**Dinuclear Ruthenium and Platinum Complexes:
Design, Synthesis, Characterization
and Potential Applications**

by

Gaëtan LeClair, M.Sc.

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University
Ottawa, Ontario
August 2008

© copyright
2008, Gaëtan LeClair

Library and
Archives Canada

Bibliothèque et
Archives Canada

Published Heritage
Branch

Direction du
Patrimoine de l'édition

395 Wellington Street
Ottawa ON K1A 0N4
Canada

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

ISBN: 978-0-494-43898-5

Our file Notre référence

ISBN: 978-0-494-43898-5

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protègent cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Abstract

Near infra-red electrochromes find many applications, especially in the telecommunication industry as optical attenuators in fiber optic networks at the 1550, 1310 and 980 nm bands. Dinuclear ruthenium complexes based on the diacylhydrazide (DCH) or oxamide bridging ligands are NIR electrochromic materials that are well known.

This research project involved the preparation macromolecular materials containing dinuclear ruthenium complex moieties by polymerization of functionalized complexes that could be processed into free standing, transparent thin films which were then evaluated in prototype devices for potential applications.

Firstly, second-generation dendrimers were investigated. Unfortunately, the devised synthetic routes proved unsuccessful and only first-generation dendrimers were obtained. Subsequently, linear and hyperbranched polyurethane polymers were prepared from diol ruthenium complexes and suitable isocyanates. Crosslinked DCH ruthenium complex films were insoluble in common organic solvents and demonstrated the promising NIR electrochromic properties. Moreover, when these films were probed at 1550 nm in a reflective configuration, an optical attenuation of 17.5 dB/ μm was recorded, which corresponds to a three fold increase when compared to similar devices operating in a transmissive configuration. Biurea complex analogues absorb near 1200 nm, and films were prepared. However, due to lower electrochromic material loading and incomplete crosslinking, the optical attenuation at both the 980 and 1310 nm bands only reached 5 dB/ μm .

Another aspect of this project was to investigate the potential of a glucose biosensor application using glucose oxydase while monitoring the NIR absorption. The response time of an all-solution configuration was rather slow, relying only on slow diffusion dynamics. Response time was even slower with previously prepared thin films.

Finally, the same DCH ligand system was used to prepare a series of dinuclear platinum complexes to investigate their emissive properties. It was found that the bridging ligand had negligible effects on the photoluminescence of the complex. Increasing the electron donating potential of the peripheral ligand did promote a bathochromic shift, its magnitude dependant on the ligand. Contrary to the ruthenium complexes, the platinum complexes did not exhibit a mixed valence state. While emission at 600 nm was achieved, NIR phosphorescence could be attained by using other peripheral ligands.

Acknowledgments

Although the path to a PhD degree is filled with obstacles and trials, it provides an unequivocal learning opportunity and in all my years as a university student, never did I learn so much. Research does not follow a straight path and things may go awry, and it will, possibly for long periods of time, but learning from these mistakes and mishaps provides the occasion to develop extremely valuable troubleshooting skills. In the grand scheme of things, everything eventually falls in place.

I would like to express my gratitude towards my supervisor Dr Zhi Yuan (Wayne) Wang for giving me the opportunity to pursue my graduate studies in the field of material science. I had the freedom to pursue ideas and when I lost focus from the possibilities, he pointed me in the right direction with constructive advice.

Next in line is my partner, Annick, whom has been a solid foundation in my life for almost nine years. She has helped me grow and mature into the person I am today. I thank you dear, for believing in me and supporting me in my times of need.

My thanks go to my lab mates and friends who made the last 5 years of my life in Steacie Building 'interesting' to say the least. It was a first for me to be part of a large group, made up of people from various parts of the world, permitting me to experience and learn about other cultures without travelling half way across the world.

I wish to thank my family for their guidance and moral support throughout the years. The world is increasingly more complicated and their wisdom has proven invaluable towards my life experiences.

I would like to express my gratitude to Carleton University and the Ontario government for financial support throughout this endeavour.

Lastly, I am grateful to the technicians and support staff of the Ottawa-Carleton Chemistry Institute for spectral acquisition, ‘MacGyvering’ gadgets and making sure that essential forms were properly and timely filled so that I could eventually graduate.

Table of Contents

Abstract	i
Acknowledgments	iii
List of Figures	vii
List of Tables	ix
List of abbreviations	x
Chapter 1 – Introduction	1
1.1 – Electrochromic materials	1
1.2 – Electrochemical characterization of electrochromic materials	2
1.3 – Other characterization parameters	7
1.4 – NIR-active electrochromic materials	9
1.4.1 – Metal oxides	9
1.4.2 – Hexacyanometallates: Prussian blue	11
1.4.3 – Radical anions of conjugated diimides and diquinones	13
1.4.4 – Porphyrins and phthalocyanines	14
1.4.5 – Conjugated polymers	16
1.4.6 – Transition metal complexes	19
1.5 – Applications	25
1.6 – Rationale and objectives	29
Chapter 2 – Bridging and peripheral ligands	30
2.1 – Introduction	30
2.1.1 – Synthetic methods for bridging ligands	31
2.1.2 – Synthetic methods for non-bipyridine peripheral ligands	34
2.2 – Results and discussion	35
2.2.1 – Bridging ligands	35
2.2.2 – Peripheral ligands	41
2.3 – Conclusion	42
2.4 – Experimental	42
Chapter 3 – Dinuclear ruthenium and platinum complexes	53
3.1 – Introduction	53

3.2 – Results and discussion	55
3.2.1 – Ruthenium complexes	55
3.2.2 – Platinum complexes	69
3.3 – Conclusion	83
3.4 – Experimental	84
Chapter 4 – Macromolecular materials of ruthenium complexes	95
4.1 – Introduction	95
4.2 – Results and discussion	98
4.2.1 – Dendrimers	98
4.2.2 – Linear polymers	103
4.2.3 – Hydrogels and sol-gels	108
4.2.4 – Hyperbranched polymers	110
4.3 – Conclusion	111
4.4 – Experimental	113
Chapter 5 – Device applications based on dinuclear ruthenium complexes	122
5.1 – Introduction	122
5.2 – Results and discussion	126
5.2.1 – Glucose biosensor	126
5.2.2 – Reflective NIR variable optical attenuator	129
5.3 – Conclusion	135
5.4 – Experimental	136
Claim to original research	139
References	141
<u>Appendices</u>	153
Appendix 1 – ^1H and ^{13}C NMR spectra of ligands	153
Appendix 2 – NMR of green impurity from biurea complex	184
Appendix 3 – NMR of piperidine biurea complex soluble in DCM	186
Appendix 4 – Quantum yield determination of 44	188
Appendix 5 – Crystallography data of 46	190
Appendix 6 – Reflective VOA attenuation measurement apparatus	199

List of Figures

Figure 1.1 – Simulated CV of a reversible one-electron redox couple ³	3
Figure 1.2 – Solvent optimal voltametric operating range ⁴	5
Figure 1.3 – OTTLE cell assembly: a) innards, b) side view, and c) assembled cell	7
Figure 1.4 – Schematic representations of a) response time and b) contrast ratio and electrochemical stability	8
Figure 1.5 – 3-D model of PB and corresponding redox reactions	12
Figure 1.6 – General structure of a) diimides and b) diquinones	13
Figure 1.7 – Structure of quinone-imine EC	14
Figure 1.8 – Structures of a) porphyrin, b) phthalocyanine and c) metallized porphyrin (β and meso positions are defined)	14
Figure 1.9 – Selected conductive polymers	17
Figure 1.10 – Polyaniline redox states	18
Figure 1.11 – Partial MO diagram for an octahedral complex: a) LMCT and b) MLCT	20
Figure 1.12 – Bis-dithiolene square planar complexes.	21
Figure 1.13 – Various dinuclear metal complexes (counter ions omitted for clarity)	22
Figure 1.14 – Example of a dinuclear molybdenum complex	24
Figure 1.15 – The a) trinuclear and b) hexanuclear ruthenium complexes	25
Figure 1.16 – NIR window in a) OFF mode and b) ON mode	26
Figure 1.17 – Night vision system	28
Figure 2.1 – General synthetic routes to symmetric and unsymmetric DCH ligands	31
Figure 2.2 – Alternative biurea ligand synthesis	32
Figure 2.3 – Oxamide ligand synthesis	33
Figure 2.4 – Synthesis of 2-phenylpyridine and quinoxaline peripheral ligands	35
Figure 2.5 – Diol-DCH synthesis via ethyl acetoacetate coupling	37
Figure 2.7 – Variable temperature effect on amide ¹ H region of 17	40
Figure 2.8 – Peripheral ligands considered	41
Figure 3.1 – Model of a) DCH and b) OXA dinuclear ruthenium complexes	54
Figure 3.1 – CV of 30 , 31 and 36	56
Figure 3.2 – Potential energy curves of a weakly coupled (a) and a strongly coupled (b) mixed valence state	59
Figure 3.3 – Spectroelectrochemistry of 36 and Ru ^{II} /Ru ^{III} states of 33 and 38	62
Figure 3.4 – Spectroelectrochemistry of 36G and CV (inset)	63
Figure 3.5 – ESI-MS of 36G	64
Figure 3.6 – CV of 39S and 39I	66
Figure 3.7 – Spectroelectrochemistry of 39 , 39S and 39I	67
Figure 3.8 – ESI-MS of 35	69
Figure 3.9 – Structures of platinum complexes 44-46	70
Figure 3.10 – ESI-MS of 46	71
Figure 3.11 – Photoluminescence spectra of 44-45 and absorption spectra (inset) of 44-46 (1x10 ⁻⁶ M solutions in DCM, not degassed)	72
Figure 3.12 – ORTEP drawing of 46	75
Figure 3.13 – CV of 44 in DCM (0.1M TBAH, 200 mV scan rate)	76
Figure 3.14 – TGA of 44-46	77
Figure 3.15 – Structure of 47-49 and stereoisomers	78
Figure 3.16 – ESI-MS of isolated fractions of 47	80

Figure 3.17 – Absorption spectra of 47-49 in DCM (inset: spectra expansion)	81
Figure 3.18 – Visible PL of 47-49 (excited at 365 nm)	82
Figure 3.19 – PL spectra of 47-48 in DCM (excited at 360 nm)	82
Figure 3.20 – Visible PL of 49 and ligand mpbq (350 nm excitation)	83
Figure 4.1 – Dendrimer depiction showing generation levels (C = core)	97
Figure 4.2 – G2 dendron 51 reaction scheme	99
Figure 4.3 – G2 dendrimer 57 pathway via Suzuki coupling	100
Figure 4.4 – Stick (top) and 3-D model (bottom) of ruthenium complex of 53 (hydrogens omitted for clarity)	101
Figure 4.5 – Tetra DCH G1 dendrimer synthesis	102
Figure 4.6 – Spectroelectrochemical properties of 59 (CV in inset)	103
Figure 4.7 – Polyester and polyurethane synthesis (bpy omitted for clarity)	104
Figure 4.8 – Hydroxyacid complex synthesis	105
Figure 4.9 – Ligand 61 and triazole ‘click’ chemistry (showing possible isomers)	106
Figure 4.10 – ESI-MS of the attempted complexation of 61	107
Figure 4.11 – Absorption spectra of solgel films containing 35 (inset: picture of ‘A’ films)	110
Figure 4.12 – Sample spin-coated crosslinked films containing 41	111
Figure 5.1 – Glucose oxidase sensing scheme considered	122
Figure 5.2 – GOX active site mechanism	123
Figure 5.3 – a) transmissive and b) reflective VOA constructs	124
Figure 5.4 – ITO NIR reflectance (100 nm thick coating)	125
Figure 5.5 – Oxidation of 34 with hydrogen peroxide	126
Figure 5.6 – Enzymatic oxidation of 34 by GOX at various glucose concentrations	127
Figure 5.7 – CV of crosslinked polyurethane film of 41	130
Figure 5.8 – Chronoamperometry of a crosslinked polyurethane film of 41 using a 5 second stepping time	132
Figure 5.9 - Chronoamperometry of a crosslinked polyurethane film of 41 using a 2.5 second stepping time	133
Figure 5.10 – Chronoamperometry at 1310 nm of a crosslinked polyurethane film of 39 using a 5 second stepping time	134
Figure 5.11 – Chronoamperometry at 980 nm of a crosslinked polyurethane film of 39 using a 5 second stepping time	134

