated to the Faradaic charge passed \(Q(t)\) as follows:

\[
A(t, \lambda) = Q(t) \frac{\varepsilon}{nF \alpha}
\]  

(5)

where \(\alpha\) is the electrode area in cm\(^2\), the other symbols have their usual meaning and the absorptivity \(\varepsilon\) is given units of cm\(^2\)mol\(^{-1}\) (= 10\(^3\) M\(^{-1}\)cm\(^{-1}\)).

Since both \(A(t, \lambda)\) and \(Q(t)\) represent the integral of the flux of equation 1, the derivative of the absorbance with respect to time is directly related to that of the charge with respect to time, namely, the current \(i(t)\),\(^48\) i.e.

\(^1\) We acknowledge however, that the experiments are more correctly described as photoelectrochemistry rather than spectroelectrochemistry under these circumstances.
Thus \( \frac{dA(\lambda,t)}{dt} \) provides an alternative measure of the flux associated with the redox reaction and, in contrast to the electrochemical signal, does so with both insensitivity to non-faradaic charge-consuming processes and enhanced the molecular specificity associated with the use of spectroscopic techniques.

In the system under study here, both the oxidised and reduced forms of the materials absorb at the wavelength of analysis, consequently the true absorbance due to the Ru\(^{2+}\) form alone, must be extracted from the data if quantitative information is required. This can be readily accomplished, if the absorptivities of both species are known, by applying an appropriate correction factor. This is derived below for the present situation, where the decrease in absorbance due to electrolysis of a species is being monitored. A similar argument applies for systems where the absorbance of an electrolysis product is monitored. Firstly, the total absorbance at any given wavelength and time is given by

\[
A = \varepsilon_{\text{Ru}^{2+}} \Gamma_{\text{Ru}^{2+}} + \varepsilon_{\text{Ru}^{3+}} \Gamma_{\text{Ru}^{3+}} \tag{7}
\]

where \( \Gamma_{\text{Ru}^{2+}} \) and \( \Gamma_{\text{Ru}^{3+}} \) are the surface concentrations (mol cm\(^{-2}\)) of the oxidised and reduced forms of the complex. Since, at any time, the total surface coverage \( \Gamma_T \) is given by

\[
\Gamma_T = \Gamma_{\text{Ru}^{2+}} + \Gamma_{\text{Ru}^{3+}} \tag{8}
\]

Substituting for \( \Gamma_{\text{Ru}^{2+}} \) we get

\[
A = \varepsilon_{\text{Ru}^{2+}} \Gamma_{\text{Ru}^{2+}} + \varepsilon_{\text{Ru}^{3+}} \left( \Gamma_T - \Gamma_{\text{Ru}^{2+}} \right) = \varepsilon_{\text{Ru}^{2+}} \Gamma_{\text{Ru}^{2+}} + \varepsilon_{\text{Ru}^{3+}} \Gamma_T - \varepsilon_{\text{Ru}^{3+}} \Gamma_{\text{Ru}^{2+}} \tag{9}
\]

Prior to electrolysis, the initial absorbance, \( A_i = \varepsilon_{\text{Ru}^{2+}} \Gamma_T \), so the change in the absorbance signal, \( \Delta A \) is given by

\[
\Delta A = A - A_i = \varepsilon_{\text{Ru}^{3+}} \Gamma_{\text{Ru}^{3+}} - \varepsilon_{\text{Ru}^{2+}} \Gamma_{\text{Ru}^{2+}} = \left( \varepsilon_{\text{Ru}^{3+}} - \varepsilon_{\text{Ru}^{2+}} \right) \Gamma_{\text{Ru}^{2+}} \tag{10}
\]
or
\[
\Gamma_{\text{Ru}^{3+}} = \frac{\Delta A}{E_{\text{Ru}^{3+}} - E_{\text{Ru}^{4+}}}
\]  

(11)

Therefore, the absorbance due to Ru\(^{3+}\) is given by
\[
A_{\text{Ru}^{3+}} = \Delta A \left(\frac{E_{\text{Ru}^{3+}}}{E_{\text{Ru}^{4+}} - E_{\text{Ru}^{3+}}}\right)
\]  

(12)

Since the absorbance due to Ru\(^{2+}\) alone, \(A_{\text{Ru}^{2+}} = A - A_{\text{Ru}^{3+}}\), it follows that
\[
A_{\text{Ru}^{2+}} = \Delta A \left(\frac{E_{\text{Ru}^{2+}}}{E_{\text{Ru}^{4+}} - E_{\text{Ru}^{3+}}}\right) + A_i
\]  

(13)

The absorptivities \(E_{\text{Ru}^{3+}}\) and \(E_{\text{Ru}^{2+}}\) were determined using equation 5 by measuring the absorbance before and after exhaustive oxidation of the attached solid in a slow scan rate voltammetric experiment, such as that shown in Figure 4.14. \(Q_T\) (and thus \(\Gamma_T\)) was evaluated from the area under the background corrected voltammetric peak. The values obtained \(E_{\text{Ru}^{3+}}\) for and \(E_{\text{Ru}^{2+}}\) for \([\text{Ru(dpp)}_3](\text{PF}_6)_2\) were \(3.15 \times 10^7\) cm\(^2\) mol\(^{-1}\) and \(5.66 \times 10^6\) respectively, giving a correction factor of 1.219. The value for the absorptivity of the reduced form of the solid is similar to that obtained for the complex dissolved in acetonitrile (29500 M\(^{-1}\)cm\(^{-1}\)).

The upper graph in Figure 4.14 shows the voltammetric response (dotted line) at slow scan rate for a layer of immobilised microparticles of \([\text{Ru(dpp)}_3](\text{PF}_6)_2\). The simultaneously collected absorbance signal at 460 nm (solid line) is also shown with the correction factor \(\frac{E_{\text{Ru}^{2+}}}{E_{\text{Ru}^{3+}} - E_{\text{Ru}^{3+}}}\) from equation 13 above applied.

The lower graph of Figure 4.14 represents the derivative (dA/dE) of the corrected absorbance signal shown in the upper curve. Plots of this type are often referred to as derivative cyclic voltabsorbammograms, (DCVA).\(^{48}\) The data has been multiplied by the factor \(\frac{nF \alpha v}{\epsilon}\) from equation 4, to show the equivalence of, and directly compare the voltammetric and spectroscopic
signals. (The scan rate, \( \nu \) simply converts between \( dA/dE \) and \( dA/dt \)). Unlike the current, which includes contributions from capacitive charging and other background processes, the derivative absorbance signal originates solely from the redox processes embodied in equation 1. If the derivative in Figure 4.14, is regarded then, as a perfectly background subtracted voltammogram, both signals are in very satisfactory agreement with one another. Drawing a linear baseline between both sides of the foot of the voltammetric peak gives a value of 7.5 \( \mu A \) for the peak current \( (i_p) \), whereas the peak derivative signal \( (dA/dV)_p \), (when multiplied by the factor \( nFA\nu/\epsilon \), has a value of 6.7 \( \mu A \).
Figure 4.14 Cyclic voltabsorptometry (upper graph), derivative cyclic voltabsorptometry (DCVA) (lower graph) and cyclic voltammetry (lower graph) for immobilised micro-particles of [Ru(dpp)_3](PF_6)_2. Scan starts at 0.6 V, the scan rate (ν) is 0.05 Vs\(^{-1}\), the electrode area (a) is 0.25 cm\(^2\), the surface coverage (Γ\(_T\)) is 1.32 x 10\(^{-9}\) mol cm\(^{-2}\) and the absorptivity of the Ru\(^{2+}\) form of the solid (ε) is 3.15 x 10\(^7\) cm\(^2\) mol\(^{-1}\). The absorbance signal was corrected to account for the absorbance of the Ru\(^{3+}\) species according to equation 3.
Figure 4.15 shows the CV and DCVA responses for a layer of immobilised [Ru(dpp)_3](PF_6)_2 at the relatively fast scan rate of 0.5 V s\(^{-1}\). Also, the surface coverage, and therefore the thickness of the deposit, in this experiment is 9% higher than that shown in Figure 4.14. A feature of these materials which we have noted is that the voltammetric peaks become less distinct and smaller in magnitude relative to the case for thinner deposits cast from a smaller volume of deposition solution. This is presumably related to an impediment to the flux of charge compensating counter ions in the thicker deposits, resulting in a diminished rate of charge transport. As a result of this phenomenon, the forward voltammetric peak in Figure 4.15 is poorly resolved from the background making peak height (i_p) or peak potential (E_p) determination a somewhat subjective affair. However the derivative signal allows both of these parameters to be measured with relative ease. The DCVA signal displays several features which distinguish it from the corresponding signal in Figure 4.14. Namely the peaks exhibit tailing rather than being symmetrical and the derivative absorbance signal does not return to zero as it does slow scan rate experiment. These observations are consistent with a transition to semi-infinite diffusional type behaviour, which one would expect to observe as the timescale of the experiment decreases and / or the thickness of the deposit increases.
Figure 4.15 Solid-state CV and DCVA responses for [Ru(dpp)$_3$](PF$_6$)$_2$ immobilised on ITO at the a scan rate of 0.5 Vs$^{-1}$ where the electrode area (a) was 0.2 cm$^2$ and the surface coverage $\Gamma_T$ was 5 x 10$^{-9}$ mol cm$^{-2}$.

This advantage of the spectro electrochemical approach is further illustrated in Figure 4.16. In this case the potential of the working electrode has been deliberately driven past the solvent limit to 2.0 V vs. Ag/AgCl, where the voltammetric signal consists almost entirely of current due to the electrolysis of the solvent. Care was taken not to scan far enough such as to cause evolution of gas bubbles. As expected under these conditions the oxidative wave of the CV is indistinct with tail of the peak significantly convoluted with the solvent electrolysis current. The derivative absorbance signal is however
unaffected by this background process and provides a signal morphologically identical to a CV regardless of solvent limit. While acknowledging that the materials under study here can, under most conditions, be studied by conventional techniques without being gravely affected by the solvent limit, the potential applications of this technique in situations where the voltammetric signal is closer to or even buried within the solvent electrolysis current is obvious.

**Figure 4.16** Solid-state CV and DCVA responses for [Ru(dpp)₃](PF₆)₂ immobilised on ITO in contact with aqueous 0.1 M LiClO₄ at the a scan rate of 0.1 V s⁻¹ where the potential was reversed at 2.0 V vs Ag/AgCl. The electrode area was 0.3 cm².
The solid-state voltammetric responses and corresponding derivative absorbance responses for a layer of immobilized [Ru(bpy)$_2$(dpb)](PF$_6$)$_2$ micro-particles at scan rates of 0.005 V s$^{-1}$, 0.1 Vs$^{-1}$ and 0.5 V s$^{-1}$ are shown in Figure 4.17. Note that while the peak currents ($I_p$) in the voltammograms increase with increasing scan rate, the opposite trend applies for the variation of $(dA/dV)_p$ with scan rate as expected.$^{48}$ As observed for [Ru(dpp)$_3$](PF$_6$)$_2$, there is a distinct variation in peak shape on going from high to low scan rate. This is most readily seen in the derivative absorbance signals where the slow scan rate gives a narrow and reasonably symmetrical response, whilst the two faster scan rates result in broader tailed peaks. Whilst ohmic effects undoubtedly account for much of the peak broadening, there is little doubt but that the relatively rapid return of the signal to baseline in the slow scan rate response is due to the exhaustive electrolysis of the deposit, consistent with thin layer type behaviour.
Figure 4.17 Solid-state voltammetric responses (upper graph) and corresponding derivative absorbance responses for a layer of immobilized [Ru(bpy)$_2$(dpb)]PF$_6$ micro-particles at scan rates of 0.005 V s$^{-1}$, 0.1 V s$^{-1}$ and 0.5 V s$^{-1}$. 
Potential step techniques such as chronoamperometry and chronocoulometry are also commonly used in the characterization of modified electrodes. For example, as we have seen, the charge transport characteristics can readily be extracted from a plot of current versus $t^{1/2}$ in the case of chronoamperometry or charge versus $t^{1/2}$ in the case of chronocoulometry. Similar to voltammetry, the efficacy of these techniques may be adversely affected by charge consuming background processes, particularly if, in order to completely step over the wave, it is necessary to step the potential to a value where solvent is electrolysed, as is the case for the ruthenium complexes examined here. Therefore it is of interest to explore the use of spectro electrochemical approaches to circumvent such potential problems.