List of Tables

Table 1.1 – Coloration efficiency dependence of WO ₃ electrochromes	11
Table 1.2 – Optical properties of some polythiophenes	19
Table 2.1 – Identification, melting points and yields of hydroxyl ligands prepared	36
Table 2.2 – Identification, melting points and yields of other ligands	38
Table 3.1 – Electrochemical properties of the ruthenium complexes	57
Table 3.2 – Spectroelectrochemical properties of ruthenium complexes	61

List of abbreviations

AIBN	Azobisisobutyronitrile
Alq ₃	tris(8-hydroxyquinolino)aluminium
AM	acrylamide
APS	ammonium persulfate
ATR	attenuated total reflectance
bpy	2,2'-bipyridine
CDI	1,1'-carbonyldiimidazole
CE	counter electrode
COSY	correlation spectroscopy
CTAB	cetyl trimethylammonium bromide
CV	cyclic voltammetry
DABCO	1,2-diazabicyclo[2,2,2]octane
dB	decibel
DCC	dicyclohexylcarbodiimide
DCH	diacyl hydrazide
DCM	dichloromethane
DEAD	diethylazodicarboxylate
DIAD	diisopropylazodicarboxylate
DMAP	dimethylamino pyridine
DME	1,2-dimethoxyethane
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
DW	distilled water
EC	electrochromic
ECD	electrochromic display
EDOT	3,4-ethylenedioxythiophene
EI	electron ionisation
E _{PA}	anodic potential
E _{PC}	cathodic potential
ESI	electrospray ionisation
ESR	electron spin resonance
FAD	flavin-adenine dinucleotide
FT-IR	Fourier transform infrared
GOX	glucose oxidase
GPC	gel permeation chromatography
η _D	refractive index
HMBC	heteronuclear multiple bond correlation
HMDI	hexamethylene diisocyanate
HOMO	highest occupied molecular orbital
HSQC	heteronuclear single quantum correlation
ICP-MS	inductively coupled plasma mass spectrometry
IR	infrared
ITO	indium-doped tin oxide
IVCT	inter-valence charge transfer
LMCT	ligand-to-metal charge transfer

LUMO	lowest unoccupied molecular orbital
MBA	methylene bisacrylamide
MeCN	acetonitrile
MLCT	metal-to-ligand charge transfer
MMLCT	metal-metal-to-ligand charge transfer
Mp	melting point
mpbq	2-Methyl-3-phenyl-benzo[g]quinoxaline
mpq	2-Methyl-3-phenylquinoxaline
MS	mass spectrometry
NHE	normal hydrogen electrode
NIR	near infrared
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
ORTEP	Oak Ridge thermal ellipsoid program
OTTLE	optically transparent thin layer electrode
OXA	oxamide
PB	prussian blue
PC	polycarbonate
PG	prussian green
PL	photoluminescence
ppy	2-phenylpyridine
pq	2-phenylquinoline
PW	prussian white
PX	prussian brown
RBF	round bottomed flask
RE	reference electrode
R _f	retention factor
SCE	standard calomel electrode
TBAH	tetrabutylammonium hexafluorophosphate
TEA	triethylamine
terp	terpyridine
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TLC	thin layer chromatography
TMED	tetramethylene ethylene diamine
TMP	trimethylolpropane
TMP-NCO	trimethylolpropane, carbamate with xylene diisocyanate
Tris	2-Amino-2-(hydroxymethyl)-1,3-propanediol
UV	ultraviolet
Vis	visible
VOA	variable optical attenuator
WE	working electrode

Chapter 1 – Introduction

1.1 – Electrochromic materials

Electrochromism, a term first used by Platt¹, is defined as a reversible change in absorbance produced by electroactive materials when switching between oxidation states. One example is aqueous ferrous cyanide which is pale yellow but, upon oxidation, becomes bright yellow due to the ferric cyanide formed². This change in absorbance can be at any wavelength in the electromagnetic spectrum although most electrochromes (EC) absorb in the visible portion of the spectrum. Since two differently-colored states are always considered, these are often referred to the bleached and colored states where the former represents the lesser colored or colorless form of an EC. This coloration can develop through anodic (oxidative) or cathodic (reductive) processes. For example, tungsten, titanium, molybdenum and cobalt oxides change color cathodically while iron, iridium and niobium oxides change color anodically³. The coloration mechanism of these oxides and other electrochromes will be discussed in more detail in section 1.4.1.

Electrochromes are typically divided in three categories. Electrochromes that remain in solution following a redox reaction are of type I, those soluble in bleached form but become colored solid electrodeposits are of type II, and lastly, type III electrochromes are defined as being solid in both redox states³.

Chapter 1 – Introduction

1.2 – Electrochemical characterization of electrochromic materials

Electrochromes can be studied either by chemical or electrochemical means. However, the latter is more practical since foreign species are not introduced into the equation (assuming high chemical purity). Electrochemical cells can be made up of two (static) or three (dynamic) electrodes. In a two electrode system, the potential at both electrodes is altered by current flowing through the cell which must be controlled with a high degree of precision. This is however not possible when using a two electrode system due to a potential drop across the cell arising from the solution resistance and polarization of the counter electrode (CE) completing the circuit. Control can be ensured by using a third electrode. The potential of the cell where the electrochemical reaction of interest occurs, is measured not by the potential difference between the working electrode (WE) and the CE, but rather between the WE and the third electrode, the reference electrode (RE), which no net current passes through, effectively keeping the potential constant. The shape of the current-voltage curve (*i.e.* voltammogram) obtained is dictated by the flux of materials at the electrode which can be described by Fick's law. Fick's first law relates the flux of materials, j_i , to its concentration gradient, $(\partial c_i / \partial x)$, by

$$j_i = -D_i \left(\frac{\partial c_i}{\partial x} \right) \quad \text{Equation 1.1}$$

where D is the diffusion coefficient of the species. It should be stated that the concentration gradient arises from consumption of species near the electrode².

In cyclic voltammetry, the current is monitored against an applied potential. When scanning towards more positive potentials, oxidation occurs and the current

generated peaks near the redox potential of the material analyzed. Once the end of the potential range is reached, it is reversed and the reduction peak is observed. Figure 1.1 depicts a typical cyclic voltammogram (CV). Usually, the current is cycled from negative to positive and back, but the initial scanning direction is subject to the material analyzed and user preferences. The anodic potential, E_{pa} , is the potential at which the anodic current, I_{pa} , reaches its apex. In the same way, the cathodic potential, E_{pc} , is the potential at which the anodic current, I_{pc} , reaches its minimum value. Comparing the shape and amplitude of both redox waves yields additional information about the system stability. Potential discrepancies between both waves denote some irreversibility and can be caused by product degradation, and more commonly, by adsorption or deposition of the electroactive species on the electrode. To obtain the redox potential, E , the average of E_{pa} and E_{pc} is taken.

Figure 1.1 – Simulated CV of a reversible one-electron redox couple³

Chapter 1 – Introduction

Redox potentials are normally referenced against aqueous-based electrodes such as the normal hydrogen (NHE) or the saturated calomel (SCE) electrodes. Since organic compounds are mostly insoluble in water, CV is generally done in compatible organic solvents, which renders aqueous based reference electrodes unusable and, unfortunately there are no reliable reference electrodes for use in organic solvents. To overcome this, a silver (or platinum) wire can be used as a pseudo reference electrode. The IUPAC-recommended reference materials of choice are the ferrocene/ferrocenium (Fc^+/Fc) or bis(biphenyl)chromium(0)/ bis(biphenyl)chromium(I) couples^{4, 5}. The reference value of the Fc^+/Fc system depends on the solvent and supporting electrolyte employed. Tetraalkyl ammonium hexafluorophosphate or perchlorate salts are commonly used as electrolytes and, fortunately, formal potentials of Fc^+/Fc in selected solvents have been conveniently tabulated by Connely⁶. While the choice of solvent and electrolyte depends on the analyte, both must be of high purity. Even in trace amounts, impurities can drastically affect electrochemical measurements either by interacting with the analyte in question or by diminishing the usable potential range of the solvent (see Figure 1.2). For instance, anhydrous propylene carbonate which generally has a potential range of -3.6 to 3.2 V, which is reduced to -2.5 to 2.5 V when contaminated with 0.1 M water⁴. Granted, in this scenario, the usable range is adequate for most analytes but the effects are still significant. Another example, acetonitrile, a versatile solvent for electrochemical measurements, is often contaminated by water, ammonia, acetic acid, propionitrile, acrylonitrile, allyl alcohol, acetone and benzene⁴. Dissolved oxygen can also be problematic; being redox active itself, it can form reactive species which can interfere

Chapter 1 – Introduction

with the analyte of interest. Purging the solvent with inert gas such as nitrogen or argon tackles this issue.

Figure 1.2 – Solvent optimal voltametric operating range⁴

Spectroelectrochemistry, the spectral analysis of the different EC material oxidation states, is done by hyphenating a potentiostat to a spectrophotometer. An optically transparent thin layer electrode (OTTLE) cell (Figure 1.3) is used to house the three electrodes and the solution or the solid film to be analyzed (both situation still require a supporting electrolyte to ensure conductivity between electrodes). Thin platinum wire manually braided and arranged to form a crude mesh, act as the WE while another piece of platinum wire makes up the CE. The RE is composed of a silver wire and serves as a pseudo-reference. These electrodes are kept in place via a two layer

Chapter 1 – Introduction

lamine low-density polyethylene spacer (light gray area of Figure 1.3a). This laminate is produced by arranging all the pieces between microscope slides, clamping the unit and heating at 120°C in an oven for a few minutes, until both plastic layers melt into one another. The resulting thickness is normally less than a millimeter and the path length can be measured accurately using a digital caliper. Heating for too long results in distorting the spacer's shape causing irreversible damage since the thickness of the plastic will equal that of the electrodes and prevents adequate sealing. Two quartz windows, one with drilled filling holes, form a sandwich (Figure 1.3b) with the spacer. Appropriate rubber spacers at the metal-glass interface are placed to prevent damage to the windows from over tightening. The assembled cell (Figure 1.3c) fits into standard cell holders and *in situ* optical measurements can then be made at different potentials to observe the optical properties of the different oxidation states of the EC. Even with such a small volume, the diffusion rate of the electroactive species is quite limited and the electrolysis of the entire sample is very slow. The area of interest is encompassed by the mesh of the WE where the oxidation process is rapid and the electrochromic specie within this area is uniformly of the same state. Opaque tape can be used to mask the area around the WE so that the incident beam of the spectrometer passes through this area only.

Figure 1.3 – OTTLE cell assembly: a) innards, b) side view, and c) assembled cell

1.3 – Other characterization parameters

Unfortunately, the chromism of a material does not guarantee direct applications. It must also be stable and provide efficient switching between the targeted redox states. The optical performance of an electrochrome is evaluated by applying square wave potential steps that switch the material's redox states. Integrating the current-time trace generated by the potential pulse and measuring the film area yields the injected charge density, Q ($\text{C}\cdot\text{cm}^{-2}$). The color efficiency, η , is described as the amount of color formed (change in absorbance) between redox states for a given Q (equation 2) and should be as high as possible.

$$\text{Absorbance} = \eta \times Q \quad \text{Equation 1.2}$$

The response time is defined as the time required to attain the colored state from its bleached state (or vice versa) and the order of magnitude of this parameter may dictate the applications of the electrochrome in question particularly when fast switching times are required (Figure 1.4a). The intensity of the colored state will gradually diminish with

Chapter 1 – Introduction

each ON/OFF cycle due to material degradation (electrochrome and/or electrode). It is also possible that the coulombic efficiency of the redox process is less than 100% and thus a small portion of one state will not switch to the other. After a certain number of cycles (figure 1.4b), the device is deemed inoperable and it is this number of cycles that defines the cycle life. The contrast ratio, which is another mean to evaluate the color intensity, can also be determined using Figure 1.4b and is defined as the transmission ratio between bleached and colored states. For example, in Figure 1.4b, the bleached state has 100% transmittance while the colored state has 20% transmittance, giving a contrast ratio of 5. Finally, when power requirement is an important parameter, such as in display or memory applications, the memory effect may be considered and electrochromes that do not require a continuous potential to maintain their colored state, are used.