As suggested by equation 4, the absorbance signal during electrolysis is directly related to the charge passed, therefore like the analogous relationship used in the coulometric technique, the absorbance transient varies with the square root of time according to

$$A = \frac{2\varepsilon C \sqrt{D_{CT}} \sqrt{I}}{\sqrt{\pi}}$$

where $C$ is the concentration of redox active centres in the deposit and $D_{CT}$ is the charge transport diffusion coefficient. Therefore chronocoulometry and its sister technique chronospectrometry may be compared directly without the necessity to derivatise the data. One advantage of potential step techniques is that, unlike most voltammetric methods, the effect of experimental timescale may be probed in a single experiment. We have compared the responses from these two techniques with simulated spectro electrochemical data, in order to gauge the relative merits of the two approaches. Chronospectrometry simulations were performed using DigiElch, a commercial software package which uses a box method to perform electrochemical simulations. Since, as suggested by equation 5 and 14 above, the chronospectrometry and chronocoulometry responses ought to be morphologically identical and directly proportional, simulations were performed by inserting the constant $\frac{e}{nFA}$ in the space where the value of the
Figure 4.18 shows the change in absorbance monitored at 460 nm and the accumulation of charge, associated with the oxidation of solid deposits of [Ru(dpp)_3](PF_6)_2, with respect to time, during a potential step experiment. The upper and lower graphs represent the response for thick and thin deposits respectively. The thickness was varied in order to assess the extent to which the layer solution boundary influences the response. In the upper graph where the deposit is thick, both the absorbance and the charge vary linearly with the square root of time up to approximately 1.0 s^{1/2}. The chronocoulometry and chronospectrometry slopes from this portion of the graph give values of 1.7 x 10^{-9} mol sec cm^{-3} and 1.8 x 10^{-9} mol sec cm^{-3} for $\sqrt{D_{CT}C}$ respectively, $\sqrt{D_{CT}C}$ being a measure of the rate of charge transport. These values are in good agreement with chronoamperometric analysis (using the Cottrell equation) which gave a value of 1.8 x 10^{-9} mol sec cm^{-3} and CV data from Figure 4.11 which gave a value of 2.2 x 10^{-9} mol sec cm^{-3} using the Randles Sevcik equation.

At longer times, as the thickness of the depletion layer approaches that of the deposit itself, the absorbance drops below that predicted by equation 14 and the charge falls below that predicted by the integrated Cottrell equation. At even longer experimental time scales (greater than 2.0 s^{1/2}) whilst the absorbance signal begins to plateau, significantly the slope of the coulometry signal increases. Since unlike the electrochemical signal, the spectroscopic signal is sensitive only to changes in the concentrations of the ruthenium centres, the apparent excess charge past at long timescales is most likely associated with background processes such as solvent electrolysis. The solid red line in the upper graph is the simulated spectroscopic response for a layer thickness of 4.3 x 10^{-6} cm. Both signals are in good agreement with the simulated response at short times. However, at intermediate experimental timescales, the charge deviates significantly both above and below the idealized response, whereas the absorbance exhibits only negative deviations, which get smaller at even longer times.
The lower curve in Figure 4.18, where a smaller quantity of material was drop coated on the electrode and thus the thickness of the deposit is smaller, also shows good agreement between the optical and electrochemical signal at short times (< 0.25 s\(^{1/2}\)). The slopes of both the electrochemical and spectroscopic signals from this short time portion of the graph yields a value of 3.8 \times 10^{-9} \text{ mol sec cm}^{-3} for \sqrt{D_{CT}C} in agreement with our earlier observation of faster charge transport rates for thinner layers. As in graph (a) there is significant disagreement between the spectroscopic and electrochemical signals at times scales longer than about 1.0 s\(^{1/2}\). While the absorbance reaches a constant value as the deposit becomes fully oxidized, the charge continues to increase, presumably due to charge consuming processes unrelated to the redox switching of the layer. The simulated response, in good agreement with both signals at short times, is in good agreement with the absorbance signal at both short and long times, with some significant deviation at intermediate times. The negative deviation of the absorbance from the model at these intermediate times may be explained by the fact that the model response assumes a perfect layer of uniform thickness with a well defined layer solution boundary. In reality however, these deposits are not monolithic and likely contain a distribution of particle sizes, with the result that, the depletion zone may be influenced by the layer solution boundary at intermediate times as well as at longer times, as the more remote portions of the immobilized material are electrolysed over a longer period of time.
Figure 4.18 Chronocoulometry (dashed line), chronospectrometry (open circles) and simulated chronospectrometry (solid line) for high (upper graph) and low (lower graph) surface coverage [Ru(dpp)$_3$](PF$_6$)$_2$ immobilised on ITO in contact with aqueous 0.1 M LiClO$_4$. In the upper graph the electrode area (a) was 0.49 cm$^2$ and $\Gamma_T$ was $4.7 \times 10^{-9}$ mol cm$^{-2}$. In the lower graph (a) was 0.45 cm$^2$ and $\Gamma_T$ was $1.6 \times 10^{-9}$ mol cm$^{-2}$. The absorbance was monitored at 460 nm. Simulation parameters are as stated in the main text of page 173.
4.3 Conclusion

Micro-particles of the ruthenium phenanthroline complexes, \([\text{Ru}(\text{dpp})_3](\text{PF}_6)_2\) and \([\text{Ru}(\text{tmp})_3](\text{PF}_6)_2\), show stable, reversible electrochemistry when immobilised on glassy carbon, ITO or boron-doped diamond electrodes in the presence of aqueous perchlorate, tetrafluoroborate or hexafluorophosphate electrolyte solution. The solution phase electrochemical and spectroscopic properties of a novel bipyridine complex of Ruthenium, \([\text{Ru}(\text{bpy})_2(\text{dpb})]^{2+}\) are similar to those of \([\text{Ru}(\text{dpp})_3]^{2+}\) and \([\text{Ru}(\text{bpy})_3]^{2+}\). It also showed stable, reversible electrochemistry when immobilised on ITO electrodes.

*In situ* electrochemical AFM studies show that the increase in peak current observed during the initial break-in period of the deposit (first 50 scans) is accompanied by small/subtle morphological changes to the layer including the appearance of small particles presumably formed by electrocrystallisation.51

The scan rate dependence of the voltammetric responses and the solid-state spectro electrochemistry both suggest that charge percolation through these deposits can be treated as a diffusion-like process, where the electrochemical reaction is assumed to start at the three-phase electrode–particle–solution boundary, and the subsequent growth of the reaction zone follows a semi-infinite linear diffusion into the particles.52 Moreover, finite diffusional (thin layer) type behaviour may be exhibited at sufficiently long experimental timescale. Spectro electrochemical experiments demonstrate that the deposits are exhaustively oxidised during a slow cyclic voltammetric scan. Spectral changes monitored during a slow cyclic voltammetric scan confirm the exhaustive oxidation of the Ru\(^{2+}\) species to the Ru\(^{3+}\) form which is signalled by the disappearance of the MLCT band and simultaneous growth of a MC band at lower wavelength. The spectral changes are reversible over many oxidation–reduction cycles.

Both the reversible potential \(E^{\text{1/2}}\) of the Ru\(^{2+/3+}\) couple and the rate of charge transport through the solid \(D_{\text{CT}}\) are sensitive to electrolyte concentration, although the dependence is weaker in the case of the tetramethyl
phenanthroline complex, which has a denser structure. The charge transport
data suggest that ion transport, rather than self-exchange between
neighbouring metal centres, represents the rate determining step for the
propagation of charge through these materials. The dependence of $E_{\text{1/2}}$ on
electrolyte ion concentration is Nernstian, reflecting the fact that a single extra
counter ion per ruthenium centre enters or leaves the solid on electrolysis, in
order to maintain electroneutrality. Weakly hydrated anions such as
perchlorate or hexafluorophosphate are thermodynamically easier to
assimilate into the particles in response to redox switching. Thus, the anion
desolvation energy influences the energetics of redox switching.

The derivative of the absorbance signal monitored at a single wavelength
during potential cycling is morphologically identical to a cyclic voltammogram
with no background. This technique is shown to be useful when peaks of
small magnitude are obscured by capacitive background or when peaks close
to the solvent limit are obscured by solvent electrolysis current. The
technique effectively increases the electrochemical window available for
voltammetric measurements. This will be useful for studies of compounds
with high (or low) formal potentials, in cases where oxygen cannot be
removed from solution and studies at high or low pH.

Since the relationship between $dA/dt$ and the Faradaic current ($i$) is known,
quantitative as well as qualitative information may be obtained under
favourable conditions. As both the oxidized ($\text{Ru}^{3+}$) and reduced ($\text{Ru}^{2+}$)
species absorb at the wavelength of analysis, a correction factor of
$$\frac{\varepsilon_{\text{Ru}^{3+}}}{\varepsilon_{\text{Ru}^{2+}} - \varepsilon_{\text{Ru}^{3+}}}$$
must be applied. The derivation of this correction factor also
presented.

Chronospectrometry experiments can provides the equivalent to a
chronocoulometric response. Moreover, due to the “invisibility” of charge
consuming processes unrelated to the redox reaction, the response is closer
the ideal simulated response than the electrochemical signal. Spectro
electrochemical responses may be easily simulated using commercially available electrochemical simulation software. Absorbance transients from thick and thin deposits of [Ru(dpp)_3](PF_6)_2 on ITO show best agreement with simulated data at very short and very long timescales. This observation in conjunction with the observations from the potential scan experiments, suggest that the absorbance, charge or current versus time behaviour of the system can be adequately described by a semi-infinite diffusional model when 
\[ \sqrt{2D_{CT}t} \ll \text{the average particle size} \] and by a finite diffusional model when 
\[ \sqrt{2D_{CT}t} \gg \text{the average particle size}. \]

Solid-state electrochemiluminescence is observed when the material is oxidized in the presence of a co-reactant such as oxalate or a suitable amine. Since the co-reactant cannot penetrate the solid, the ECL reaction occurs only at the surface of each particle resulting in diminished intensity relative to a similar solution phase experiment. Annihilation ECL between the sequentially oxidized and reduced forms of the material is far more intense because the reaction occurs in the bulk of the solid rather than at the surface. The ECL and photoluminescence spectra show that the same excited state is populated regardless of the mode of excitation.
Chapter 4 Solid-state electrochemical properties of ruthenium polypyridyl complexes

References

(41) Knight, A. W.; Greenway, G. M. Analyst. 1996, 121, 101R.
(50) The blocked right boundary (BRB) condition was specified, i.e. no concentration gradient at the right-hand boundary.
CHAPTER 5 Characterisation of Electrochemically Addressable 2D Luminescent Sensing Interfaces

5.0 Introduction

Ruthenium complexes based on diimine ligands such as bipyridine, terpyridine and phenanthroline have been the subject of countless studies due to their often exceptional optical and redox properties. While the majority of investigations have focused on the solution phase properties of these materials, their immobilisation on surfaces represents a major concern for real world technological applications in fields such as energy conversion, electrocatalysis and electrochemical / optical sensors.¹

In the specific area of electrochemiluminescence (ECL) sensing, electrodes which have the luminescent moiety immobilised directly on their surfaces are potentially very attractive because the active (Ru³⁺) form of the chemiluminescent reagent may be constantly regenerated in situ by the electrode to enhance sensitivity. In addition, only minute amounts of costly luminescent reagent are used (though the local concentration may be very high) and the need for a reaction cell and pumps to deliver a reagent to the reaction zone is eliminated. Moreover, such a simplified experimental set-up can enable the development of miniature and integrated sensor devices.