Figure 1.4 – Schematic representations of a) response time and b) contrast ratio and electrochemical stability

Chapter 1 – Introduction

1.4 – NIR-active electrochromic materials

1.4.1 – Metal oxides

Many metal oxides express electrochromism^{7, 8} but only oxides of tungsten^{2, 3, 9}, iridium¹⁰, molybdenum¹¹, vanadium¹², titanium¹³, niobium¹⁴, cobalt¹⁵, tin¹⁶, copper¹⁷ and iron¹⁸ have significant activity beyond the visible region of the electromagnetic spectrum (>700 nm). Tungsten oxide is by far the most widely employed electrochrome in visible applications. It is colorless or light blue in the bleached state, but intense blue in the reduced form. To maintain charge neutrality, this reduction also involves ion insertion; the redox reaction taking place is

where M is the inserted cation which can be an alkaline metal or H⁺ and where x is the degree of insertion. This system is fully reversible when x < 0.2. Higher degree of insertion irreversibly leads to ‘bronze’ formation, i.e. a golden-brown reflective metallic surface³. It is widely accepted that the color formation mechanism stems from an intervalence transition by the W^V electrons hopping to neighbouring W^{VI} sites. However, electron spin resonance (ESR) spectroscopy, recorded at 4.2K, of a H_xWO₃ film with a low degree of insertion, did not detect unpaired electrons on the W^V sites. Therefore it has been proposed that ground state electrons are paired or that electrons are localized over larger regions of W^V sites¹⁹.

The visible blue color of reduced WO₃ implies absorbance of the longer wavelengths and thus, not surprisingly, its λ_{max} appears at 980 nm. The morphology of

Chapter 1 – Introduction

WO₃ and the introduction of impurities can impact the position of λ_{max} which can range from 900 nm to 1300 nm^{20, 21}. While a fast reduction of this oxide is achieved, its re-oxidation to the bleached state is dependent on the morphology of the material and can require a longer time period to reach an acceptable level. This slower response time can limit its potential applications, particularly when speed is not an important issue such as it would be the case with smart glass³. While a variety of preparation methods could improve the switching speed of derived films, it was the development of faster liquid crystal displays that shattered any hopes of using WO₃ in display technologies²².

Nevertheless, metal oxides do present some advantages. Their main advantage is their high photostability in comparison to most organic-based electrochromes, giving metal oxides the upper hand on cycle life. However, metal oxides are not without issues as they do demonstrate some photodegradation, are chemically unstable, especially towards water, form brittle films regardless of the preparation method, and have low color efficiencies³.

Preparation of metal oxide films is achieved via numerous methods such as thermal evaporation, chemical vapour deposition, sputtering, electrodeposition, and sol-gels³. Each method has its advantages and will influence the resulting film morphology from amorphous to crystalline. Once again, using tungsten oxide as the exemplar material, Table 1.1 shows the colour efficiencies (η) obtained via various preparation techniques. The insertion coefficient (x) also governs η , but since this value is restricted to $x < 0.2$, to maintain reversibility, increasing η relies on improving preparative methods.

Table 1.1 – Coloration efficiency dependence of WO₃ electrochromes

Preparative route	Morphology	η (cm ² C ⁻¹)	λ_{obs} (nm)	Reference
Electrodeposition	Amorphous	118	633	23
Thermal evaporation	Amorphous	115	633	24
Sputtering	Polycrystalline	42	650	24
Sol-gel	Crystalline	70	685	25
Sol-gel	Crystalline	167	800	26
Spin-coated gel	Crystalline	64	650	27

It is interesting to note that high η values can be achieved for both amorphous and crystalline films. Amorphous films have some degree of porosity and facilitate cationic diffusion, explaining the high η values. The surface area may also be playing a role. It is unclear why the crystalline film, obtained by the sol-gel methodology, has a η value of 167 cm²C⁻¹, but since it was evaluated at a longer wavelength, the direct comparison to the other preparative routes is unreliable.

1.4.2 – Hexacyanometallates: Prussian blue

Prussian blue, PB, ferrocyanide or iron(III) hexacyanoferrate(II) is the main metallate of this family of electrochromes. PB was discovered by Diesbach in 1704 and has been used in paints as a blue pigment and was the main component of ‘blueprints’ for several decades³. It is simply prepared by mixing solutions of hexacyanoferrate(III) salt with iron(II) chloride followed by the collection of the insoluble blue precipitate. However, in this state, PB can only be used as a pigment. PB is characterized by a mixed-valence system where iron(III) is chelated by cyanide ligands, while the iron(II) is chelated to the nitrogen of the cyanides. The resulting conjugation between the iron atoms (Figure 1.5) makes it ideal for intervalence charge-transfer (IVCT) and it is this

electron hopping that generates the coloring transition. The absorbance resulting from the IVCT is centered near 700 nm and its onset extends to 1200 nm³. Thin films of PB can be prepared using various techniques, but electrodeposition is preferred²⁸⁻³³.

Figure 1.5 – 3-D model of PB and corresponding redox reactions

When fully oxidized to Fe(III)-Fe(III), PB presents a white/transparent color and is named Prussian white (PW). The chromism of this cyanometallate does not stop here: the fully reduced PB turns brown and is similarly called Prussian brown (PX). Moreover, there is also an intermediate form between PB and PW where partial oxidation is achieved and a green color develops – this one is cleverly called Prussian green (PG). Polychromism, the ability of an electrochrome to display multiple colours, is somewhat of a rare property. Since the discovery of electrochromic properties of PB, many mixed metal analogues of PB have been prepared, either by mixing the usual iron(II) salt to M(III)CN_6 or by electrochemical means. The resulting materials were not as impressive as PB: some of which demonstrate electrochromism only in the UV spectrum, some are

only capable of two- or three-colors (no PG analogue) and others, such as the palladium-iron cyanometallate analogue, only show redox activity from the iron atoms³.

1.4.3 – Radical anions of conjugated diimides and diquinones

Both diimides and diquinones (Figure 1.6) can be reduced to radical anions and their extended conjugation promotes a low bandgap transition that appears in the NIR region. The diimide radical anions absorb broadly at 1250 nm; additionally when its concentration within the polymer matrix is increased, this absorbance is extended well past 2.5 μm ³⁴. Conversely, the absorbance of diquinone radicals is a function of substituents and can range from 900 to 1700 nm³⁵. Both have been incorporated into polymers and used to make films.

Figure 1.6 – General structure of a) diimides and b) diquinones

These compounds make great electrochromes, but as is the case with most organic-based ECs, they are susceptible to photodegradation³. Moreover, their radical anions can also undergo oxidative degradation, increasing their manufacturing costs³⁶. Electrochromes containing both quinones and imides have also been prepared, combining their properties into one single molecule (Figure 1.7)³⁷. The 6-nitro anthraquinone imide radical anion absorbs from 500 nm and has an onset of 1700 nm while its neutral form

has no optical absorbance past 400 nm. Substituting the nitro group for a bromide causes a hypsochromic shift, effectively tuning the absorbance.

Figure 1.7 – Structure of quinone-imine EC

1.4.4 – Porphyrins and phthalocyanines

Porphyrins are a naturally occurring ring systems built from four pyrroles which are conjugated through methynes (Figure 1.8). These can be prepared with various functional groups at the eight β positions and four meso positions. Their phthalocyanine (PC) cousins have an extra phenyl moiety fused to the two β positions of each pyrrole ring. Given their highly delocalized π system, these are highly coloured molecules and are often found bound to metals such as magnesium in chlorophyll and iron in haemoglobin.

Figure 1.8 – Structures of a) porphyrin, b) phthalocyanine and c) metallized porphyrin (β and meso positions are defined)

Chapter 1 – Introduction

These complexes are usually blue or green and consequently the absorbance maximum is found in the far red region. If the metal center is small, it can lie within the ring cavity; however larger metals such as lanthanides, form sandwich-type molecules akin to ferrocene. The most studied complex of this type is bis(phthalocyaninato)lutetium(III) which was discovered in 1970³⁸. Not only does this complex exhibit a visible electrochromism process ranging from green in its reduced form to yellow-tan in oxidized form, it also shows broad NIR absorbance most intense between 1200 and 1400 nm³⁹. Metalloporphyrins constituted of the smaller metals barely break the NIR barrier, absorbing between 600 and 700 nm.

It is also possible to prepare meso-meso fused arrays to redshift the absorbance maximum but, due to an almost 90° dihedral angle between porphyrin units, the conjugation effect does not extend from one ring to another⁴⁰. To permit the overlap of the π orbitals, the dihedral angle must be eliminated; this can be achieved through oxidative double ring closure of the meso-meso linked porphyrins⁴¹⁻⁴³. These triply fused dimers and oligomers (porphyrin tape) do exhibit NIR absorbance due to an extended conjugation and are also redox active⁴⁴. However, literature on their electrochromic or spectroelectrochemical properties is not yet available. Other than fusion through the meso positions, rigidification has also been achieved through the β positions by tetraamino benzene condensation with a diketone porphyrin⁴⁵, through a phenyl fused to two pyrroles⁴⁶, and finally through a pyrrolo[3,4-c]pyrrole⁴⁷ (fused pyrrole dimer). Yet, even though these systems are rigid, their absorbance past 800 nm was not recorded. Without this information, comparison with the triple-fused system is not possible though it is

expected that a three point fusion would enhance orbital overlap more efficiently than a two point fusion.

1.4.5 – Conjugated polymers

Extended conjugation is key in red-shifting the absorbance of organic molecules. In fact, each double bond added to an existing π system induces a bathochromic shift of approximately 30 nm⁴⁸. In theory, a molecule's absorption could be tailored quite precisely. Unfortunately, conjugation requires π orbital overlap for electron delocalisation and the σ bonds that separate the π bonds can rotate, weakening or even nullifying the electron mobility based on the dihedral angle. This also holds true in conjugated polymers where many unsaturated monomers are bound together in linear fashion although with so many long chains interacting and potentially becoming entangled, twisting due to steric repulsion is inevitable. Nevertheless, with hundreds, even thousands of repeat units in each chain, the probability of sections of polymer that remain planar is quite high and every variant length of planar section is possible. As the absorption is dictated by the extent of conjugation, the resulting absorbance completely encompasses the visible and NIR regions and polymers are often black in appearance.

The first prepared conductive polymer was polyacetylene which is actually an insulator but when exposed to iodine a 10⁸-fold increase in conductivity is observed⁴⁹. Following this discovery, it was thus understood that conjugated polymers required doping, in order to create formal charges on the polymer backbone and to truly render them conductive. Polyacetylene, like any other alkene, is unfortunately susceptible to oxidation and thus has seen few applications. In contrast, aromatic structures are very

stable and so conjugated polymers derived from aniline, thiophene, 3,4-ethylenedioxythiophene (EDOT), pyrrole, furan and fluorene were of interest (Figure 1.9). Of these, thiophene and aniline polymers are the most frequently encountered electrochromes in the literature³.

Figure 1.9 – Selected conductive polymers

At first glance, all the structures presented in Figure 1.9 are conjugated except for polyaniline which requires oxidative doping (through chemical or electrochemical processes) to become conductive and conjugated. Interestingly, by controlling the level of doping in polyaniline, it is possible to observe four redox states (Figure 1.10): the initial form (leucoemeraldine), is yellow in color and absorbs mainly in the UV region; the first oxidation specie (emeraldine salt) is green and is conductive; the second oxidation form named emeraldine base, is blue and partially conjugated, with some absorption in the NIR region; the fully oxidized and conjugated form of polyaniline (pernigraniline), is black and exhibits increased absorbance in the NIR region.

Figure 1.10 – Polyaniline redox states

Because of their rigid structure, the solubility of conjugated polymers is often poor and is an issue when material processing is considered. However, this can be overcome by the addition of aliphatic pendant chains on the monomers⁵⁰. This solution is not without disadvantage as the symmetry of the monomer is usually lost and the polymerization can proceed via head-to-head, head-to-tail or tail-to-tail.