As described previously, various immobilisation methods for ECL reagents have been investigated using a wide variety of ruthenium-based, as well as other luminescent complexes. These include drop or spin coating of pre-formed polymers,²⁻¹³ electropolymerisation from solutions of the monomer,¹⁴,¹⁵ monolayer self-assembly,¹⁶⁻¹⁸ sol gel composites,¹⁹⁻²³ Langmuir-Blodgett techniques,²⁴ carbon pastes²⁵ and solid deposition techniques²⁶⁻³². Unfortunately, the utility of many of these approaches is compromised by structural changes to the film over time, thermal instability, leaching effects (in the case of some polymeric systems) and limited potential window due to oxidative cleavage (especially alkanethiol SAMS).³³ Recently there have been several reports describing the covalent attachment of
moieties, which are both redox active and luminescent to electrode surfaces. This work includes diazonium salts,\textsuperscript{34,35} click chemistry\textsuperscript{36-41} and attachment schemes enabled by nano materials which have been extensively reviewed by Vivekchand et al.\textsuperscript{42}

Electrochemically assisted covalent modification of carbon surfaces is a relatively recent development in modified electrode research.\textsuperscript{43} A report by Barbier et al. in 1990\textsuperscript{44} was the first to describe electrochemical generation of a solution radical which appeared to couple to the carbon surface forming a covalent bond between a surface and the modifier.\textsuperscript{43} Grafting species which contain aryl amine or carboxy groups to the surface makes this initial covalently attached monolayer very suitable for further chemistry. A number of monolayer systems covalently attached in this way have been reported. The method has been used to develop molecular electronic concepts,\textsuperscript{45,46} link bioactive molecules for bio-sensing applications\textsuperscript{33} and immobilize organic acids and heterocyclic ligands to help increase selectivity and/or sensitivity in electrochemical detection systems.\textsuperscript{43,47} Since the commencement of the work described in this chapter, a few reports have appeared describing the attachment of electroactive \textit{metal centered polypyrydyl} complexes to an electrode surface via the diazonium reduction method. A recent report by Leech et al.\textsuperscript{48} showed the promise of attaching an amine derivatised bipyridyl osmium complex to an aryl carboylic acid grafted carbon surface to demonstrate its stability and electrochemical properties for possible sensing applications. Furthermore, Jousselme et al.\textsuperscript{1} demonstrated the use of diazonium chemistry by direct reduction of the ruthenium diazoinium salt onto SWCNT for ECL sensing applications. Attachment to various electrode surfaces has been achieved via Sharpless’ “Click chemistry”, this is a particularly promising approach because it affords quantitative yields and no side products.\textsuperscript{38} This concept has been used to link ferrocene derivatives to alkyl thiols\textsuperscript{38,41} or graphite\textsuperscript{36} and iridium complexes to copolymers\textsuperscript{39} (via a covalent bond) on an electrode surface.

Nanomaterials have been widely studied due to their potential applications in biochemical, biomedical,\textsuperscript{49} nano-scaled optical and electrical devices.\textsuperscript{50} In recent times a large amount of work has focused on their surface modification in order to aid the solvation of CNTs due to poor solubility\textsuperscript{42,51} or for further manipulation
involving sensing strategies.\textsuperscript{42} The generation of functional groups on the surface of CNTs can be achieved through chemical oxidation and cleaving of the capped ends. Such surface functionalisation enhances the reactivity and provides an avenue for further chemical modification of the carbon nanotubes via ion adsorption, metal deposition or grafting reactions.\textsuperscript{52} Carboxylic acid functionalised carbon nanotubes have been recently been used to link luminescent Ru(II) polypyridyl derivatives as a electrochemiluminescence sensor.\textsuperscript{50,52}

In this chapter, we will discuss the use of the novel functionalised ruthenium bipyridine complexes described in chapter 2 to modify carbon electrodes in order to explore different routes to electrode modification for ECL sensing. The two major routes for electrode modification described here, are the use of diazonium chemistry and carboxylated multiwall carbon nanotubes (MWCNT-COOH) on carbon surfaces. These two approaches were used to attach electro-active / luminescent complexes to conductive surfaces, with the goals of furthering our understanding of such systems and their potential for sensing applications.

Our initial investigation involved electrode functionalization using diazonium chemistry to prepare a platform for our tailored ruthenium complexes. The glassy carbon (GC) surface was derivatised with either a phenyl carboxyl or amine moieties. In the first approach the coupling chemistry involved the use of N,N'-carbodiimidazole (CDI) with ferrocene carboxylic acid, which was used as a model for comparison of our [Ru(bpy)\textsubscript{2}(L)]\textsuperscript{2+} derivatives where, L = bpy with NH\textsubscript{2} or COOH functionality. In the second approach to electrode modification, carboxylated multi walled carbon nanotubes (MWCNTs) were treated with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) in an aqueous solution and then functionalised with a ruthenium complex before or after their deposition on an electrode surface. Both of these systems were spectroscopically and electrochemically characterized to understand and explore their potential as a basis for ECL sensing devices.
5.1 Materials, Apparatus and Methods

General

All commercial reagents (Sigma-Aldrich) were of analytical grade or higher and were used without further purification unless otherwise stated. All ruthenium(II) complexes (complex 6,7,13) used in this investigation were synthesized as described previously in chapter 2. Ferrocene carboxylic acid (99%) and 1,4-diaminobenzene were used as received from Sigma-Aldrich. The coupling agents: N’,N’-carbodiimazole (CDI), 1-Ethyl-3-[3-dimethylaminopropyl]carbodiimidehydrochloride (EDC), N-hydroxysuccinamide (NHS) were analytical grade and used without further purification. Phosphate buffers and perchlorate electrolyte solutions were prepared in deionised water (18 MΩ cm⁻¹) and stored for no longer than 1 week at 5 °C. Reagent grade ethanol, nitric acid (50%) and deionised water (18 MΩ cm⁻¹) were used consecutively for rinsing of electrochemical glassware. For further details of the potentiostats and other apparatus used for electrochemical measurements, please refer to Chapter 3.1 page 7.

General instrumentation

ToF-SIMS analysis was performed on a ToF-SIMS IV (Ion-TOF GmbH, Germany) instrument. A bismuth cluster liquid metal ion gun operating at 25 kV was used as the primary ion source, the source was capable of producing a range of ion clusters including $^{209}$Bi⁺, $^{209}$Bi₃⁺, $^{209}$Bi₅²⁺, $^{209}$Bi₇²⁺ ions. $^{209}$Bi⁺ was the primary ion used with $^{209}$Bi₃⁺ used for high m/z (>800 Da) investigations. The ion source was pulsed at 2.5 pA, with the primary ion dose density kept below the static SIMS limit of $10^{13}$ ions/cm². Surface charge neutralization was performed with the use of a pulsed electron flood gun. The analysis chamber pressure was kept at or below $10^{-9}$ torr. High mass resolution spectra (> 7500 at m/z = 29) were recorded.
For standard electrochemical and ECL measurements a conventional three-electrode configuration was used, as described in Chapter 3. The working electrode was a 3 mm GC disc shrouded in Teflon, (CH Instruments). The counter electrode was a platinum wire which was flame cleaned before each experiment and the reference electrode was Ag / AgCl (3 M KCl). For surface analysis studies, 15 mm GC disc substrates (Sigradur-G) were used as the working electrode. These were electrochemically addressed in a modified Teflon cell (see Appendix Figure 5.0) normally used for Quartz crystal microbalance (QCM) measurements (CH instruments). The cell exposed a 4 mm diameter portion of the disc to the solution. All glassy carbon based electrodes were cleaned by polishing with 0.3 and 0.05 µm alumina slurry on a felt pad, then 2 min of consecutive ultrasonic treatment in Milli-Q H20, HNO3 and then Milli-Q H2O.

Electrochemical impedance spectroscopy was performed using a CH660B potentiostat over a frequency range of 1-10^5 Hz. Impedance data were analysed by fitting to equivalent circuits simulated using EIS Spectrum Analyser. Carboxylated multiwall carbon nanotubes (MWCNT-COOH) functionalised screen printed electrodes (SPEs) were purchased from DropSens®. The SPE includes a three-electrode configuration, comprising: (1) a 4 mm carbon disc working electrode coated with MWCNT-COOH; (2) a carbon auxiliary electrode of the same materials as the working electrode; (3) a silver pseudo-reference electrode. The substrate is ceramic-based and the contact pads are made from silver. The other carbon SPEs used in this work were purchased from Zensor® R&D (Taiwan) via eDAQ Pty. These SPEs also contain three electrodes as described above. In this case the substrate is flexible plastic and the contact pads are carbon-based.

All ECL measurements on modified MWCNT SPEs were carried out using a modified setup (Appendix Figure 5.1). Before any electrochemical measurements, the electrolyte was spiked to contain 0.1 M KCl to minimise potential drift for the Ag reference electrode. The electrical contact pads on a DropSens® electrode requires the fitted connector piece from the supplier to be used with the potentiostat since regular alligator clips were too large and would complicate the connection during measurements. However, regular alligator clips could be used with the MCNT modified Zensor® SPEs during electrochemical measurements.
5.2 Experimental

Figure 5.0 Overview of carbon electrode modification strategies used in this chapter.
5.2.1 Electrode modification of GC surfaces via the reduction of functionalised diazonium salts.

Scheme 5.1 Mechanism for the attachment of diazonium salts to carbon.

*In situ* formation and deposition of a diazonium species. (Step 1a) In situ preparation of aryl diazonium salt in electrochemical cell; (Step 1b) preparation of diazonium salt prior to grafting process; (step 2a) electrochemical reduction of diazonium salt forms radical; (Step 2b) aryl radical + carbon surface forms new C-C bond.
**Procedure 5.I** (Step 1a) An electrochemical cell containing 1, 4-phenylenediamine (0.054 g, 0.49 mmol) was charged with 10 mL of cold 0.5 M HCl solution. Nitrogen was bubbled through the liquid until the mixture dissolved. To this solution, 0.045 g (1.3 equiv) of sodium nitrite (NaNO₂) was added and the solution was then allowed to react for 2 minutes under nitrogen. Alternatively, (Step 1b) the diazonium salt is isolated and purified prior to the electrochemical deposition. The *in-situ* generation was advantageous due to minimal synthetic steps and reagent degradation. (Step 2a,b) The in situ reduction experiment where glassy carbon was modified potentiostatically at 0.14 V with one step, for either 10, 25, 50, 100 or 250 s. The electrode was then thoroughly rinsed and sonicated (1 min) with Milli-Q water and used promptly. The barrier properties of unmodified and modified glassy carbon electrodes were evaluated in a 5 mM K₃[Fe(CN)₆] in 0.1 M KCl electrolyte.
Scheme 5.II Coupling of ferrocene carboxylic acid with amine derivatized glassy carbon surface in the presence of CDI / CH$_3$CN under nitrogen.

**Procedure 5.II** An oven dried three-necked round bottom flask fitted with a condenser and quick-fit nitrogen inlet was charged with dry acetonitrile (10 mL). While the flask was warm, 0.0115 g of ferrocene carboxylic acid was added. The solution was stirred vigorously until the acid dissolved completely. The solution was then cooled to ambient temperature and N,N’-carbodiimazole (CDI) (0.012 g) was added and the mixture was left to stir for 10 min.
Figure 5.1 Setup used for modification of conventional electrodes with ferrocene-COOH (Fc-COOH) or ruthenium(II) derivatives.

Figure 5.2 Setup used for modification of 15 mm disc substrates with ferrocene or ruthenium derivatives. Electrode disc sits on center of customized Teflon sheet.

Due to the different electrodes used for this project, the reaction flask was utilised in different ways. (1) In Figure 5.1 a derivatised conventional 3 mm GC electrode was then fixed to a rubber septum, which was able to fit in a quick fit slot and submerged
in the solution without disturbing the magnetic stirrer. (2) For modification of the 15 mm diameter GC disc substrates, as shown in Figure 5.2 above, a Teflon based circle sheet with cut-outs was used to allow the solution to pass through and was inserted so that it sat at the lowest point of the round bottom flask above the magnetic stirrer. The cut-outs in the Teflon sheet created a vortex so that the solution could come in contact with the disc and not be damaged by the magnetic stirrer. A modified GC disc electrode was then carefully inserted with the modified layer in the upright position. The reaction was left to stir at RT for 24 h. The modified electrode was then rinsed first with Milli-Q water, then with acetone and once again with Milli-Q water.
Scheme 5.III Coupling of $\text{[Ru(bpy)₂(mba-bpy)](PF}_6)_2$ with amine derivatised glassy carbon surface in the presence of CDI / CH$_3$CN under nitrogen.

Procedure 5.III Refer to scheme 5.II for coupling conditions except that $\text{[Ru(bpy)₂(mbpyb)](PF}_6)_2$ (0.012 g, 5 mM) was added in place of Fc-COOH
5.2.2 Electrode modification with MWCNT-COOH followed by functionalisation with \([\text{Ru(bpy)}_2(L)]^{2+}\) complex.

Scheme 5.IV Electrode substrate modification with MWCNTs followed by CNT-Ru(II) coupling.

In scheme 5.IV, Step (A): MWCNT-COOH (1 mg / mL) solution onto Zensor SPE or GC electrode. Step (B): electrode activation in the presence of 40 mM EDC / 45 mM NHS. Coupling of \([\text{Ru(bpy)}_2(\text{mab-bpy})](\text{PF}_6)_2\) to activated carboxylated MWCT coated electrodes.
Procedure 5.IV: Zensor®, GC and DropSens® electrode modification

1. Fresh Zensor® electrodes were first thoroughly rinsed with Milli-Q water and were left to stand at RT in a sealed container for 24 h. In the case of conventional GC electrodes, they were firstly polished with 0.3 and 0.05 µm alumina and then rinsed with Milli-Q water.

DropSens® electrode modification: This scheme is similar to Zensor® / GC electrode modification although step 1-5 was omitted as the DropSens® SPEs already have MWCNT-COOH deposited on the working electrode. Manufacturer details can be viewed in materials 5.1.

2. A solution of 1 mg / mL 5% carboxylated MWCNTs was suspended in 50% H$_2$O:DMF. This suspension was sonicated for 3 h prior to deposition. The deposition must be done promptly after sonication in order to achieve a fully dispersed solution.

3. Step (A) MWCNT-COOH deposition: A micro-pipette was used to transfer 2.5 µL of the dispersed solution and drop coated onto the carbon surface of the SPE.

4. The freshly prepared electrodes were left undisturbed in a sealed container and left to dry for 24 h.

5. All electrodes were visually inspected for even homogeneous deposition before the complex attachment stage.

6. Step (B) Ru-CNT modification: A 5 mL reaction vial was fitted with a circular Teflon insert at the top of the lid to allow a support rod to be fitted which held the SPE in place with the aid of an o-ring. Please see Figures 5.3 and 5.4 for electrode and vial setup example (setup is shown for SPEs). The electrodes were incubated in a solution of 40 mM EDC and 45 mM NHS at room temperature for 1 h. The electrode was then carefully removed from the chamber and rinsed thoroughly with Milli-Q water.

7. Step C: The electrode was then immediately submerged in the second reaction vial containing a solution of the Ru(II) complex (5 mM) in phosphate buffer at pH 6 / 30% DMSO with gentle stirring for 24 h in complete darkness. See figure 5.5 for details. After incubation, the electrode was
rinsed with Milli-Q water, 1 M HCl, 1 M NaOH, 30% DMSO and then finally Milli-Q water.

8. Electrodes which were not to be used straight away were stored in 0.2 M PBS at pH 7.

Figure 5.3 shows the pre-assembly of the electrode before it enters the reaction chamber. Figure 5.4 depicts the general reaction chamber setup with a DropSens® electrode.
Scheme 5.V Synthesis of CNT-Ru(II) adduct and carbon electrode deposition.

Procedure 5.V

1. **Step (A) CNT activation**: To a centrifuge tube MWCNT-COOH (20 mg), 40 mM EDC / 45 mM NHS in Milli-Q H₂O (10 mL) were stirred at RT for 1 h.
2. The tube was centrifuged (5 min) and the supernatant was decanted. Then Milli-Q water (10 mL) was added, stirred (2 min) and centrifuged (5 min) and the supernatant was decanted.
3. **Step (B) Ru-CNT modification**: To this centrifuge tube containing the multiwall nanotubes, 5 mM [Ru(bpy)₂(mab-bpy)](PF₆)₂ was added in a solution of phosphate buffer at pH 6 / 30% DMSO with gentle stirring for 24 h in complete darkness.
4. Step 2 was repeated.
5. A solution of 30% DMSO / H₂O (10 mL) was added then stirred (5 min), before centrifuged (5 min) and supernatant decanted. This step was repeated with 1 M HCl (10 mL). Repeated once again using 0.1 M NaOH solution (10 mL). Step 2 repeated.

6. **Step (C) MWCNT-COOH deposition:** Finally, 50% H₂O / DMF added and solution centrifuged for 2 h prior to deposition on electrode surface. Refer to steps 1-5 for further details (scheme 5.IV for electrode preparation).

### 5.3 Results and Discussion

#### 5.3.1 Electrode modification using diazonium chemistry

The initial work for this chapter as shown in Figure 5.0 involved electrochemically assisted modification of a glassy carbon surface with 1,4-phenylenediamine via diazonium chemistry. The amination of the surface was desired so that it could be used as a platform to immobilize electro-active / luminescent materials for potential sensing applications. The attachment method was first optimised using ferrocene carboxylic acid before attempting to bind the less readily available ruthenium complex [Ru(bpy)₂(mbpyb)](PF₆)₂. Although it should be noted that the immobilization of ferrocene derivatives on electrodes is also potentially useful in a sensing context.⁵⁴-⁵⁶

As outlined in scheme 5.I, a GC working electrode substrate was first primed by electrochemically bonding a reactive group to the surface. The first investigation involved the use of 1,4-diaminobenzene in order to facilitate the subsequent coupling of our carboxylic acid functionalised metal complexes.

One equivalence of NaNO₂ was used to generate the mono-diazonium species. This reaction, which has been extensively analysed in other reports,⁵⁷ leaves the other amine group on the phenyl ring intact for coupling via amide bond formation with our acid functionalised metal complexes. The appropriate choice was to use the in-situ method as opposed to preparing and isolating the relatively unstable diazoniunm species, as it was simpler, less time consuming and generally more conducive to sensor fabrication.
The attachment was achieved electrochemically using *in situ* generated diazonium salt of the 1,4-diaminobenzene in acidic media. This diazonium is reduced at a potential of 0.14 V vs. Ag/AgCl to a radical species which, reacts with the electrode to form a stable carbon-carbon bond. The mechanism has been described as a one electron electrochemical reduction on carbon electrodes, which results in the formation of a phenyl radical and N₂; the phenyl radical reacts with the carbon surface by coupling to an unsatisfied valence or adding across a double bond. It is likely that a short-lived neutral phenyl-N₂ species exists as an intermediate, but it rapidly and irreversibly dissociates to the much more stable N₂ and phenyl radical⁵⁸ as shown in scheme 5.1.

![Figure 5.5](image.png)

*Figure 5.5* CV deposition (10 cycles (initial scan = dashed line) of *in situ* generated \(^{1}\text{N}_2\text{-C}_6\text{H}_4\text{-NH}_2\) on a 3 mm diameter conventional glassy carbon electrode surface; potential scanned from 0.5 to -0.2 V versus Ag/AgCl at 0.1 Vs\(^{-1}\).
The response from the corresponding CV in Figure 5.5 exhibits a broad reduction peak assigned to the formation of the aryl radical, which then attaches to the surface. The initial scan from the formation of the aryl radical attaching to the carbon surface gave a surface coverage of $1.2 \times 10^{-10}$ mol cm$^{-2}$ based on the charge passed. After the first scan, the reductive peaks due to the diazonium formation decrease in magnitude as does the capacitive current. While the decreased capacitance is a well-known effect of electrode passivation, the decreased faradaic current can be explained as the inhibition of further reduction of diazonium molecules, once the initial layer is formed. Having said this, as suggested by Solak et al.$^{59}$, electron tunneling may occur through an aryl monolayer layer, providing a means by which newly attached phenyl rings can react with the electrochemically generated radical species. These factors depend on the relative rates of the reaction with the newly formed layer versus the bare carbon surface and may result in the formation of a multilayer through an additional C-C or azo-bond formation.$^{58,60}$

The surface coverage of attached amino-phenyl groups was also evaluated by using integrated current data from experiments, such as that shown in Figure 5.6, at different deposition times. The surface coverage ($\Gamma$) in mol cm$^{-2}$ is calculated using equation 1.

$$\Gamma = \frac{Q}{nFA} \quad (1)$$

where the charge (Q) in coulombs is obtained from the integrated chronoamperogram; (n) is the number of electrons transferred; F the Faraday constant and (A) the area of electrode in cm$^2$. 

200
Figure 5.6 Integrated response from a typical chronoamperometric deposition experiment. The potential of a 3 mm diameter GC electrode was stepped to -0.14 V in a solution containing \textit{in-situ} generated $^*\text{N}_2\text{-C}_6\text{H}_4\text{-NH}_2$ in 0.1 M HCl electrolyte.
Figure 5.7 Typical results of single step chronoamperometric deposition experiments on 3 mm glassy carbon electrode with varying times (10, 50, 100, 250 sec), plotted versus the charge passed (Q).

The surface coverages ($\Gamma$), of the amine on conventional GC electrodes ($A = 0.0707$ cm$^2$) were estimated based on the charge passed ($Q$) during the diazonium deposition and are shown in Figure 5.7. The theoretical value$^{58,61}$ estimated for a closely packed phenyl based monolayer is $12\text{–}13.5 \times 10^{-10}$ mol cm$^{-2}$ based on the geometric size of the phenyl ring and minimal spacing between molecules on a flat surface. In the literature$^{58}$ quantitative estimates of coverages are generally lower than this value, and have been between 4 and $6 \times 10^{-10}$ mol cm$^{-2}$ for such systems. This is possible due to the differences in substrates used, which may influence the deposition conditions of the diazonium species. Our shortest deposition times of 10 seconds gave values of $2.9 \pm 0.43 \times 10^{-10}$, which is significantly lower than the typical monolayer coverage. As described earlier in Figure 5.5 the use of CV
deposition with a potential range of 0.5 to -0.2 V at 0.1 V s\(^{-1}\), the typical surface coverages were between 1 and 5 \(\times 10^{-10}\) mol cm\(^{-2}\) after 1 scan from the in situ generation of the phenyl amine diazonium salt. Furthermore, depending on which GC electrode used on the day, the charge passed estimated can give surfaces coverages 1 order of magnitude lower. We observed values of 9.8 \(\times 10^{-9}\), 19 \(\times 10^{-9}\), 26 \(\times 10^{-9}\) mol cm\(^{-2}\) at longer deposition time scales of 50, 100 and 250 seconds respectively, which are well over the typical values for monolayer coverage, as suggested earlier. These values suggest that at shorter deposition times, sub monolayer coverages are likely to occur which may be due to incomplete depositions at the surface. At longer time scales (>10 sec) it will give rise to multilayer growth on the glassy carbon surfaces, which is supported in Figure 5.6. The slope on the graph is consistently smaller on the later time period indicating that the rate of hydrolysis has diminished to negligible levels and parasitic side reactions are still occurring.

5.3.2 Barrier effect on the grafted layer of \(H_2NC_6H_4\)-electrode

In order to assess the extent and quality of the deposition for the amino-phenyl grafting process, the blocking properties of the layer were probed electrochemically. This was done by observing the effects of layer deposition on the voltammetric behaviour of \([\text{Fe(CN)}_6]^{3-}\). This redox species was used as it has well established properties which make it ideal as a surface sensitive probe. Most importantly it shows heterogeneous electron transfer rates which are reasonably fast yet slow enough to be easily manifested on the time scale of an electrochemical experiment.\(^{58}\) On the other hand, \([\text{Ru(NH}_3)_6]^{3+}/^{2+}\) is not an ideal probe as its rate of electron transfer is much faster.\(^{58}\) Figure 5.8 shows the CV responses for a 5 mM solution of ferricyanide for a bare and an amino-phenyl grafted electrode at different deposition times.
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Figure 5.8 Cyclic voltammogram responses from segments 3-4 at 0.1 Vs\(^{-1}\) in 0.1 M KCl pH 7.5 for a 5 mM \([\text{Fe(CN)}_6]\)\(^{3-}\) (vs. Ag/AgCl). (A) bare electrode and \(\text{C}_6\text{H}_4\text{NH}_2\) grafting; (B) deposition at 10 seconds; (C) deposition at 50 seconds; (D) deposition at 100 seconds.