Finally, conductivity is closely related to response time which depends on the regular stacking of the chains in solid state. A regio-regular polymer is able to crystallize properly, or at least has a better chance of forming crystallite regions. The thiophene class of polymers can illustrate the optical effects of stereo-control over the polymer properties and a few examples are provided in table 1.2⁵¹. The effects of head-to-head and tail-to-tail assembly are purely steric and induce a dihedral angle at the common σ bond of the polymer. This obviously reduces the electron delocalisation potential and a hypsochromic shift is observed for highly hindered oligomers³. As expected, regio-regular polythiophenes are more redshifted due to minimized steric hindrance and smaller

dihedral angle. Other configurations result in hypsochromic shifts, some of which are less pronounced than others.

Table 1.2 – Optical properties of some polythiophenes

Monomer used	$\lambda_{\max}$ (nm) of undoped polymer	Polymer color (reduced)	Polymer color (oxidized)
530	Purple	Pale blue
415	Yellow	Violet
505	Red	Blue
450	Orange	Blue
425	Yellow	Blue

1.4.6 – Transition metal complexes

If metal oxides are the most studied electrochromes, transition metal complexes would stand in second place. Coordination complexes are typically easier to purify as their color makes it possible to visually track their evolution through a chromatography column – no fraction collection is required (unless overlap with another coloured compound occurs). The optical transitions that are responsible for the color involve the metal center and the coordinating ligands. The electronic transitions caused by light

absorption can either be $d-d$ transitions or charge transfer bands. In a $d-d$ transition, a d orbital electron from the metal is excited and promoted to a more energetic d orbital. The charge transfer bands require the participation of both the ligand and metal – when an electron from the ligand is excited to an empty orbital of the metal, ligand to metal charge transfer, or LMCT occurs⁵². There are normally four types of possible LMCTs (A, B, C and D) and they depend on electron and empty orbital availability (Figure 1.11a). The opposite, a metal to ligand charge transfer, or MLCT, where an electron from the metal is promoted to an empty ligand orbital is also possible but, as the name implies, it requires that the empty ligand orbital is of higher energy than the occupied metal orbital involved (Figure 1.11b). MX_6 complexes, where X is a halogen, exhibit LMCT due to the halide low-energy occupied orbitals. MLCTs are observed when the coordinating ligands contain CO, CN or aromatic amines such as bipyridines, which all have high energy empty orbitals⁵².

Figure 1.11 – Partial MO diagram for an octahedral complex: a) LMCT and b) MLCT

All the transitions shown in Figure 1.11 are allowed transitions even though G is not a charge transfer transition, but a $d-d$ transition. The Laporte⁵³ rule states that when a

molecule has a center of symmetry, transitions within a given set of p or d orbitals are forbidden. However, a complex is almost never symmetric, in part due to the Jahn-Teller effect and asymmetric vibrations, and thus the normally forbidden G transition is allowed. Even so, these transitions have the same optical characteristics as any other $d-d$ transitions⁵². Charge transfer transitions are normally of high energy and fall in the UV-Vis spectrum.

The first reported series of NIR absorbing metal complexes are the square planar Ni, Pd and Pt dithiolenes (Figure 1.12) which, once oxidized to the radical anion, show an intense, broad, low energy transition that can range from 700 to 1400 nm depending on the nature of the dithiolate ligand³.

Figure 1.12 – Bis-dithiolene square planar complexes.

Because MLCTs and LMCTs are usually high energy transitions and thus only $d-d$ transitions have the required energy to be observed in the NIR region. However, $d-d$ transitions are much weaker than charge transfer transitions and experimentally, high molar extinction coefficients with the NIR active redox state of the dithiolene complexes are observed⁵⁴. The weak $d-d$ transitions are present and can be observed when the metal dithiolate is in a redox state that is not NIR active. Otherwise, the strong NIR transitions of the radical anion overlap and mask them completely. Schrauzer and Mayweg⁵⁵ assigned the strong NIR transitions of the anion to $\pi \rightarrow \pi$ transitions while Gray⁵⁶⁻⁵⁸ and

coworkers assigns them to $L(\pi) \rightarrow \pi^*$ demonstrating that the transition assignment matter is subject to controversy and no definite answer is available although low bandgap charge transfers should be involved⁵². One thing is certain: electron delocalisation plays an important role in these NIR transitions and it has been shown through various complexes that the inductive effect of the R functional groups (Figure 1.11) on the λ_{max} is significant⁵⁴.

Also of interest are the dinuclear ruthenium complexes. These complexes are coordinated through a bridging ligand and show strong electronic coupling of the two metal centers. Since the discovery of the Creutz-Taube⁵⁹ complex, also known as 22-F-VII, which shows some degree of electron transfer between the two metals, many analogues using various bridging ligands have appeared in the literature (Figure 1.13)^{3, 52,}

60-65

Figure 1.13 – Various dinuclear metal complexes (counter ions omitted for clarity)

What makes these dinuclear complexes NIR active? To answer this question, redox properties must be considered. Since most of the above examples are symmetrical,

Chapter 1 – Introduction

a single redox couple might be expected, but in fact, two couples are observed in these systems. All of the dinuclear ruthenium complexes shown above are usually isolated in the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ state and can be oxidised to a $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ mixed-valence state with further oxidation to the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ state. As well as being electropolychromic in the visible region, monitoring of the mixed-valence oxidation state in the NIR region shows a broad intense NIR absorbance that ranges from 1100 to 2000 nm. This transition is attributed to an inter-valence charge transfer, IVCT, between the two metal atoms, due to the electron on the Ru^{II} that can transfer to the Ru^{III} ^{52, 59}. Even though NIR research has focused primarily on ruthenium complexes because of their relatively simple synthesis and ideal electrochemical properties³, in theory any other metal that can undergo a one-electron oxidation is a potential candidate for NIR activity.

So far, the only other metal explored for such application is molybdenum⁶⁶⁻⁷¹. Ward, McCleverty and coworkers have prepared a series of tris(pyrazolyl)borato-oxo molybdenum(V) complexes bridged by various conjugated diphenolates (Figure 1.14)⁶⁶⁻⁷¹. These also show two one-electron redox couples and, not only is the mixed valence $\text{Mo}^{\text{V}}\text{-Mo}^{\text{VI}}$ NIR active (from 900 to 1554 nm), the fully oxidized $\text{Mo}^{\text{VI}}\text{-Mo}^{\text{VI}}$ state is NIR active as well (832 to 1033 nm) via a low energy LMCT^{3, 67, 68}. Interestingly, two Mo-Mo complexes, in their fully oxidized state, based on the 2,5-(4-hydroxyphenyl)thiophene and 4,4'-dihydroxy azobenzene bridging ligands, absorb in the red and blue respectively. The azo group seems to be increasing the bandgap to the point that the LMCT appears near the UV region⁶⁸.

Figure 1.14 – Example of a dinuclear molybdenum complex

The various dinuclear complexes described above are proving to be good electrochromes, but is there room for improvement? If two metal centers are good, wouldn't three be better? Ward and coworkers have made a hexaphenolic conjugated bridging ligand, chelated with three ruthenium cations (Figure 1.15a) and instead of having two redox couples, three are now observed which represent the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ states which are all accessible at fairly low potentials, e.g. 1.03 V for the fully oxidized state. What is really interesting with this complex is that all four states are NIR active and that their molar extinction coefficients in the NIR are significantly higher than any previously reported dinuclear complex⁷². Wang⁷³ and coworkers have prepared a hexanuclear dendrimer-like ruthenium complex (Figure 1.15b), where the three inner ruthenium atoms are conjugated with the phenyl core, which only displays two redox couples. The close proximity of the six ruthenium atoms and the sheer steric bulk of the bipyridines force a dihedral angle that is large enough to interrupt any possible electron delocalisation through the phenyl core⁷³.

Figure 1.15 – The a) trinuclear and b) hexanuclear ruthenium complexes

1.5 – Applications

Visible electrochromes find uses in smart glass (chemical curtains)⁷⁴⁻⁷⁶, electrochromic displays (ECD)⁷⁷⁻⁷⁹, light modulation⁸⁰⁻⁸², and sensors⁸³⁻⁸⁶. These applications are based on modifying light transmission, optical contrast or the redox color changes. The only commercialized visible electrochromic devices are rear-view mirrors, developed by the Gentex Corporation, which attenuate glare from vehicle head lights via a sensor or manual switch²⁴. This principle is being implemented to sunglasses, ski goggles, and motorcycle helmets^{75, 87, 88}. NIR electrochromes find similar applications, but in a different region of the electromagnetic spectrum. A classic example is that of NIR active smart windows that can keep buildings cool in the summer by dissipating the thermal energy either by absorption or reflection, and warm in the winter by allowing the heat radiation to pass through (figure 1.16)^{75, 89, 90}.

Figure 1.16 – NIR window in a) OFF mode and b) ON mode

NIR active materials show promising results in the energy generation domain. With a significant portion of the solar irradiance spectrum being in the NIR region, any compound that absorbs in this region, coupled to current photovoltaic (PV) systems, would increase the efficiency of solar panels by expanding the energy range of photons harvested⁹¹. Granted, these materials do not need to be electrochromic, but only NIR absorbent⁹². A recent paper by Yan and coworkers discusses a PV cell containing NIR active phthalocyanines that has a 1.95% energy conversion efficiency⁹². While this is a relatively small percentage, particularly when compared to current silicon-based commercial solar panels which achieve about 10% efficiency, the phthalocyanine-based device absorbs from 400 to 1000 nm and could still be improved by the introduction of materials that can absorb lower wavelength to cover a broader range of the solar irradiation spectrum.

NIR wavelengths also show great potential in medical applications as a diagnostic tool since they can penetrate biological tissue up to a few centimeters^{93, 94}. Biomolecules, tagged with a NIR marker can be tracked and monitored via absorbance; however, since

Chapter 1 – Introduction

photoluminescence is significantly more sensitive than absorption monitoring, research into NIR emitting molecules is on the rise. As such, NIR tags are normally used in biosensors. For example, NIR biosensor schemes, coupled to oxidase enzymes, can be used to monitor blood sugar levels⁹⁵. Further details on biosensors will be presented in chapter 5.

Another application of NIR active compounds is through night vision gear which can unveil the night's darkest secrets. This technology is based on collecting the IR light that is invisible to the human eye and rendering it visible. The process starts by collecting the invisible photons onto a photocathode that is capable of ejecting multiple electrons for each photon absorbed (signal amplification). Those electrons are then accelerated by a strong electric field and impact on a phosphor screen which recreates the invisible image into visible green light (Figure 1.17). The third generation technology utilize a gallium arsenide photocathode that is sensitive for both NIR and IR photons (800 nm and up), resulting in a 30000-50000x increase in amplification⁹⁶⁻⁹⁸. Although these devices are generally used in the military by troops to 'see' in the dark, they can also be used in aircrafts' targeting systems to 'lock-on' air and ground targets because of the heat radiating from the vehicle engines^{99, 100}.

Since the NIR region is the most sensitive to night vision equipment, the ability to mask these wavelengths would result in effective camouflage⁹⁹. A patterned NIR electrochromic insignia could be used to send messages to friendly troops via switching to simulate Morse code or simply as identification. A NIR ECD would permit troops to receive and send text messages without the risk of unveiling their position due to visible light from a display or sounds from audio transmitters. On the other hand, the matter of

masking heat signature is more complex since there is much more energy to ‘mask’ in a vehicle, not to mention that targeting systems can detect a broader range of heat wavelengths^{99, 100}. Such a countermeasure system would require an electrochromic material that would span the entire NIR-IR region to ensure ‘invisible’ status⁹⁹.

Figure 1.17 – Night vision system

Lastly, a very popular application of NIR electrochromes is in light modulation or variable optical attenuators (VOA) used by the telecommunication industry to convert electrical signals into optical signals and vice-versa. Silica fibre optics has its highest transparency in the NIR region and so redox materials have become important in achieving faster information encoding as bandwidth demands increase¹⁰¹. This application will also be discussed in further detail in chapter 5.