At the bare electrode surface, the formal potential \(E^\circ\) is 0.231 V for the \([\text{Fe(CN)}_6]\)\(^{3-}\) redox couple and the peak-to-peak separation, \(\Delta E_p\), of the cyclic voltammogram at 0.1 V s\(^{-1}\) in 0.1 M KCl pH 7.5 for a 5 mM \([\text{Fe(CN)}_6]\)\(^{3-}\) solution is 62 mV. After the 10-second deposition the ferri/ferrocyanide redox couple is significantly affected compared to the bare electrode. As the deposition time increases we can noticeably see that the ferricyanide oxidation/reduction waves become increasingly inhibited where the \(\Delta E_p\) at 10 sec deposition was estimated to be 400 mV and at 50, 100 sec deposition there was no ferricyanide peaks visible. The redox behaviour of \([\text{Fe(CN)}_6]\)\(^{3-}\) seen for a 10 sec deposition can be explained by slow heterogeneous kinetics. It should be acknowledged that a previous study has also shown that the morphology of this type of diazonium used on gold gives a relatively
inhomogeneous and rough organic layer. Deposition times of 50 and 100 seconds showed highly irreversible electrochemistry suggesting virtually complete blocking, consistent with their surface coverage values estimated from the charge passed during deposition. The fact that long deposition times longer than 50 seconds is required to fully block the electrode surface suggests that a heterogeneous layer is being generated on the carbon surface. This leads to the idea that the grafting process is not equal in all areas of the bare working electrode surface and that all new C-C bonds generated will not necessarily originate from the bare surface. This is a concern at longer deposition times because this allows the reactive material to keep depositing onto the underlying surface. Heterogeneous growth has been suggested for similar systems on glassy carbon, highly ordered pyrolytic graphite (HOPG), gold (Au), and indium tin oxide (ITO) electrodes.

The mechanism for the electrochemical reduction of the in situ generated aminophenyl mono-diazonium cation is analogous to that of other diazonium species, which have been investigated. Figure 5.9 outlines the proposed mechanism by which 1,4-diaminophenyl group attaches to glassy carbon and forms a multilayer system: Firstly in step 1, the functionalized aryl radical is electrochemically generated precisely where it is most likely to react with the electrode surface. Step 2 shows the bonding arrangement between the carbon surface and the adjacent aminophenyl group. The attachment is strongly bound through a covalent bond. It was difficult to reproducibly control the layer thickness, as has been noted in other studies, the tendency to form multilayers and the thickness of the modified layer depends on the nature of the non-derivatised surface, deposition conditions, diazonium ion concentration, deposition scans, potential range and scan rate. Thus, in step 3, it shows the multilayer growth that would exist on the electrode surface after the initial derivatisation if the aryl radical was not to react with the bare surface. Furthermore, it has also been shown in recent XPS analysis that diazo bridges can occur (C-N=N-C) as part of the multilayer growth for this type of diazonium which may be present in our system.
5.3.3 Impedance spectroscopy of the grafted layer of $\text{H}_2\text{NC}_6\text{H}_4$-electrode

Electrochemical impedance spectroscopy (EIS) measurements can be used to evaluate the effect 4-amino phenyl groups on the kinetics of a redox reaction at a glassy carbon electrode. Ferrocyanide / ferricyanide couple is an outer sphere redox system and therefore can be used as a redox probe for pinholes and defects on the modified surfaces. Figure 5.10 shows the (EIS) response in the form of Nyquist plots for a bare and a series of $\text{C}_4\text{H}_4\text{NH}_2$ coated glassy carbon electrode in contact with a ferricyanide solution. The shape of these plots is typical for the redox response of a solution phase species.\textsuperscript{57,69} The impedance plot for the bare electrode is characterized by a semicircle of 250 $\Omega$ in the high frequency domain, indicating a kinetically controlled interfacial electron-transfer reaction, while the straight line portion of the graph on the right hand side indicates semi-infinite diffusional control at lower frequencies.\textsuperscript{57} The Nyquist plot for the GC electrode after 10 sec deposition shows an increase in the charge transfer resistance $R_{\text{CT}}$ manifested by an increase to 540 $\Omega$ in the diameter of the semicircle. This indicates an extension of kinetic
control to lower frequencies compared to the bare electrode as a result of slower interfacial electron transfer caused by the passivating effect of the layer.

Figure 5.10 Impedance spectroscopy performed with a 5 mM $[\text{Fe(CN)}_6]^{3-}$ / 0.1 M KCl / pH 7.5 at a potential of 0.231 V; (a), bare GC electrode; deposition of $^+\text{N}_2\text{C}_6\text{H}_4\text{NH}_2$ cation: (b), 10 sec deposition; (c), 50 sec deposition; (d), 100 sec deposition. Frequency range: 1-10$^5$ Hz. Key: (■) fitted spectra, (Δ) experimental spectra. Units for $Z'$ and $Z''$ are in ohms
Figure 5.11 Randles equivalent circuit used to model the electrochemical impedance data where $R_s$ is the solution resistance, $R_{CT}$ is charge transfer resistance, Warberg resistance ($Z_w$), $C_{dl}$ is double layer capacitance (modeled as a constant phase element, CPE). (Image taken from reference 70)

A Randles equivalent circuit representing both bare and 4-amino phenyl modified electrodes is shown in Figure 5.11. It comprises of the solution phase resistance, $R_s$, the charge transfer resistance, $R_{CT}$, the Warburg resistance $Z_w$ and a constant phase element, CPE, which likely accounts for the heterogeneity of the electrode. The experimental impedance spectra were fitted with Randles equivalent circuit simulation. $R_s$, $R_{CT}$, $Z_w$, CPE were determined using the following fitting parameters: Newton algorithm, Amplitude function with maximum iterations of 10000. Figure 5.10 shows the ferro/ferri cyanide electron transfer reaction in 0.1 M KCl on the GC-C$_4$H$_4$NH$_2$ surface overlaid with the modeled data obtained from the Randles equivalent model circuit in the high frequency range. The bare electrode model is also in good agreement (>95%) with the experimental data, indicating that after grafting, the rate of electron transfer is slowed considerably due to the passivation of the electrode surface.

As shown previously in Figure 5.10, for the longer deposition times of 50 sec and 100 sec, $R_{CT}$ rises dramatically from values of the order of $10^3$ $\Omega$ to $1.12 \times 10^4$ and $1.47 \times 10^4$ $\Omega$ respectively. At high depositions times the shape of the Nyquist plot is altered, with the apparent appearance of an unexplained second RC element at high frequencies. It is evident that deposition of the diazonium for periods longer than 10 sec results in more complex behaviour, clearly the charge transfer resistance increases with deposition time. In Figure 5.12 the difference in $R_{CT}$ for a bare / non-derivatised and modified glassy carbon surface is evidently seen. The increase of
RCT with electrolysis time demonstrates that the film becomes more compact and thicker with increasing electrolysis time.

RCT can be used to evaluate the heterogeneous rate constant, \( k^\circ \) for the \([\text{Fe(CN)}_6]^{3-}\) redox couple as shown in equation (2). Thus, R_CT is determined where R constant is 8.314 J K\(^{-1}\) mol\(^{-1}\), temperature in Kelvin (T), electrons transferred (n), Faraday constant (96485 C), area (A) in cm\(^2\), heterogeneous rate constant (\( k^\circ \)) and concentration (mol cm\(^{-3}\)).

\[
R_{CT} = \frac{RT}{(nF)^2A k^\circ C}
\]

In Figure 5.12 it shows that R_CT increases with deposition time. The R_CT values calculated for \([\text{Fe(CN)}_6]^{3-}\) at a bare GC electrode (\( \Omega = 244.61 \)) and deposition at 10 50 100 sec are 510.75, 11250, 14736 \( \Omega \) respectively. Thus, \( k^\circ \) decreases with increasing layer thickness on the electrode. As pointed out on page 207, the rate at which basal and edge planes are modified by the diazonium reaction, differ significantly.\(^5\) Since the electron transfer kinetics of ferrocyanide are known to be sluggish at the basal planes, this fact should also be borne in mind when interpreting these results.
Figure 5.12 $R_{CT}$ versus Deposition time of amino-phenyl grafted layer on 3 mm glassy carbon electrode. The inset graph shows a magnified view for $R_{CT}$ values at a bare GCE (0 sec) and deposition time of 10 sec.

5.3.4 Ferrocene linked with grafted aminophenyl groups on glassy carbon

![Diagram showing ferrocene linked with grafted aminophenyl groups on glassy carbon](image)

Figure 5.13 Ferrocene covalently linked to C₆H₄NH₂ grafted glassy carbon electrode.
We initially used ferrocene carboxylic acid (Fc-COOH) as a model to demonstrate the possibility of attaching carboxylic acid functionalised redox active compounds. Following the attachment scheme 5.II, ferrocene carboxylic acid was coupled to the amino phenyl derivatised GC surface by the use of a coupling agent, N,N'-carbodiimidazole (CDI) in dry CH$_3$CN.

**Voltammetric behaviour**

Figure 5.14 shows the cyclic voltammograms of the ferrocene-CONH-phenyl-electrode coupled adduct compared with the solution phase response both in 1.0 M LiClO$_4$ electrolyte. The immobilized species has a formal potential $E^\circ$, of 0.402 V which is similar to that of the solution phase species (0.334 V). Furthermore, there was no significant change in the background capacitance before and after ferrocene attachment. The $\Delta E_p$ is $50.2 \pm 5.2$ mV, which is less than the 59 mV expected for a freely diffusing species. This observation is consistent with a surface confined response. The ideal FWHM is $90.6 / n$ mV, where $n$ is the number of electrons transferred. The higher than expected FWHM (104 mV) could be due to repulsive interactions between the individual ferrocene molecules on the electrode surface. On the other hand, both the greater than ideal FWHM and a non-zero peak separation ($\Delta E_p$) (ideally $\Delta E_p$ should equal 0 at slow scan rates) could be explained by a kinetic dispersion model with the redox species being in a range of environments with a range of values of $k^\circ$ and $E^\circ$. Figure 5.15 shows that the peak current ($i_p$) was linear with scan rate, which is also indicative of a surface bound species.
Figure 5.14 Cyclic voltammograms of: (top) solution phase Fc-COOH; (bottom) surface confined Fc-COOH covalently attached to a 3 mm disc glassy carbon electrode grafted with amino-phenyl groups via a 100 sec diazonium deposition; in 1.0 M LiClO₄ electrolyte at 0.1 V s⁻¹.
The charge \( Q \) under the background corrected peaks of the cyclic voltammogram in Figure 5.14 gave a surface coverage \( (\Gamma) \) of \( 1.8 \pm 1.5 \times 10^{-10} \) mol cm\(^{-2}\) using equation (1), which is in good agreement with \( 0.25 \times 10^{-10} \) mol cm\(^{-2}\) and \( 0.1 \times 10^{-10} \) mol cm\(^{-2}\) reports based on ferrocene self-assembled monolayers reported by Liu et al.\(^{71}\) and Rowe et al.\(^{72}\), respectively. The amino benzene deposition time of 100 sec was best suited for modification of the Fc electro-active species due to the consistent blocking properties, and high surface coverage it produced.

![Cyclic voltammograms](image)

**Figure 5.15** (Left) Cyclic voltammograms of attached Fc-CONH\(^{-}\) on a diazonium modified glassy carbon surface at scan rates of 5, 20, 50, 80 and 100 mV s\(^{-1}\); (Right) scan rate study plot of \( I_{p,a} \) vs scan rate (V s\(^{-1}\)); \( R^2 \) is 0.997.

The redox stability of the coupled ferrocene to an aryl-amine amine surface via an amide bond showed moderately good stability and reproducibility with repetitive cycling in 1.0 M LiClO\(_4\) electrolyte at 0.1 Vs\(^{-1}\) which can be seen in Figure 5.16. The peak currents for the ferrocene couple decreased by 10% after a 10 min of repetitive
cycling and decreased to 50% after 2 h. The cyclic voltammetry and stability data suggest that the coupled metal complex is covalently bound.

Figure 5.16 Stability plot after 500 cycles from Fc-COOH coupled to aryl-amine GC surface via -CONH- bond. The electrode was scanned from 1.0 to -0.1 V in 1.0 M LiClO₄ electrolyte at 0.1 Vs⁻¹.

This system was further characterized by ToF-SIMS. The positive ion peaks found are summarized in Table 5.0 from the splitting pattern of ferrocene attached to the glassy carbon surface. Characteristic peaks at 55.93, 120.07 and 186.01 mass / u all include Fe in their ion mass. Ion peaks at 65.03, 92.05, 94.04 and 108.06 are consistent with pentadiene rings splitting from the ferrocene structure covalently attached through a –CONH-bond to a phenyl ring on the glassy carbon surface. The spectrum is presented in Appendix Figure 5.3.
Since the barrier properties changed with increasing deposition time of the underlying phenylamine layer at the electrode surface, this suggests a possible means to control electron transfer at modified electrodes of this type. We investigated the electron transfer rates from two different deposition times while keeping the coupling reaction of ferrocene carboxylic acid constant.

<table>
<thead>
<tr>
<th>Mass / units</th>
<th>Ion structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.93</td>
<td>Fe</td>
</tr>
<tr>
<td>65.03</td>
<td>C₅H₅</td>
</tr>
<tr>
<td>92.05</td>
<td>C₆H₄NH₂</td>
</tr>
<tr>
<td>94.04</td>
<td>C₅H₅COH</td>
</tr>
<tr>
<td>108.06</td>
<td>C₅H₅CONH</td>
</tr>
<tr>
<td>120.97</td>
<td>C₅H₅Fe</td>
</tr>
<tr>
<td>186.01</td>
<td>C₁₀H₁₀Fe</td>
</tr>
</tbody>
</table>

Table 5.0 ToF-SIMS positive ion mass peaks of Fc-CONH- on 15 mm sigradur-G glassy carbon substrate.
Figure 5.17 Dependence of $\Delta E_p$ on scan rate for ferrocene (Fc) monolayers covalently linked to a GC substrate via an underlying layer of electro-deposited H$_2$NC$_6$H$_4$ on glassy carbon. Responses for two phenylamine deposition times are shown: (●) 250 s; (●) 100 s. The solid lines represent the responses predicted for 133 s$^{-1}$ and 313 s$^{-1}$ using DigiElch electrochemical simulation package.

Figure 5.17 demonstrates the effect on electron transfer for covalently coupled ferrocene moieties by varying the deposition times for derivartising a GC surface with C$_6$H$_4$NH$_2$ groups (Scheme 5.II). The apparent rate constant for the electron transfer rate was calculated using Laviron’s method, which assumes Butler-Volmer kinetics and a Langmuir adsorption isotherm. The values of $k$ at 100 sec and 250 sec were calculated to be 313 s$^{-1}$ and 133 s$^{-1}$ respectively. These values were confirmed by digital simulation of the scan rate dependence on $\Delta E_p$ as shown in Figure 5.17. The rate constant varies with the thickness of the underlying multilayer,
consistent with the distance dependence of electron transfer rate predicted by Marcus theory. However, shorter deposition times did not further increase the rate of heterogeneous electron transfer, suggesting that the reasons for the dependence on deposition time may be more complex than this.

5.3.5 Ru(II)(bpy)$_2$(L)$^{2+}$ linked with grafted aminophenyl groups on glassy carbon

![Diagram of Ru(II)(bpy)$_2$(mab-bpy)$^{2+}$ linked with grafted aminophenyl groups on glassy carbon electrode.]

**Figure 5.18** [Ru(bpy)$_2$(mab-bpy)]$^{2+}$ covalently linked to H$_2$NC$_6$H$_4$ grafted glassy carbon electrode.

Having successfully attached ferrocene carboxylic acid to the carbon surface we next focused on our luminescent ruthenium complex of interest. Thus, the carboxylic acid derivative [Ru(bpy)$_2$(mab-bpy)](PF$_6$)$_2$, (Complex 6) was attached to phenylamine derivatised conventional GC electrodes using the same coupling strategy used for Fc-COOH. The promising solution phase luminescence and redox properties for this complex (see chapter 3) suggested it might be a good candidate for modified electrode based ECL sensing. Early attempts showed promise from CV measurements of the layer as seen in Figure 5.19, which was performed in 1.0 M LiClO$_4$ electrolyte on a conventional 3 mm GC electrode. The $E^o$ for the Ru$^{2+/3+}$...
couple was 1.034 V versus Ag/AgCl which is similar to 0.84 V (versus ferrocene) found for the solution phase response. The peaks for the Ru$^{2+/3+}$ couple are distinct from the capacitive current although are very close to the solvent limit. The ΔEp was 52 mV at 0.1 V s$^{-1}$, which is consistent with a surface confined response with contributions from ohmic effects and/or slow heterogeneous kinetics due to the underlying grafted layer thickness, which proved a difficult parameter to control. The voltammogram in Figure 5.19 shows that [Ru(bpy)$_2$(mba-bpy)](PF$_6$)$_2$, coupled through a –CONH- bond on a carbon surface has substantial redox stability over a series of scans. The voltammograms show a faradaic current change for the Ru$^{2+/3+}$ redox couple with repetitive cycling in 1.0 M LiClO$_4$ electrolyte. It shows a 10% loss after 100 repetitive scans and 50% loss of the peak current after 200 scans. The capacitive current does not decrease during the time progressive scans show a loss in the Faradaic waves for the Ru$^{2+/3+}$ couple. This suggests that the underlining grafted layer of phenyl-NH$_2$ is not being stripped off, but the Ru(II) species is being slowly degraded during repetitive electrochemical cycling. Due to the low surface coverages and the somewhat irreproducible results associated with the coupling attachment method, this route to electrode modification was not perused further.
Figure 5.19 Cyclic voltammetry of [Ru(bpy)$_2$(mba-bpy)](PF$_6$)$_2$, (complex 6), covalently linked to a H$_2$NCO$_6$H$_4$-GC electrode surface in 1.0 M LiClO$_4$ electrolyte at 0.1 V s$^{-1}$. Electrode diameter (3 mm); the scans shown are of 1, 20, 50, 70, 100, 200, 500 cycles (outer to inner).
5.3.6 $[\text{Ru(II)(bpy)}_2(L)]^{2+}$ - MWCNT adducts immobilised on carbon electrodes

The relatively low surface coverage produced using the diazonium route prompted us to attempt a strategy involving electrodes with a much larger microscopic area. We explored the use of MWCNT-COOH deposited on carbon substrates to couple to a Ru(II) polypyridyl complex. The SPEs used in this study comprise a traditional three-electrode configuration. DropSens® SPEs that were also used in this study have the same configuration but already contain MWCNT-COOH functionality. Glassy carbon electrodes and Zensors®, which have the same configuration as DropSens® SPEs, but both required carboxylated MWCNTs to be deposited onto the surface prior to coupling the Ru complex were also used. We chose to utilise screen-printed electrodes in order to emulate a low cost and simple sensor platform. After covalently binding the Ru complex to the MWCNT-COOH coated electrode surface, as described in scheme 5.IV, the electrochemical and spectroscopic properties were characterised.
Voltammetric behaviour

The electrochemical behaviour of functionalised MWCNT- [Ru(bpy)$_2$(mab-bpy)]$^{2+}$ films on carbon SPEs was studied using cyclic voltammetry. In Figure 5.21 a CV measurement in 1.0 M LiClO$_4$ electrolyte vs. Ag/AgCl of [Ru(bpy)$_2$(mab-bpy)]$^{2+}$ (complex 7) coupled via an amide bond to carboxylated MWCNTs, that had been initially applied to the SPE carbon substrate. This figure also shows a solution phase CV response on a glassy carbon (GC) electrode for the freely diffusing ruthenium complex for comparison.

**Figure 5.21** (Blue): CV response at 0.05 V s$^{-1}$ in 0.1 M LiClO$_4$ electrolyte for [Ru(bpy)$_2$(mab-bpy)]$^{2+}$ attached to the carboxylated MWCNTs immobilized on a SPE. (Red): Solution phase CV for 1 mM [Ru(bpy)$_2$(mab-bpy)](PF$_6$)$_2$ dissolved in CH$_3$CN / 0.1 M TBAPF$_6$ electrolyte at 0.8 V s$^{-1}$ at a 3 mm GC electrode.
Figure 5.21 shows that the Ru$^{2+/3+}$ redox peaks exhibited by the immobilised Ru-CNT adduct (left) using scheme 5.IV are 250% larger than that obtained using the diazonium method used for the covalent attachment of the carboxylic acid derivative [Ru(bpy)$_2$(mba-bpy)](PF$_6$)$_2$ complex (scheme 5.III). The Ru$^{2+/3+}$-CNT redox couple in Figure 5.21 is reversible and the peaks display a Gaussian shape. The formal potential $E^0$ for the Ru$^{2+/3+}$ redox couple is 0.95 V vs Ag/AgCl and shows $\Delta E_p$ value of 40 mV at a scan rate of 0.1 V s$^{-1}$. Other electrolytes such as KPF$_6$, KCl and phosphate gave relatively poor voltammetric responses, possibly due to a more favourable ion-pairing interaction with the perchlorate ion.

The solution phase CV in Figure 5.21 for [Ru(bpy)$_2$(mab-bpy)](PF$_6$)$_2$ showed a pre-peak before the Ru(II) oxidation which continues to increase with repetitive cycling (Appendix Figure 5.4). Our solution phase CV results suggest that the amine complex begins to passivate the electrode surface due to the free amine being oxidized just before the Ru(II) redox wave. We do not observe this behaviour on the nanotubes, which confirms that the amine has been converted into an amide bond.

The linear scan rate dependence of the peak current ($i_p$), as shown in Figure 5.22, for both DropSens® and Zensor® electrodes demonstrate the redox reaction is surface confined, as expected for a surface confined system. The voltammetric peak areas were integrated, to obtain the charge passed (C) and used to calculate the apparent surface coverage ($\Gamma$) based on the geometric area (A) of the electrode, using equation (1). A typical surface coverage found for a DropSens® and Zensor® modified Ru-CNT SPE was estimated to be $7.89 \times 10^{-9}$ and $3.71 \times 10^{-9}$ (mol cm$^{-2}$) respectively.
Figure 5.22 Cyclic voltammograms of $[\text{Ru(bpy)}_2(\text{mab-bpy})]^2^+$, attached to drop coated MWCNT-COOH on screen printed Zensor® and DropSens® electrodes, as describe in Scheme 5.IV, and on GC, as describe in Scheme 5.V, at scan rates of 0.05 - 0.1 V s\(^{-1}\) (inner to outer) in 1.0 M LiClO\(_4\) electrolyte vs. Ag/AgCl. (bottom right corner) Scan rate dependence plots for Zensor® (O) $R^2$ 0.993; DropSens® (□), $R^2$ 0.995; GC (Δ), $R^2$ 0.994.

The $\Gamma$ results that were estimated for the Zensor® modified CNT SPEs were lower than the DropSens® electrodes as shown in Table 5.1. This might be due to the difference in the coating procedure of MWCNT-COOH onto the carbon surface of the SPEs. Overall, the surface coverages of Ru on SPEs were far higher than that of a typical monolayer system on the basis of geometric electrode area. This is due to the high surface area associated within the carbon nanotubes\(^{51}\) (see SEM results later).
Table 5.1 surface coverages (Γ) of Ru-CNT on DropSens®, Zensor® and 3 mm glassy carbon (GC) electrodes.

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>Charge</th>
<th>Area</th>
<th>Γ x 10⁻⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DropSens</td>
<td>1.06 x 10⁻⁴</td>
<td>0.1397</td>
<td>7.89</td>
</tr>
<tr>
<td>Zensor</td>
<td>4.5 x 10⁻⁵</td>
<td>0.1256</td>
<td>3.71</td>
</tr>
<tr>
<td>GC</td>
<td>2.43 x 10⁻⁵</td>
<td>0.07068</td>
<td>3.56</td>
</tr>
</tbody>
</table>

An alternative approach to forming an electrode modified with MWCNT - Ru(II) is described in Scheme 5.V where coupling the nanotubes with [Ru(bpy)₂(mab-bpy)](PF₆)₂ is carried out prior to depositing the Ru-CNT adduct onto a carbon surface. This was done in order to explore any electrochemical or other differences between the two types of preparations. It was found that Scheme 5.V was easier to utilize although, the Ru(II) complex loading was estimated to be lower compared to electrodes prepared via Scheme 5.IV. The voltammetric behavior for a GC electrode modified with functionalized [Ru(bpy)₂(mab-bpy)]²⁺-CNTs as described in Scheme 5.V is shown in Figure 5.22. The redox peaks from the Ru²⁺/³⁺ couple are well defined and the electrochemical properties were identical to the SPEs. The surface coverage of Ru on a GC surface is 3.56 x 10⁻⁹ mol cm⁻² which is lower than that found for DropSens® and Zensor® electrodes. The capacitance for each electrode increase in the order of DropSens® < Zensor® < GC suggesting that the amount of MWCNTs on the surface (and therefore the microscopic area) is different in each case.