1.6 – Rationale and objectives

Dinuclear ruthenium complexes, based on DCH, oxamides and other analogues have been previously extensively studied. This research project involved the preparation of macromolecular materials containing the dinuclear complexes in order to evaluate their solid state optical properties and performance. The potential of using other metals with these bridging ligands was also investigated by studying the properties of DCH complexes of platinum.

The results reported in this dissertation pertain to the optical properties of polymerized dinuclear ruthenium complexes as well as those of small molecules of novel dinuclear platinum complexes. Performance of the ruthenium complexes was evaluated by NIR attenuation and optical sensor configurations. The objectives of this project are:

1. to prepare film-forming macromolecular materials, containing the dinuclear ruthenium moiety, using newly synthesized hydroxyl-functionalized complex monomers and maximize their ruthenium content;
2. to evaluate the NIR optical properties of solid films in a reflective VOA design and to compare its performance to that of analogue transmissive VOAs;
3. to develop a redox biosensing scheme using an oxidase enzyme and dinuclear ruthenium complex to evaluate the advantage of a NIR optical sensor compared to traditional amperometric sensors; and
4. to develop a viable synthetic route to analogous dinuclear platinum complexes to assess their physicochemical, electrochemical, and emissive properties.

Chapter 2 – Bridging and peripheral ligands

2.1 – Introduction

Polymers containing the DCH-Ru moiety can be prepared via two pathways. The simplest approach is to first synthesize the polymer then perform a complexation step. Even small molecular weight polymers have long chains which can get tangled and knotted preventing the bulky $\text{Ru}(\text{bpy})_2$ of approaching each and every ligand site, limiting the uptake of metal¹⁰². There are also solubility issues due to hydrogen bonding of the amide function that can interfere. Although the percentage of metal within the final product can be measured via various methods, such as acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis¹⁰³, the fact remains that the polymer ligand sites may not be fully complexed and will introduce batch to batch variability. Cheng¹⁰⁴ and coworkers prepared a ligand polymer and obtained a very high degree of metal uptake with only a small percentage of vacant ligand sites, showing that the complexation of a polymer ligand is viable. The second method, still simple in concept, is to prepare the polymer using polymerizable complexes. This approach ensures that every ligand site is complexed, yielding materials having a high metal content.

The main inconvenience of the first method is that the low molecular weight of the polyhydrazide as it precipitates as oligomers, even in high boiling, high polarity solvents¹⁰⁵. Thus the second method's potential will be assessed in this study by preparing a series of difunctionalized ligands that will be polymerisable, even after the complexation. The first method has already been explored by our group with limited success.

2.1.1 – Synthetic methods for bridging ligands

The bridging ligands considered for this project are diacyl hydrazides, also known as dicarbonyl hydrazines (DCH), biureas (an extension of the DCH group), and oxamides (OXA). Many viable routes to DCH ligands exist and the most common method is to combine a monoacyl hydrazide, which is prepared by hydrazinolysis of methyl or ethyl esters, with an acid chloride to yield the desired ligand¹⁰⁶. Symmetrical ligands are obtained by using reagents that have identical R groups. The reaction of the same acid chloride to hydrazine monohydrate also yields a symmetrical ligand, however the ‘wet’ condition can induce by-products that may be difficult to remove (Figure 2.1). Another straightforward method to obtain simple symmetrical ligands is through hydrazinolysis of anhydrides¹⁰⁷. Ligands having aromatic R groups are normally hydrophobic and have limited solubility in organic solvents due to extensive hydrogen bonding while aliphatic ligands can be water soluble. Also, hydrazide ligands can be dehydrated to cyclic oxadiazoles, which are themselves useful as luminescent materials¹⁰⁸⁻¹¹⁰ and enzyme inhibitors¹¹¹⁻¹¹⁴, although they no longer function as ligands.

Figure 2.1 – General synthetic routes to symmetric and unsymmetric DCH ligands

Chapter 2 – Bridging and peripheral ligands

Chloroformates can be used with hydrazine hydrate or hydrazides to produce a urethane type ligand which is essentially the same as the DCH system. Similarly, if an isocyanate is utilized, semi-biureas and biureas are obtained¹¹⁵ (Figure 2.1). Isocyanates react very rapidly with nucleophiles and so the preparation of functionalized biureas through this route is very limited. One method capable of overcoming this obstacle is aminolysis of dialkylazodicarboxylates, such as diethylazodicarboxylate (DEAD) or diisopropylazodicarboxylate (DIAD), by primary or secondary aliphatic amines¹¹⁶. The resulting azobiurea is converted to the biurea by reducing the azo bond with a hydrazine hydrate at room temperature¹¹⁷ (Figure 2.2). The reduction of the azo bond can also be achieved through the oxidation of iodides¹¹⁶ by the azo group although an extra purification step is necessary compared to the reduction using hydrazine which produces nitrogen gas. While this method only forms symmetrical ligands, it permits the introduction of isocyanate-unfriendly functional groups such as carboxylic acids, alcohols and other amines.

Figure 2.2 – Alternative biurea ligand synthesis

Less common methods to prepare DCH ligands include oxidative coupling of aromatic hydrazides using oxone¹¹⁸⁻¹²⁰, sodium perborate¹²¹ or arylsulphonyl peroxides¹²² and enzymatic coupling of hydrazides to carboxylic acids¹²³.

Chapter 2 – Bridging and peripheral ligands

Lastly, OXA based ligands, which are structural analogues of the DCH series of ligands, also form dinuclear metal complexes and can be prepared by aminolysis of diethyl oxalate or by the simple action of oxalyl chloride with amines. The use of diethyl oxalate is more versatile as it allows the introduction of many functional groups and does not produce inorganic by-products. Unsymmetrical oxamides are obtained using ethyl chlorooxoacetate and its reaction with one equivalent of an amine. Once this intermediate is isolated, aminolysis of the ethyl group is achieved using a second amine (figure 2.3). Oxamides are formed readily at room temperature with aliphatic amines but aminolysis using aromatic amines necessitates heat due to their lower nucleophilicity from conjugation with the aromatic ring. Another route to oxamides is through the reductive coupling of isocyanates using samarium diiodide¹²⁴. However, as with any isocyanate, functionalisation is limited. Lastly, a method using diisopropenyl oxalate¹²⁵ also yields oxamides via aminolysis though it is rendered obsolete by the inexpensive diethyl oxalate which performs just as well if not better.

Figure 2.3 – Oxamide ligand synthesis

All these systems act as bridging ligands, between oxygen and nitrogen to form the desired dinuclear complexes (to be discussed in chapter 3).

Chapter 2 – Bridging and peripheral ligands

2.1.2 – Synthetic methods for non-bipyridine peripheral ligands

2,2'-Bipyridine (bpy) is a very popular ligand, often used as the starting point of many octahedral complexes. As discussed in chapter 1, bipyridines have high energy, empty orbitals and when complexed to a metal, the resulting optical transitions are MLCTs. Functionalization of bipyridine modifies the energy levels of these empty orbitals such that the transition energies also change. For instance, $(\text{bpy})_3\text{Ru}^{\text{II}}$, has a MLCT band at 452 nm in acetonitrile, while the 4,4'-dicarboxylic acid derivative is red-shifted to 483 nm^{126, 127}. The absorption can also be red-shifted by extending the conjugation of the bpy ligand¹²⁸. Adding electron donating groups to bpy, such as amines, has an opposite effect, blue-shifting the absorbance. These modifications require much effort with little effect and it is for this reason that all ruthenium complexes studied in the scope of this project are of the $\text{Ru}(\text{bpy})_2\text{L}_2$ nature and electronic tuning of the bandgap will be studied through the bridging ligand.

Moreover, probing the electronic effects of both bridging and peripheral ligands is also applicable for the novel dinuclear platinum complexes. Platinum cyclometallation using 2-phenyl pyridine is often encountered in the literature and is a reference point to study the electronic effects of the peripheral ligand. Commercially available 2-phenyl pyridine can be synthesized by Suzuki coupling of 2-chloro-pyridine to phenylboronic acid¹²⁹. Since extending the conjugation seems to induce the largest bathochromic shifts, commercially available 2-phenylquinoline, also readily available via Suzuki coupling methodology, was chosen to evaluate the red-shifting potential. The hypsochromic shift (blue-shift) was evaluated using quinoxaline derivatives, having an extra heteroatomic

nitrogen. This diaza ligand is simply synthesized by iodine-catalyzed, condensation of the adequate 1,2-diamine to 1,2-dione (Figure 2.4)¹³⁰.

Figure 2.4 – Synthesis of 2-phenylpyridine and quinoxaline peripheral ligands

2.2 – Results and discussion

2.2.1 – Bridging ligands

When choosing a functional group to act as the polymerizable moiety, several criteria such as commercial availability, price and foreseeable reactivity of the final product should be considered. As such, hydroxyl-containing hydrazides and amines were chosen to prepare the target hydroxyl ligands (Table 2.1). Aliphatic hydroxyl amines having various main chain lengths are commercially available to prepare diol biurea and diol oxamide ligands. In preparing diol DCH ligands, the usual acid chloride method is obviously not available unless a monohydroxyl ligand is the target. Additionally, all of the oxidative hydrazide coupling methods previously mentioned failed to produce the desired aliphatic diol ligand. In fact, these methods are reported to be efficient when using an aromatic hydrazide; however, they were not evaluated for aliphatic hydrazides^{118, 121, 122}.

Chapter 2 – Bridging and peripheral ligands

Table 2.1 – Identification, melting points and yields of hydroxyl ligands prepared

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{N}-\text{N}-\text{C}-\text{R}^2 \\ \quad \\ \text{H} \quad \text{H} \end{array}$		Mp (°C) ^a	Yield (%) ^b	Remarks	Ref.
R ¹ = (CH ₂) ₃ OH; R ² = CH ₂ CH ₃	1	102-103	58	e	-
R ¹ = (CH ₂) ₅ OH; R ² = CH ₂ CH ₃	2	98-99	36	e	-
R ¹ = (CH ₂) ₃ OH; R ² = NH(CH ₂) ₂ CH ₃	3	122-123	90	e	-
R ¹ = (CH ₂) ₅ OH; R ² = NH(CH ₂) ₂ CH ₃	4	125-126	93	e	-
R ¹ = R ² = (CH ₂) ₅ OH	5	147-148	21	f	-
R ¹ = R ² = NH(CH ₂) ₃ OH	6	252-253	78 ^d	f	-
R ¹ = R ² = NH(CH ₂) ₅ OH	7	258-259	82 ^d	f	-
R ¹ = R ² = NHC(CH ₃)(CH ₂ OH) ₂	8	141-142	56 ^d	g	-
R ¹ = R ² = O(CH ₂) ₂ OH	9	165-166	51	f	131
R ¹ = R ² = N OH	10	212-213	27	h	-
R ¹ = R ² = N CH ₂ OH	11	186-187	55 ^d	h	-

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{N}-\text{C}-\text{N}-\text{R}^2 \\ \quad \\ \text{H} \quad \text{H} \end{array}$		Mp (°C) ^a	Yield (%)	Remarks	Ref.
R ¹ = (CH ₂) ₅ OH; R ² = CH ₂ CH ₂ CH ₃	12	133-134	60	e	-
R ¹ = R ² = (CH ₂) ₃ OH	13	162-163	73	f	132
R ¹ = R ² = (CH ₂) ₅ OH	14	157-158	47	f	132
R ¹ = R ² = OH	15	350 ^c	44	f	133

^a uncorrected melting points from this project;

^b isolated yields from this project;

^c decomposed

^d based on starting azodicarboxylate dihydroxyl ligand;

^e monohydroxyl ligand – useful as a pendant or side group in polymer;

^f useful as monomers for linear polymers;

^g tetrahydroxyl ligand – useful for hyperbranched polymers;

^h secondary amide biurea to solve a problem discussed in chapter 3

These ligands were considered and prepared for use in various types (pendant groups, linear polymers, hyperbranched, crosslinked and dendrimers) of polymerization by their respective ruthenium complex. Their syntheses vary little within a category and yields are modest to excellent. The modest yields can be explained to loss due to high water solubility during the workup, especially for short aliphatic chain ligands. All of the

hydroxyl ligands were white powders or microcrystals that precipitated from the reaction medium and thus only required filtering and washing with solvent to obtain them in pure form. Uncorrected melting points are high for most ligands, reflecting their high tendency to hydrogen bonding, and are lower for ligands having longer alkyl chains.