In order to understand the functional stability and attachment properties of these electrodes, redox stability studies were carried out. As shown in Figure 5.23, the ruthenium modified CNT (Ru-CNT) DropSens® electrode shows outstanding long-term stability based on the background current measured in cyclic voltammetry of the ruthenium modified CNT DropSens® electrode in 1.0 M LiClO₄ at 0.1 V s⁻¹. In Figure 5.23, each data point corresponds to the current measured during a series of continuous cyclic voltammetric experiments over a 5-day period.
There is an initial decrease in surface coverage, probably due to the loss of physisorbed material or loosely attached nanotubes on the DropSens® electrode. However, once the voltammetric signal had stabilized, there was virtually no change in signal upon repeated scanning over a 5 day period. These electrodes have also shown that they can be repeatedly scanned in LiClO₄ electrolyte and demonstrate a 10% of the Ru²⁺/³⁺ voltammetric response after 100 scans.

![Figure 5.23](image)

**Figure 5.23** This shows the (\(i_p\)) current change (%) for functionalized [Ru(bpy)₂(mab-bpy)]²⁺-MWCNTs DropSens® SPE cycled using cyclic voltammetry for a 5 day period.
Figure 5.24 (Top) CV response for the Ru\textsuperscript{2+/3+} redox couple on a DropSens\textsuperscript{®} SPE electrode activated with EDC / NHS activation and then treated with 1 mM [Ru(bpy)\textsubscript{2}(mab-bpy)](PF\textsubscript{6})\textsubscript{2}. (bottom) This CV shows the response for the Ru\textsuperscript{2+/3+} redox couple of [Ru(bpy)\textsubscript{2}(mab-bpy)](PF\textsubscript{6})\textsubscript{2} when the EDC/NHS activation step is omitted.

Control experiments were carried out without EDC / NHS activation. In each case, an SPE electrode was immersed in the 1 mM [Ru(bpy)\textsubscript{2}(mab-bpy)](PF\textsubscript{6})\textsubscript{2} solution for 24 h. In Figure 5.24 redox active peaks were found for the Ru\textsuperscript{2+/3+} couple of [Ru(bpy)\textsubscript{2}(mab-bpy)](PF\textsubscript{6})\textsubscript{2} with the aid of EDC / NHS activation. Although, the case of the later control experiment (no coupling agents) the redox peak currents for Ru\textsuperscript{2+/3+} of [Ru(bpy)\textsubscript{2}(mab-bpy)](PF\textsubscript{6})\textsubscript{2} are barely present after the washing step, demonstrating that covalent attachment is achieved and linking can increase the loading density of Ru(II) on functionalized MWCNTs.
Layer morphology

We investigated the nature of the micro and nano-structured surface of Zensor® SPE, glassy carbon disc and DropSens® electrodes modified with MWCNT-COOH using scanning electron microscopy. Our intention was to gain insight into relationship between the surface nanostructure and the electrochemical properties. DropSens® carboxylated MWCNT SPEs were compared with our Zensor® and GC customized MWCNT-COOH deposited electrodes. In Figure 5.25, the DropSens® electrodes have the appearance of a disordered ensemble of carbon nanotubes on a surface composed of larger graphitic platlets. There are no graphite particles not covered by the nanotubes. The porous nature of the MWCNT layer is apparent on high magnification.

In Figure 5.26 a bare Zensor® SPE is characterised by rough graphite sheets overlaid on each other. After drop coating with MWCNTs a disordered layer of carbon nanotubes can be seen, similar to Figure 5.25. Unlike the DropSens® electrodes, the underlining features of the electrode are fully masked by the drop coated layer. This might be due to differences in the deposition method used by us compared to the commercial CNT-SPEs. Furthermore, the surface would possibly be subjected to various drying effects upon deposition and the necessary drying time at ambient temperature which could influence the dispersion of nanotubes on the surface. The modified GC disc electrodes showed similar morphology to our modified Zensor® SPEs (Appendix Figure 5.5). SEM was also performed after modification with [Ru(bpy)$_2$(mab-bpy)]$^{2+}$ to reveal any changes to the electrode surface as a result of this procedure. These SEMs showed small areas of the carbon surface that appear to have been stripped of the nanotubes (c.f. Zensor-MWCNT-COOH) which may have been washed away or moved to others areas of the electrode during their modification (Appendix Figure 5.5).
Figure 5.25 SEM images of a DropSens® electrode with drop coated MWCNT-COOH layer (A) 5,000 x magnification; (B) 10,000 x magnification; (C), 20,000 x magnification; (D), 50,000 x magnification.
5.3.7 ECL Properties of $[\text{Ru(bpy)}_2(X)]^{2+}$-MWCNT adducts on carbon electrodes

**ECL behaviour**

The solution phase ECL properties of $[\text{Ru(bpy)}_2(\text{pht-bpy})](\text{PF}_6)_2$ (complex 13), $[\text{Ru(bpy)}_2(\text{mab-bpy})](\text{PF}_6)_2$ (complex 7) are presented in chapter 3. The ECL efficiency $\Phi_{\text{ECL}}$, measured in acetonitrile for complex 13 with the phthalate protecting group was 0.074 while complex 7 as the free amine gave an $\Phi_{\text{ECL}}$ of 0.001 which is significantly lower than that found for $[\text{Ru(bpy)}_3]^{2+}$. However, the low ECL efficiency
for complex 7 is thought to be due to the passivation from the free amine group on the electrode surface (see section 5.3.6, voltammetric behaviour). Therefore, this figure will not reflect the efficiency of the complex after attachment via amide bond formation.

Taking 2-(dibutylamino) ethanol (DBAE), a tertiary amine, as a model analyte, preliminary ECL experiments were performed on the Ru-CNT/ DropSens© SPEs using cyclic voltammetry with simultaneous light detection. The DropSens© SPEs were chosen for this study due to their high faradaic currents seen for the Ru^{2+/3+} redox couple during the voltammetric characterization. In Figure 5.27 a CV / ECL-potential profile for a solution of 100 µM DBAE in 0.1 M LiClO₄ electrolyte is shown. The left side of Figure 5.27 shows the CVs for a Ru-CNT electrode with and without the co-reactant. The Ru^{2+/3+} redox couple becomes irreversible with the addition of the co-reactant due to the reaction of Ru^{3+} with the co-reactant (or a species derived from the co-reactant). Electrochemiluminescent emission is observed in conjunction with the change in the redox state of the Ru center as shown on the right side of Figure 5.27. The conversion of the NH₂ group to an amide probably increases the ECL signal compared to solution phase because parasitic reactions involving the amine are no longer present. In the control experiment, ECL emission is not observed in the absence of DBAE in the same solution medium.
Figure 5.27 (Left) CVs of Ru-CNT / DropSens® SPE without (−) and with (---) DBAE co-reactant vs Ag/AgCl. (Right) Corresponding ECL-potential curves in the absence (A) and the presence (B) of 100 µM DBAE in 0.1 M LiClO4 electrolyte, with a scan rate of 0.1 Vs⁻¹.

Figure 5.28 shows the ECL spectra of the Ru-CNT adduct on a DropSens® electrode in the presence of 40 mM DBAE as the co-reactant when the electrode was held at a bias potential above 1.0 V Vs Ag/AgCl. The emission peak maximum of the Ru-CNTs appears at 640 nm. This $\lambda_{\text{max}}$ is red-shifted by 15 nm compared with the free [Ru(bpy)₂(mab-bpy)](PF₆)₂ dissolved in acetonitrile (625 nm). The change in $\lambda_{\text{max}}$ for the ECL spectra is probably due to the Ru centers being in different dielectric environments in the layer, compared with the solution phase.⁵⁰

The intense ECL emission led us to investigate the potential use of these functionalised nanotubes on a SPE for sensing applications. The ECL of
[Ru(bpy)$_3$]$^{2+}$ and its derivatives has become an attractive detection tool for biochemical substances containing amine functional groups, such as amino acids and alkaloids.\cite{73} Codeine phosphate is an important pharmaceutical compound and has been detected using ECL.\cite{73} The ECL emission from the modified electrodes in the presence of codeine at concentration ranging between $1 \times 10^{-6}$ and $5 \times 10^{-6}$ M is shown on the right side of Figure 5.29. The ECL signal is clearly distinct from the baseline at all concentrations used. Figure 5.29 shows a calibration curve (left) plotted for codeine concentrations vs. ECL intensity using the functionalized [Ru(bpy)$_2$(mab-bpy)]$^{2+}$-CNT adducts deposited on DropSens® SPEs. The ECL intensity varies linearly with the codeine concentration in this range. The limit of detection (S/N=3) for codeine using this approach was $6 \times 10^{-6}$ M and the ECL measurements demonstrated reproducible results for repetitive measurements on a Ru-CNT / DropSens® SPE (RSD = 2.7%).
Figure 5.28  (Red) ECL spectra of a functionalised $[\text{Ru}(\text{bpy})_2(\text{mab-bpy})]^2^+\cdot\text{CNT}$ adduct giving a ECL $\lambda_{\text{max}}$ of 640 nm on a 4 mm DropSens® SPE electrode with 40 mM DBAE at pH 7.5 in phosphate buffer. (Dotted line) Solution phase ECL spectra of 1 mM $[\text{Ru}(\text{bpy})_2(\text{mab-bpy})](\text{PF}_6)_2$, (complex 7) in CH$_3$CN / 0.1 M TBAPF$_6$ electrolyte using annihilation ECL giving a ECL $\lambda_{\text{max}}$ of 625 nm on a 3 mm conventional glassy carbon (GC) electrode.
Figure 5.29 (left) Calibration curve for codeine phosphate at the Ru-CNT / DropSens® SPE in 0.1 M LiClO₄ (pH 6) containing 0.1 M KCl, R² = 0.998. (Right) ECL emissions from codeine phosphate at the Ru-CNT / DropSens® surface using chronoamperometry. Potential was stepped from 0.0 V to 1.1 V vs. Ag/AgCl.
5.3 Conclusion

Two main approaches to electrode modification were explored for the formation of ECL-active electrode interfaces. This included the use of diazonium salts and functionalised nanomaterials. Multilayer coverages were obtained at long deposition times during the electrografting of $^*\text{N}_2\text{C}_6\text{H}_4\text{NH}_2$ to a GC surface. The surface coverages obtained for grafting phenyl amine groups at short and long deposition times at a GC surface were examined through their blocking behaviour during impedance and cyclic voltammetry with $[\text{Fe(CN)}_6]^{3-}$. At short deposition time (< 10 sec), limited blocking behaviour was observed, as the $[\text{Fe(CN)}_6]^{3-}$ redox wave was still present, but not typical, for a fully reversible cyclic voltammogram. At longer deposition times no redox waves were present for the $[\text{Fe(CN)}_6]^{3-}$ redox couple which suggested complete blocking behaviour at the surface of the electrode. The impedance data showed that $R_{CT}$ increased with deposition time of the grafting layer and $R_{CT}$ is inversely proportional to the heterogeneous rate constant ($k^\circ$). Ferrocene-COOH was coupled to these amine phenyl grafted GC surfaces and demonstrated a reversible surface confined response for the ferrocene redox couple. The electron transfer rates of coupled ferrocene decreased when the underlying grafted layer was increased due to longer deposition times used. Unfortunately, preliminary results for the covalent attachment of Ru(II) polypyridyl complex salts to functionalised (i.e. $-\text{C}_6\text{H}_4\text{NH}_2$, $-\text{C}_6\text{H}_4\text{COOH}$) carbon substrates demonstrated some promise but were very variable in their response.

Nanomaterials such as carboxylic acid MWCNTs proved to be a better choice for electrode modification. Carbon nanotubes proved very attractive due to their unique structural, superior mechanical and electronic properties. Stability, reproducibility, robustness, electrochemical properties, kinetics and sensitivity are key factors in any electrochemical sensing application. Three types of electrodes were used which included Zensor® and DropSens® SPEs and GC electrodes. The cyclic voltammetric responses for Ru-CNT adducts on these electrode substrates gave well-defined surface confined responses which were stable with continuous cyclic over a 5 day period. Thus, scheme 5.IV proved to be a better approach for the preparation of these modified electrodes. SEMs showed the carbon nanotube network deposited on a
carbon surface and that the MWCNTs deposited on Zensors® and GC were similar to that found for DropSens® electrodes. Finally, intense ECL was observed for codeine phosphate when the Ru-CNT SPE was cycled with the analyte in LiClO₄ electrolyte. Overall, this system showed good electrochemical behaviour, high stability and intense ECL emission for the use in a sensing application.
References

(49) Yang, W.; Thordarson, P.; Gooding, J. J.; Ringer, S. P.; Braet, F. Nanotechnology 2007, 18, 412001.
Chapter 6 Conclusion and future Work

6.1 Summary

Due to its exceptional properties, tris(2,2ʹ-bipyridine)ruthenium(II) \([\text{Ru}(\text{bpy})_3]^{2+}\), has been the focus of research interest for the majority of solution phase and solid state ECL systems. We have used this complex both as a starting point from which to explore new structures, \(\{[\text{Ru}(\text{L})_3]^{2+}\) and \([\text{Ru}(\text{bpy})_2(\text{L})]\)\(^{2+}\), and as a reference for benchmarking the properties of these new ruthenium complexes. Our interest here lies in the design and synthesis of complexes, suitable for surface confined ECL based sensing strategies, which retain their favorable electrochemical and luminescence properties. As shown in Chapter 3, a secondary aim was to explore the extent to which these properties could be modulated in order to produce sensing molecules with for example varying emission wavelength.

In chapter 2 we describe the design and synthesis of a variety of 2,2ʹ-bipyridyl derivatives which were in turn, used to synthesis ruthenium(II) polypyridyl complexes suitable for electrode modification. As shown in Scheme 2.1 and 2.2 in chapter 2, simple entities were used to synthesis \(\alpha,\beta\)-ketone precursors which were obtainable using solventless, conventional and microwave conditions. These \(\alpha,\beta\)-ketones reacted with pyridinium salts to yield 4,6-diphenyl and 4-phenyl 2,2ʹ-bipyridine derivatives using the Kröhnke pyridine synthesis procedure. We have also demonstrated that these bipyridines can be further functionalized after their initial formation to suit the electrode modification procedure. By using Schemes 2.3 and 2.4, the lithiation towards the 4,4ʹ- dimethyl positions of bipyridine was easily controlled which allowed further manipulation. As a result, this proved to be a suitable route for the development of mono- and di-substituted bipyridine ligands with alkyl carboxylic acid and amine functionality for covalent attachment electrode modification.

In chapter 3 we used a combination of electrochemical, spectroscopic and
computational techniques to explore the fundamental properties of a series of these ruthenium diimine complexes bearing chemical attachment functionality. With appropriate choice of ligand functionality, it is possible to manipulate emission wavelengths over a significant range while keeping the redox ability of the complex relatively constant. This is important because an excited state cannot be produced unless the reaction which precedes its generation has sufficient driving force. DFT calculations showed that in the case of electron withdrawing substituents such as ester or amide, the excited state is located on the substituted bipyridine ligand whereas in the case of alkyl functionality it is localised on an unsubstituted bipyridine. The results of this chapter highlight the fact that the factors dictating annihilation ECL efficiency are interrelated. For example, the same factors that determine $\Delta G$ for the annihilation reaction (i.e. the relative energies of the HOMO and LUMO) have a corresponding effect on the energy of the excited state product. As a result, most of the complexes populate the excited state with a similar efficiency ($\Phi_{ex}$) despite the relatively wide range of emission maxima. The quantum yield of emission ($\Phi_{p}$) and the possibility of competing side reactions are found to be the main determinants of ECL intensity.

In chapter 4, we have used electrochemical, spectroscopic and surface techniques to explore the solid-state electrochemistry and solid state electrochemiluminescence (ECL) properties of ruthenium complexes with bipyridyl and phenanthroline based ligands. The ability to study ECL and related phenomena in solids is important for practical applications such as novel analytical and light-emitting devices. We employed a novel method for the characterization of solid state ECL properties by using surface bound micro-particles of these compounds. For solid-state applications, it is essential to determine the mobility of charged species; i.e. electrons and ions, and thus emphasis was given to the measurements of transport properties. In the solid state, stable voltammetric responses were observed for the ruthenium complexes studied which were characterized by semi-infinite linear diffusional charge transport at relatively short experimental timescales. The deposits could also be exhaustively oxidized at longer experimental timescales,
exhibiting finite diffusional type voltammetric behaviour. It was shown that the oxidation and reduction rate depend not only on the structure of the phenanthroline ligand, but also on the identity and concentration of the anion of the supporting electrolyte. This suggests that ion insertion/desorption into the solid is rate limiting rather than electron self-exchange. In situ electrochemical AFM reveals that initial redox cycling, necessary to “break-in” the system, is accompanied by subtle morphological changes, implying that the cycling promotes an electrochemical change in the solid phase.

ECL was observed from the micro-particle films when oxidized in the presence of a suitable co-reactant. The intensity of ECL is lower compared to the solution phase system because the reaction with the co-reactant occurs only at the surface of each particle. Annihilation between the sequentially oxidized and reduced forms of the material, which likely occurs in the bulk of the solid rather than at the surface, produces ECL which is notably more intense than in the co-reactant pathway.

Another important aspect of the work described in chapter 4 was the novel use of solid-state spectroelectrochemistry to characterize the two ruthenium complexes, [Ru(dpp)3](PF6)2, and [Ru(bpy)2(dpb)](PF6)2 in solid form. When micro-particles of these materials were immobilised on ITO electrodes, spectral changes could be monitored simultaneously with electrochemical signals providing a range of extra information. Monitoring the absorption during slow cyclic voltammetric scans confirms the exhaustive oxidation of the Ru2+ species to the Ru3+ form. The derivative of the absorbance signal monitored at a single wavelength during potential cycling is morphologically identical to a cyclic voltammogram with no background current. This technique is shown to be useful when peaks of small magnitude are obscured by capacitive background or when peaks close to the solvent limit are obscured by solvent electrolysis current. The technique effectively widens the electrochemical window available for voltammetric measurements. After suitable correction of the signal, the value of the voltammetric peak height (i_p), as well as peak potential (E_p), may be obtained from the derivative absorbance signal. Chronospectrometry is demonstrated to provide the
equivalent to a chronocoulometric response, but is closer to the ideal simulated response. A facile method for simulating time or potential-dependant spectro electrochemical responses using commercial electrochemical simulation software (e.g. DigiElch or DigiSim) was described. Absorbance transients monitored during the electrolysis of solid particles of \([\text{Ru}(@dpp)_3](\text{PF}_6)_2\) show best agreement with simulated data at very short and very long timescales. This observation, in conjunction with the observations from the potential scan experiments, provides strong evidence that the absorbance, charge, or current vs. time behaviour of the system can be adequately described by a semi-infinite diffusional model at short experimental timescales and by a finite diffusional model at sufficiently long timescales.

In chapter 5 we show that by exploiting both functionalized ruthenium complexes and covalent attachment schemes to create a sensing interface, we can tailor of the necessary properties required to suit specific needs while achieving the best possible sensor performance. We used diazonium chemistry for the electrochemically assisted modification of carbon electrode surfaces with reactive amine groups. These aminated surfaces served as a convenient and highly stable platform to immobilize ferrocene carboxylic acid and an alkyl carboxylic acid ruthenium complex. The blocking behaviour of the electrografted layer was characterized using AC impedance spectroscopy and cyclic voltammetry. From these investigations, we found that the increase in \(R_{CT}\) values calculated from impedance measurements and loss of the ferricyanide redox waves during a CV scan showed that the grafted layer becomes thicker and more compact when the deposition time for the \textit{in-situ} generated \(\text{N}_2\text{C}_4\text{H}_4\text{NH}_2\) ion is long. These investigations were performed to ensure that the underlining electrode had been fully modified. We also found that, when a redox moiety is attached, the heterogeneous electron transfer rate can be, to an extent, controlled by varying the thickness of the grafted layer.

Other attachment modes included the use of carboxylic acid functionalized multi-walled carbon nanotubes (MWCNT-COOH) on screen printed electrodes
and GC electrodes. In this scheme, amine functionalised ruthenium complexes were covalently linked, through an amide bond, to the surface of the CNT either before or after deposition on the electrode. The voltammetry, surface morphology and ECL properties were examined for this system. The high surface area of the nanotubes gave rise to well-defined redox waves for the Ru$^{2+/3+}$ couple, which were stable over several days with repetitive cycling. SEM imaging showed a random arrangement of MWCNT on a carbon substrate after their deposition. Intense ECL was seen from these modified stable electrodes which proved suitable for the detection of model analytes and pharmaceutical compounds at micro-molar concentrations.

6.2 Future work

In more recent times, the success of chemiluminescence and ECL from [Ru(bpy)$_3$]$^{2+}$ and its derivatives has spurred the development of new metal based luminescent materials with known and novel ligands. The synthesis of cyclometalated iridium complexes has attracted attention as a promising option for the search of new luminescent materials. This is due to relatively high photoluminescence efficiencies and wide range emission wavelengths of these materials. This includes the development of neutral bis-cyclometalated iridium(III) complexes with a monoanionic bidentate ligand, water soluble based Ir complexes, bis-cyclometalated iridium complexes coordinated with C,N,C or N,C,N terpyridine ligands. However, there has been no research into the coordination of N,N,C bipyridine ligands, such as the type described here. Figure 6.0 shows proposed bis-cyclometalated iridium(III) complexes using the N,N,C ligand series that we had intended to be used for the development of novel ruthenium(II) polypyridyl complexes in this thesis. The focus is now on the promising photoluminescent properties exhibited by coordinating these ligands to metals such as iridium.
Lastly, it is worth pointing out that the modification of electrode surfaces using conventional coupling chemistry with reagents such as EDC and NHS which is often taken for granted, can be in our experience be anything but straightforward and frequently low yielding. We next propose using click chemistry as an alternative mode of attachment for luminescent materials. The future focus of this research will be to covalently attach, through a 1,2,3-triazole bond linker, Ru(II) complexes, such as those described in this thesis, onto functionalized carbon nanotubes and other carbon surfaces. This will increase stability and sensitivity for ECL sensing strategies.

**Figure 6.0** Proposed iridium(III) bis-cyclometalated complexes based on the 4,6-diphenyl-2,2’-bipyridine ligands synthesized in chapter 2.
Appendix Chapter 3 Simultaneous control of spectroscopic and electrochemical properties in ECL active tris(2,2′-bipyridine)ruthenium(II) derivatives.

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Appendix Figure 3.0 Comparison of HOMO - LUMO gap (H-L) calculated by DFT and time dependant (TD) DFT with experimental data for the [Ru(bpy)2(L)]2+ complexes in acetonitrile.

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Appendix Figure 3.1 Compound 0. Mulliken population analysis of frontier molecular orbitals.
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**Appendix Figure 3.2** Compound 1. Mulliken population analysis of frontier molecular orbitals.

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**Appendix Figure 3.3** Compound 2. Mulliken population analysis of frontier molecular orbitals.
### Appendix Figure 3.4 Compound 3. Mulliken population analysis of frontier molecular orbitals.

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**Appendix Figure 3.6** Compound 5. Mulliken population analysis of frontier molecular orbitals.

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**Appendix Figure 3.8** Compound 7. Mulliken population analysis of frontier molecular orbitals.
Appendix Chapter 4  Solid state electrochemical properties of ruthenium polypyridyl complexes

Appendix Figure 4.0  Solid state UV-VIS spectro electrochemistry of microparticles of [Ru(tmp)$_3$](PF$_6$)$_2$ immobilized on an indium tin oxide (ITO) electrode in contact with 0.1 M LiClO$_4$ electrolyte. The immobilized layer was cycled using cyclic voltammetry at a scan rate of 0.005 Vs$^{-1}$
Appendix Chapter 5  Characterisation of electrochemically addressable 2D luminescent sensing interfaces

Appendix Figure 5.0 Modified Quartz micro-crystal (QCM) cell for 15 mm carbon disc electrodes used in our electrochemical laboratory investigations
Appendix Figure 5.1 SPE electrochemical cell for routine voltammetry and ECL experiments.
Appendix Figure 5.3 ToF-SIMS spectra from the positive region for ferrocene on GC substrate.
Appendix 5.4 Solution phase cyclic voltammogram of 1.0 mM [Ru(bpy)$_2$(mab-bpy)]($\text{PF}_6$)$_2$ in CH$_3$CN / 0.1 M TBAPF$_6$ electrolyte at scan rate 0.1 Vs$^{-1}$ using a 3 mm glassy carbon electrode.
Appendix Figure 5.4 these are SEM images of a glassy carbon disc electrode with MWCNT-COOH. (Left) Area was sampled with 50,000 x magnification; (Right) sample area with 20,000 x magnification.

Appendix Figure 5.5 SEM images of a Zensor electrode with MWCNT-COOH after Ru-CNT modification. (Top left) 5,000 x magnification; (Top right) 10,000 x magnification; (Bottom left), 20,000 x magnification; (Bottom right), 50,000 x magnification.