Hydrazinolysis of γ -caprolactone yields 6-hydroxyhexanoic hydrazide¹³⁴, which is useful in preparing mono-hydroxyl ligands as well as synthetic intermediates for other types of ligands. A method to dimerize this hydroxyl hydrazide was available. Patents from Broussard and coworkers cite a method to prepare symmetrical aliphatic hydrazides using a β -ketoester^{135, 136}. The reaction proceeds by hydrazone formation between the ketoester and hydrazide which increases the electrophilic nature of the hydrazide carbonyl and becomes prone to attack by the free hydrazide. The equilibrium is driven to the formation of the symmetrical hydrazide by the stabilisation by-product, 3-methyl-4-pyrazolone, that is formed (Figure 2.5). Diol **5** was only obtained in 21 % compared to the 90+% reported in Broussard's patent. However the yields in the patent were for mono phenolic and unfunctionalized aliphatic hydrazides, not aliphatic diols.

Figure 2.5 – Diol-DCH synthesis via ethyl acetoacetate coupling

Chapter 2 – Bridging and peripheral ligands

Other ligands (Table 2.2) were synthesized to prepare model dinuclear complexes in order to assess their usefulness prior to preparing the functionalized analogues. **16-19** were selected to prepare dinuclear platinum complexes, discussed in chapter 3.

Table 2.2 – Identification, melting points and yields of other ligands

DCH			Mp (°C) ^a	Yield (%) ^b	Ref.
R ¹ = R ² = (CH ₂) ₆ CH ₃	16		155-156	81	123
R ¹ = R ² = CH ₃	17		133-134	97	137
R ¹ = R ² = 4-nitrophenyl	18		293-294	50	138
R ¹ = R ² = 4-methoxyphenyl	19		228-229	36 ^d	139
R ¹ = R ² = NHCH ₂ Ph	20		275 ^c	54 ^e	140
R ¹ = R ² = HNH ₂ C- -NH ₂	21		270 ^c	60 ^c	-
R ¹ = R ² = NH(CH ₂) ₂ CO ₂ H	22		239 ^c	37 ^c	-
R ¹ = R ² = N	23		181-182	37 ^e	-
Thiocarbonyl DCH			Mp (°C) ^a	Yield (%) ^b	Ref.
24		207-208	47	141
25		148-149	78	142
OXA			Mp (°C) ^a	Yield (%) ^b	Ref.
R ¹ = R ² = (CH ₂) ₅ CH ₃	26		131-132	96	143
R ¹ = R ² = (CH ₂) ₂ CH ₃	27		160-161	98	143, 144
R ¹ = R ² = 4-nitrophenyl	28		290 ^c	25	145
R ¹ = R ² = 4-methoxyphenyl	29		266-267	38	146

^a uncorrected melting points from this project;

^b isolated yields from this project;

^c decomposed;

^d a second crop was harvested but was slightly beige and not combined with the first;

^e based on starting azodicarboxylate

Chapter 2 – Bridging and peripheral ligands

The thiocarbonyl ligands **24** and **25** were prepared in order to assess the influence of sulfur on the electrochemical and optical properties of dinuclear ruthenium complexes. The presence of the nitrogen(s) should place the NIR absorption of the resulting complexes at 1100-1200 nm. The sulfur atoms having a lower electronegativity and higher energy orbitals, could increase the highest occupied molecular orbital (HOMO) of the complex to a greater extent than its oxygen counterpart and an enhanced bathochromic shift should be observed from these complexes, potentially shifting the NIR absorption at lower wavelengths. The antagonist effects from the nitrogen and sulfur could nullify themselves.

Characterization of the ligands is straightforward: they have high melting point temperatures because of hydrogen bonding, infrared spectroscopy (IR) confirms the presence of the amide moiety (C=O @ $1630\text{-}1690\text{ cm}^{-1}$ and NH @ $3100\text{-}3300\text{ cm}^{-1}$) and the NH protons are highly deshielded (7.5-10 ppm) in ^1H NMR due in part to intramolecular hydrogen bonding but also to the positive character of the nitrogen through resonance. Mass spectrometry of these ligands is somewhat problematic at times, especially when the volatility is low. Another characteristic of the amide protons is the possibility of tautomers (Figure 2.6). This resonance process is normally faster than the NMR time scale and thus not observed. However, for the DCH ligands such as **17**, two smaller resonances at 8.9 and 9.9 ppm, in addition to the NH resonance at 9.7 ppm are observable at room temperature. Increasing the temperature of the sample to 340 K eliminates both resonances forcing them to coalesce, proving that they do not belong to an impurity (Figure 2.7).

Figure 2.6 – Tautomerization of **17** Figure 2.7 – Variable temperature effect on amide ^1H region of **17**

The piperidine-based biureas (**10**, **11** and **23**) show a high degree of complexity in the ^1H NMR splitting of the methylene protons of the ring (see appendix 1). The ring, at room temperature, is conformationally locked and the methylenic protons are no longer equivalent as observed by large ^2J coupling constants. This is also confirmed by HSQC 2D NMR where each methylenic carbon of the ring correlates to two proton signals. Furthermore, the splitting patterns of each proton of a given methylene are not identical, showing the angular dependence on the magnitude of the coupling constants. The assignment of resonances to proton groups is a routine exercise with the help of a COSY spectrum. However, a 300 MHz field does not provide sufficient resolution to be able to

observe all coupling details and so the smaller constants, are assumed to be of the same magnitude.

2.2.2 – Peripheral ligands

When platinum is involved, cyclometallating ligands are often encountered and many derivatives of 2-phenyl pyridine are synthetically or commercially available¹⁴⁷. Extending the conjugation usually induces a bathochromic shift of the metal complex, while increasing the nitrogen content has the opposite effect. Equipped with this knowledge, ligands **30-32** were chosen to probe the optical properties of dinuclear platinum complexes. Ligand **30** was obtained commercially while the two others, 2-methyl-3-phenyl-quinoxaline (**31**) and 2-methyl-3-phenyl-benzo[g]quinoxaline (**32**), were synthesized (Figure 2.8) using a published procedure based on the iodine catalyzed condensation reaction¹³⁰.

Figure 2.8 – Peripheral ligands considered

The condensation reaction was performed as described and the workup was simple. The pure ligands **31** and **32** were obtained and their spectral characterization agreed well with literature values¹³⁰. The difference between **30** and **31** is obvious enough. Ligand **32** is an interesting case where the conjugation is extended even more than **31**. The antagonist effects could nullify themselves and the resulting optical properties may be quite similar to the complex based on ligand **30**.

Chapter 2 – Bridging and peripheral ligands

2.3 – Conclusion

A series of hydroxyl-containing bridging ligands were prepared to encompass most types required for various polymerizations as well as electronic properties of the dinuclear metal complexes. Two thiocarbonyl derivatives were also prepared to establish the effect of sulfur on the optical properties of dinuclear ruthenium complexes.

Synthetic modifications of the bipyridine peripheral ligands were not explored in matters regarding ruthenium complexes since their effects are known. However, a few cyclometallating peripheral ligands were considered to generate a short series of novel dinuclear platinum complexes.

2.4 – Experimental

NMR experiments were performed on a Bruker AMX 400 MHz or Avance 300 MHz spectrometer in either DMSO-*d*₆, CDCl₃, D₂O or a D₂O/D₂SO₄ mixture when solubility was too low to record ¹³C spectra and are reported in ppm (multiplicity, integration, assignment, coupling constants). Coupling constants are given in Hertz and multiplicity terms used are: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and combinations such as dd (doublet of doublet). 2D NMR (COSY, HSQC, HMBC and NOESY) experiments were recorded when required. Infrared (IR) spectra were recorded on a Varian Scimitar 1000 series FT-IR spectrometer using an attenuated total reflectance (ATR) accessory. Mass spectra were acquired at the University of Ottawa Regional Mass Spectrometry Center on a Kratos Concept IIIH mass spectrometer in electron ionization (EI) mode (70 eV) and peaks are reported as m/z (% intensity

Chapter 2 – Bridging and peripheral ligands

relative to the base peak). Melting points were obtained on a Fisher-Johns apparatus equipped with a thermocouple (upper limit of 350°C) and are uncorrected.

All the chemicals for preparing the ligands were used as received. Solvents were ACS grade or better and used as received except for THF, which was distilled over sodium benzophenone ketyl. Triethylamine (TEA) was only distilled once a yellow coloration developed. 6-Hydroxyhexanoic hydrazide¹³⁴, 4-hydroxybutanoic hydrazide¹⁴⁸ and ligands **9**, **13-20**, **24-29** and **31-32** were synthesized by known methods (see Tables 2.1 and 2.2 for references). The other new ligands (**1-8**, **10-12** and **20-22**) were prepared by modifications of current methods.

NMR spectra can be found in Appendix 1. The spectra also include a structure of each compound with the numbering scheme used for chemical shift assignments.

General procedure for the synthesis of mono hydroxyl DCH ligands

4-Hydroxybutanoic hydrazide (1.02 g, 8.51 mmol) was dissolved in a 100 mL round-bottomed flask (RBF) with 40 mL of THF and 2 of mL H₂O (to ensure complete dissolution of the hydrazide) containing an equimolar amount of TEA. Propionyl chloride (0.95 molar equivalent), diluted in 10 mL THF was added dropwise to the hydrazide-TEA mixture as such to maintain ambient temperature under an inert atmosphere. Once the addition complete, the temperature was increased to maintain a gentle reflux for a period of two hours. The reaction solvent was evaporated using a roto-evaporator. It was found that the ligand was water soluble and so an aqueous workup was not to be considered. Instead, the solid was triturated using hot chloroform to extract the ligand. NMR of the white solid obtained after removing the chloroform showed that some TEA-

Chapter 2 – Bridging and peripheral ligands

HCl still remained (8 % in the case of 1). However, this salt will have no consequence during the complexation step and no further attempts were made to purify the ligand. Yields are corrected for TEA salt present.

4-hydroxy-N'-propionylbutanehydrazide (1). Yield: 58 %. FT-IR: 3207 cm^{-1} (NH) and 1591 cm^{-1} (C=O). ^1H NMR (300 MHz, DMSO- d_6): 9.62 (s, 2H, H5); 4.47 (t, 1H, OH, $^3J = 5\text{Hz}$); 3.38 (m, 2H, H4, $^3J = 5\text{Hz}$, $^3J = 6\text{Hz}$); 2.13 (t, 2H, H2, $^3J = 7\text{Hz}$); 2.10 (q, 2H, H7, $^3J = 8\text{Hz}$); 1.64 (m, 2H, H3, $^3J = 8\text{Hz}$, $^3J = 6\text{Hz}$) and 1.00 (t, 3H, H8, $^3J = 8\text{Hz}$). ^{13}C NMR (75 MHz, DMSO- d_6): 172.3 (C1); 171.6 (C6); 60.6 (C4); 30.4 (C2); 28.9 (C3); 26.8 (C7) and 10.1 (C8). MP: 102-103 °C. EI-MS: 174 (M^+ , 1.4 %), 156 (3.8), 125 (4.7), 100 (18), 88 (87), 69 (32) and 57 (100).

6-hydroxy-N'-propionylhexanehydrazide (2). Yield: 36 %. FT-IR: 3217 cm^{-1} (NH) and 1593 cm^{-1} (C=O). ^1H NMR (300 MHz, DMSO- d_6): 9.65 (s, 2H, H7); 4.38 (t, 1H, OH, $^3J = 6\text{Hz}$); 3.37 (m, 2H, H6, $^3J = 6\text{Hz}$); 2.11 (q, 2H, H9, $^3J = 8\text{Hz}$); 2.10 (t, 2H, H2, $^3J = 8\text{Hz}$); 1.50 (m, 2H, H3, $^3J = 8\text{Hz}$); 1.40 (m, 2H, H5, $^3J = 8\text{Hz}$); 1.30 (m, 2H, H4, $^3J = 8\text{Hz}$) and 1.00 (t, 3H, H10, $^3J = 8\text{Hz}$). ^{13}C NMR (75 MHz, DMSO- d_6): 172.3 (C1); 171.5 (C8); 61.0 (C6); 33.7 (C2); 32.7 (C5); 26.8 (C9); 25.6 (C4); 25.5 (C3) and 10.1 (C10). MP: 98-99 °C. EI-MS: 184 (2.9 %), 167 (6.2), 125 (96), 101 (15), 86 (100), 69 (33) and 57 (53).

Chapter 2 – Bridging and peripheral ligands

General procedure for the synthesis of semi biurea DCH ligands

4-Hydroxybutanoic hydrazide (1.0 g, 8.5 mmol) was dissolved in a 100 mL RBF with 40 mL THF and 2 mL H₂O (to ensure dissolution of the hydrazide). 0.95 molar equivalent of propionyl isocyanate, diluted in 20 mL THF was added dropwise to the hydrazide solution as such to maintain ambient temperature while maintaining an inert atmosphere. Stirring at room temperature was maintained for a period of two hours. The reaction solvent was evaporated using a roto-evaporator as the product was soluble in THF. It was also found that this ligand was water soluble. The solid was triturated using ethyl ether to extract any propylamine by-product that could have formed by water hydrolysis of the isocyanate. The solid was filtered and washed with 2 x 10 mL portions of acetone to remove any starting hydrazide and finally washed with ethyl ether and dried under vacuum for one hour. The solid was NMR pure.

2-(4-hydroxybutanoyl)-N-propylhydrazinecarboxamide (3). Yield: 90 %. FT-IR: 3312 cm⁻¹, 3210 cm⁻¹, 3105 cm⁻¹ (3 x NH) and 1668 cm⁻¹ (C=O). ¹H NMR (300 MHz, DMSO-*d*₆): 9.38 (s, 1H, H5); 7.58 (s, 1H, H6); 6.29 (t, 1H, H8, ³J = 6Hz); 4.49 (s, 1H, OH); 3.39 (m, 2H, H4, ³J = 5Hz, ³J = 6Hz); 2.93 (dt, 2H, H9, ³J = 7Hz, ³J = 6Hz); 2.11 (t, 2H, H2, ³J = 7Hz); 1.64 (m, 2H, H3, ³J = 7Hz); 1.37 (tq, 2H, H10, ³J = 7Hz) and 0.81 (t, 3H, H11, ³J = 7Hz). ¹³C NMR (75 MHz, DMSO-*d*₆): 172.6 (C1); 158.7 (C7); 60.8 (C4); 41.4 (C9); 30.6 (C2); 28.7 (C3); 23.5 (C10) and 11.7 (C11). MP: 122-123 °C. EI-MS: 203 (M⁺, 0.6 %), 185 (7.0), 126 (18), 118 (48), 100 (74), 87 (61), 69 (48), 58 (43) and 43 (100).

Chapter 2 – Bridging and peripheral ligands

2-(6-hydroxyhexanoyl)-N-propylhydrazinecarboxamide (4). Yield: 93 %. FT-IR: 3312 cm^{-1} , 3210 cm^{-1} , 3105 cm^{-1} (3 x NH) and 1670 cm^{-1} (C=O). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 9.36 (s, 1H, H7); 7.58 (s, 1H, H8); 6.23 (t, 1H, H10, $^3J = 6\text{Hz}$); 4.33 (t, 1H, OH, $^3J = 6\text{Hz}$); 3.37 (dt, 2H, H6, $^3J = 6\text{Hz}$, $^3J = 5\text{Hz}$); 2.95 (dt, 2H, H11, $^3J = 7\text{Hz}$); 2.07 (t, 2H, H2, $^3J = 7\text{Hz}$); 1.50 (m, 2H, H3, $^3J = 7\text{Hz}$); 1.40 (m, 2H, H5); 1.37 (m, 2H, H12); 1.28 (m, 2H, H4, $^3J = 7\text{Hz}$) and 0.82 (t, 3H, H13, $^3J = 7\text{Hz}$). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): 172.5 (C1); 158.6 (C9); 61.1 (C6); 41.4 (C11); 33.7 (C2); 32.7 (C5); 25.6 (C4); 25.3 (C3); 23.5 (C12) and 11.7 (C13). MP: 125-126 $^{\circ}\text{C}$. EI-MS: 231 (M^+ , 0.7 %), 146 (20), 112 (64), 97 (44), 69 (100) and 55 (62).

6-hydroxy- N' -(6-hydroxyhexanoyl)hexanehydrazide (5). 6-Hydroxyhexanoic hydrazide (1.46 g, 1 mmol) and methyl acetoacetate (0.58 g, 0.5 mmol) are refluxed in 10 mL toluene for three hours. The mixture is cooled to 80 $^{\circ}\text{C}$ and the organic phase is extracted with 2 mL of a 9% HCl solution to eliminate the pyrazolone impurity. According to the source patent¹³⁶, the product remains in the organic phase but due to the increased polarity of the diol, it emerged as a white precipitate as both phases cooled. It was recovered, washed with a little cold water and 5 mL cold acetone. 0.55 g of the diol was obtained, 21 % yield. FT-IR: 3215 cm^{-1} and 1593 cm^{-1} (C=O). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): 9.64 (s, 1H, H7); 4.36 (s, 1H, OH); 3.37 (t, 2H, H6, $^3J = 6\text{Hz}$); 2.09 (t, 2H, H2, $^3J = 7\text{Hz}$); 1.50 (tt, 2H, H3, $^3J = 7\text{Hz}$); 1.41 (tt, 2H, H5, $^3J = 7\text{Hz}$) and 1.21 (tt, 2H, H4, $^3J = 7\text{Hz}$). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): 171.5 (C1); 61.1 (C6); 33.7 (C2); 32.7 (C5); 25.6 (C4) and 25.5 (C3). MP: 147-148 $^{\circ}\text{C}$. EI-MS: 242 ($\text{M}^+ - \text{H}_2\text{O}$, 0.2 %), 225 (0.4), 183 (5.9), 170 (4.2), 146 (23), 115 (71), 97 (48), 69 (100), 55 (36) and 41 (49).

Chapter 2 – Bridging and peripheral ligands

General procedure for the synthesis of diol biureas

DIAD (3 g, 14.8 mmol) diluted in 10 mL ethyl ether is added dropwise to a 100 mL RBF containing 3-hydroxypropylamine (3 g, 40 mmol) diluted in 40 mL ethyl ether at room temperature with stirring. Orange solids quickly appeared. The stirring was maintained for two hours. The solids were filtered, washed with ethyl ether and air dried. The reaction solvent system varied with the solubility of the amine used, such as a 5:6 mixture of ethyl ether and methanol when preparing ligand (**10**). When methanol was involved, ethyl ether was added to the reaction, after the two hour period, to completely precipitate the azo product. Also, when secondary amines were employed (piperidines), the use of DEAD instead of DIAD was necessary for the aminolysis to proceed due to the lower nucleophilicity of the amine. **Warning:** DEAD decomposes violently when exposed to heat and reactions should always be performed at room temperature or lower.

The azo derivative was suspended (or dissolved) in 20 mL ethanol and hydrazine monohydrate was added dropwise, no more than 5 drops every 15 minutes, until the orange coloration completely disappears or in the case of the piperidine-based systems, a pale yellow fine powder was obtained. The biurea tends to degrade when too much hydrazine is added. The biurea suspension was diluted with ethyl ether and the solid was filtered, washed with ethyl ether and air dried.

*N*¹,*N*²-Bis(3-hydroxypropyl)hydrazine-1,2-dicarboxamide (**6**). Yield: 78 % (based on azodicarboxylate). FT-IR: 3389 cm⁻¹ (NH), 3207 cm⁻¹ (OH) and 1659 cm⁻¹ (C=O). ¹H NMR (300 MHz, DMSO-*d*₆): 7.59 (s, 1H, H₆); 6.36 (t, 1H, H₂, ³J = 6Hz); 4.45 (t, 1H, OH, ³J = 5Hz); 3.42 (dt, 2H, H₅, ³J = 5Hz, ³J = 6Hz); 3.09 (dt, 2H, H₃, ³J = 5Hz, ³J =

6Hz) and 1.54 (tt, 2H, H4, $^3J = 6\text{Hz}$). ^{13}C NMR (75 MHz, DMSO- d_6): 159.3 (C1); 58.9 (C5); 36.8 (C3) and 33.3 (C4). MP: 252-253 °C. EI-MS: 234 (M^+ , 0.4 %), 159 (6.6), 133 (50), 115 (12), 102 (36) and 56 (100).

N¹,N²-Bis(3-hydroxypentyl)hydrazine-1,2-dicarboxamide (7). Yield: 82 % (based on azodicarboxylate). FT-IR: 3285 cm^{-1} (NH), 3221 cm^{-1} (OH) and 1657 cm^{-1} (C=O). ^1H NMR (400 MHz, DMSO- d_6): 7.33 (s, 1H, H8); 6.08 (t, 1H, H2, $^3J = 6\text{Hz}$); 4.14 (t, 1H, OH, $^3J = 5\text{Hz}$); 3.38 (dt, 2H, H7, $^3J = 6\text{Hz}$, $^3J = 5\text{Hz}$); 3.0 (dt, 2H, H3, $^3J = 6\text{Hz}$, $^3J = 5\text{Hz}$); 1.4 (m, 4H, H4 and H6) and 1.27 (m, 2H, H5). ^{13}C NMR (100 MHz, DMSO- d_6): 158.6 (C1); 60.7 (C7); 39.2 (C3); 32.2 (C6); 29.6 (C4) and 22.8 (C5). MP: 258-259 °C. EI-MS: 290 (M^+ , 1.8 %), 260 (0.3), 187 (4.2), 161 (52), 130 (6.3), 112 (14), 102 (33), 85 (12), 69 (64), 55 (58) and 41 (100).

4-Hydroxy-N'-(4-hydroxypiperidine-1-carbonyl)piperidine-1-carbohydrazide (10). Yield: 27 % (based on azodicarboxylate). FT-IR: 3280 cm^{-1} (NH and OH) and 1626 cm^{-1} (C=O). ^1H NMR (300 MHz, DMSO- d_6): 8.09 (s, 1H, H5); 4.69 (d, 1H, OH, $^3J = 4\text{Hz}$); 3.71 (ddd, 2H, H2, $^2J = 11\text{Hz}$, $^3J = 3\text{Hz}$); 3.61 (ddd, 1H, H4, $^3J = 3\text{Hz}$, $^3J = 4\text{Hz}$); 2.86 (ddd, 2H, H2', $^2J = 11\text{Hz}$, $^3J = 3\text{Hz}$); 1.67 (ddd, 2H, H3, $^2J = 10\text{Hz}$, $^3J = 3\text{Hz}$) and 1.24 (ddd, 2H, H3', $^2J = 10\text{Hz}$, $^3J = 3\text{Hz}$). ^{13}C NMR (75 MHz, DMSO- d_6): 157.9 (C1); 66.0 (C4); 41.4 (C2) and 34.2 (C3). MP: 212-213 °C. EI-MS: 286 (M^+ , 5.0 %), 185 (99), 167 (5.9), 140 (7.9), 128 (50), 113 (22), 102 (68), 84 (49), 68 (15), 56 (100) and 42 (76).

Chapter 2 – Bridging and peripheral ligands

4-(Hydroxymethyl)-N'-(4-(hydroxymethyl)piperidine-1-carbonyl)piperidine-1-carbohydrazide (11). Yield: 55 % (based on azodicarboxylate). FT-IR: 3287 cm^{-1} (NH and OH) and 1612 cm^{-1} (C=O). ^1H NMR (300 MHz, $\text{DMSO}-d_6$): 8.04 (s, 1H, H6); 4.46 (s, 1H, OH); 3.98 (ddd, 2H, H2, $^2J = 13\text{Hz}$); 3.23 (d, 2H, H5, $^3J = 6\text{Hz}$); 2.64 (ddd, 2H, H2', $^2J = 13$); 1.59 (ddd, 2H, H3, $^2J = 12\text{Hz}$); 1.52 (m, 1H, H4) and 1.24 (ddd, 2H, H3', $^2J = 12\text{Hz}$, $^3J = 3\text{Hz}$). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): 158.3 (C1); 66.2 (C5); 44.0 (C2); 39.0 (C4) and 29.0 (C3). MP: 186-187 °C. EI-MS: 314 (M^+ , 2.5 %), 199 (67), 184 (1.6), 158 (3.6), 142 (26), 128 (6.6), 114 (72), 96 (27), 84 (49), 69 (28), 55 (100) and 43 (76).

4-Methyl-N'-(4-methylpiperidine-1-carbonyl)piperidine-1-carbohydrazide (23). Yield: 37 % (based on azodicarboxylate). FT-IR: 3238 cm^{-1} (NH) and 1634 cm^{-1} (C=O). ^1H NMR (300 MHz, $\text{DMSO}-d_6$): 8.07 (s, 1H, H6); 3.97 (ddd, 2H, H2, $^2J = 12\text{Hz}$); 2.67 (ddd, 2H, H2', $^2J = 12\text{Hz}$); 1.57 (ddd, 2H, H3, $^2J = 12$); 1.55 (ddq, 1H, H4); 1.02 (ddd, 2H, H3', $^2J = 12\text{Hz}$, $^3J = 10\text{Hz}$) and 1.24 (d, 3H, H5, $^3J = 6\text{Hz}$). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): 158.3 (C1); 44.3 (C2); 34.1 (C3); 30.9 (C4) and 22.4 (C5). MP: 181-182 °C. EI-MS: 282 (M^+ , 2.6 %), 264 (4.4), 183 (91), 168 (7.1), 142 (4.2), 126 (48), 98 (100), 84 (23), 69 (21), 55 (87) and 43 (40).

N¹,N²-Bis(1,3-dihydroxy-2-methylpropan-2-yl)hydrazine-1,2-dicarboxamide (8). DEAD (2 g, 12 mmol) diluted in 15 mL 1:1 ethyl ether:methanol is added dropwise to a 100 mL RBF containing a 2-amino-2-methylpropane-1,3-diol (2.8 g, 26.6 mmol) solution in 50 mL ethyl ether:methanol 1:1, cooled using an ice bath (removed after the addition is complete). A pale orange precipitate forms quickly and the reaction is stirred for two

Chapter 2 – Bridging and peripheral ligands

hours at room temperature. The mixture is poured in 100 mL ethyl ether. The solid is filtered off, washed with ethyl ether and air dried. The azo intermediate reduced as described above for diol biureas. The ethanol is evaporated on a roto-evaporator at low temperature (30-35°C), yielding a sticky white residue. Triturate the solid using acetone, filter the powdery solid, wash with ethyl ether and air dry. Yield: 56 % (based on azodicarboxylate). FT-IR: 3350 cm^{-1} (NH), 3231 cm^{-1} (OH) and 1672 cm^{-1} (C=O). ^1H NMR (400 MHz, DMSO- d_6): 7.71 (s, 1H, H6); 5.87 (s, 1H, H2); 4.87 (t, 2H, OH, $^3\text{J} = 5\text{Hz}$); 3.45 (dd, 2H, H5, $^2\text{J} = 11\text{Hz}$, $^3\text{J} = 5\text{Hz}$); 3.33 (dd, 2H, H5', $^2\text{J} = 11\text{Hz}$, $^3\text{J} = 5\text{Hz}$); and 1.14 (s, 3H, H4). ^{13}C NMR (100 MHz, DMSO- d_6): 158.4 (C1); 64.4 (C5); 56.8 (C3) and 18.8 (C4). MP: 141-142 °C. EI-MS: 271 (0.6 %), 246 (0.7), 190 (1.9), 164 (6.5), 141 (19), 132 (42), 114 (5.6), 100 (93), 90 (5.3), 74 (90), 56 (100) and 42 (75).

*N*¹-(5-Hydroxypentyl)-*N*²-propyloxalamide (**12**). Ethyl oxochloro acetate (4 g, 29.4 mmol) diluted in 10 mL THF was added dropwise to a cooled (ice water), stirred solution of propylamine (1.7 g, 28.8 mmol) and TEA (2.97 g, 29.4 mmol) in 70 mL of THF. The solution is warmed to room temperature following the addition and stirring is maintained for 1 hour. The reaction mixture is then chilled in an ice bath, the TEA-HCl is filtered out and the solid is washed with 20 mL of cold THF. The filtrate is concentrated to a yellow oil. A portion of this oil (2 g, 12.6 mmol) was diluted in 10 mL ethyl ether and added dropwise to a solution of 5-hydroxypentamine (1.45 g, 14 mmol) dissolved in 25 mL ethyl ether and enough methanol to ensure complete dissolution of the amine. Stirring is maintained for two hours. The mixture was then diluted with 50 mL ethyl ether, the white precipitate was filtered and washed with a 95:5 ethyl ether:methanol solution followed by

Chapter 2 – Bridging and peripheral ligands

ethyl ether and air dried. Yield: 60 %. FT-IR: 3292 cm^{-1} (NH) and 1645 cm^{-1} (C=O). ^1H NMR (300 MHz, DMSO- d_6): 8.70 (s, 2H, H2 and H9); 4.34 (s, 1H, OH); 3.37 (t, 2H, H7, $^3J = 6\text{Hz}$); 3.11 (m, 2H, H3); 3.07 (m, 2H, H10); 1.47 (m, 2H, H5); 1.45 (m, 2H, H11); 1.41 (m, 2H, H6); 1.26 (tt, 2H, H4, $^3J = 6\text{Hz}$) and 0.82 (t, 3H, H12, $^3J = 7\text{Hz}$). ^{13}C NMR (75 MHz, DMSO- d_6): 160.1, 160.0 (C1, C8); 60.6 (C7); 40.6 (C10); 38.8 (C3); 32.2 (C6); 28.7 (C11); 22.9 (C4); 22.1 (C5) and 11.3 (C12). MP: 133-134 °C. EI-MS: 216 (M^+ , 4.2 %), 188 (2.4), 171 (0.8), 159 (8.3), 143 (7.4), 130 (43), 112 (56), 103 (20), 86 (26), 69 (97), 59 (29) and 43 (100).

*N*¹,*N*²-Bis(4-aminobenzyl)hydrazine-1,2-dicarboxamide (**21**). DIAD (0.81 g, 4 mmol) diluted in 10 mL of ethyl ether is added dropwise to a 4-aminobenylamine (1.0 g, 8.2 mmol) solution in 25 mL of 9:1 ethyl ether:methanol. Stirring was maintained for 2 hours. The solvent was removed and the yellow azo solid was triturated with ethyl ether, filtered, washed with ethyl ether and air dried. Hydrazine hydrate was used as the reducing agent as described above for diol biureas. The white solid was isolated, washed with 10 mL cold methanol and 50 mL of ethyl ether. Yield: 60 % (based on azodicarboxylate). FT-IR: 3294 cm^{-1} (NH), 3219, 3091 cm^{-1} (NH_2) and 1657 cm^{-1} (C=O). ^1H NMR (300 MHz, DMSO- d_6): 7.58 (s, 1H, H8); 6.91 (d, 2H, H5, $^3J = 8\text{Hz}$); 6.53 (t, 2H, H2, $^3J = 6\text{Hz}$); 6.48 (d, 2H, H6, $^3J = 8\text{Hz}$); 4.91 (s, 2H, NH_2) and 4.03 (d, 2H, H3, $^3J = 6\text{Hz}$). ^{13}C NMR (75 MHz, DMSO- d_6): 158.6 (C1); 147.3 (C7); 128.1 (C5); 127.2 (C4); 113.6 (C6) and 42.5 (C3). MP: 270 °C (dec.). EI-MS: 165 (0.7 %), 148 (21), 132 (1.2), 121 (18), 106 (100), 94 (9.1), 78 (20), 65 (7.3), 52 (7.1) and 43 (8.4).

Chapter 2 – Bridging and peripheral ligands

3,3'-(Hydrazine-1,2-diylbis(oxomethylene))bis(azanediyldipropionic acid (22). DIAD (2.23 g, 11 mmol) diluted in 10 mL of ethanol is added dropwise to an aqueous solution (40 mL H₂O) of β -alanine (2.11 g, 23.7 mmol) and NaOH (0.96 g, mmol) in a 100 mL RBF. This was stirred at room temperature for 30 minutes and acidified with 2 M HCl. The yellow precipitate was filtered and washed with ethyl ether and air dried. The azo intermediate was dispersed in ethanol and hydrazine hydrate was added one drop at a time every five minutes until the coloration completely disappeared. Precipitate the diacid in 100 mL ethyl ether, filter and air dry. Yield: 37 % (based on azodicarboxylate). FT-IR: 3280 cm⁻¹ (NH), 3101 cm⁻¹ (COOH) and 1666 cm⁻¹ (C=O). ¹H NMR (400 MHz, D₂O): 7.75 (s, 1H, H6); 6.81 (s, 1H, H2); 3.33 (t, 2H, H3, ³J = 7Hz) and 2.35 (t, 2H, H4, ³J = 7Hz). ¹³C NMR (100 MHz, D₂O): 183.1 (C5); 163.0 (C1); 39.9 (C3) and 39.3 (C4). MP: 239 °C (dec.). EI-MS: 226 (4.6 %), 168 (0.4), 155 (6.1), 140 (1.5), 129 (86), 114 (4.9), 98 (24), 87 (45), 70 (28), 60 (15), 55 (40) and 44 (100).

Chapter 3 – Dinuclear ruthenium and platinum complexes

3.1 – Introduction

The electrochromic properties of dinuclear ruthenium complexes have been extensively studied^{3, 52, 60-65}. The IVCT of the mixed valence oxidation state appears in the NIR region of the electromagnetic spectrum and can be tuned according to the donor strength of the ligands used. As previously mentioned, the substitution effect of the peripheral ligand is modest at best, producing small optical shifts of about ± 100 nm, which represents small energy changes in the lowest unoccupied molecular orbitals (LUMO) of the complexes with little effect on the overall bandgap. Modifying the bridging ligand, on the other hand has a more pronounced effect, up to 400 nm hypsochromic shifts, which enabled the tuning of the NIR absorbance over a broader range of wavelengths¹⁴⁹. Therefore, the impact of the bridging ligands on the HOMO energy levels of the complexes is as follows: the NIR absorbance is redshifted when the electron donating potential is enhanced (HOMO increase) and vice-versa. To further study this process, a series of dinuclear ruthenium complexes, based on the ligands of Chapter 2 were prepared and characterized. The structures of some reported DCH and OXA ruthenium complexes by previous group members, were resolved by x-ray crystallography and as expected, show octahedral geometries. A simple stick structure of the DCH and OXA complexes is shown in Figure 3.1.

Figure 3.1 – Model of a) DCH and b) OXA dinuclear ruthenium complexes

Moreover, in order to study the effect of metal centers on optical properties, various dinuclear platinum complexes, with different electron donating potential, were prepared and their optical properties were evaluated. Since platinum complexes are known phosphorescent materials¹⁵⁰⁻¹⁶¹, the possibility of NIR emission by a mixed valence oxidation state was intriguing.

Many dinuclear platinum complexes based on different ligand systems are known¹⁶²⁻¹⁷⁹. However, most bridging ligands employed do not permit electronic communication between the two platinum atoms and the so-called dinuclear complex behaves as two single platinum complexes. A few mixed valence $\text{Pt}^{\text{II}}\text{-Pt}^{\text{III}}$ state complexes have been reported through crystallography but no optical studies have been performed study their NIR potential^{158, 180}. Ma and coworkers prepared dinuclear platinum complexes based on pyrazolates that form angular complexes, bringing the two platinum atoms closer together. The close proximity favours some bonding character between the two metal centers through the σ^* orbital and the resulting metal-metal-to-ligand charge transfer (MMLCT) is redshifted as the Pt-Pt distance is reduced^{181, 182}. In the cases of mononuclear platinum complexes, the usual $\pi \rightarrow \pi^*$ MLCT transition is

observed; however, for dinuclear platinum complexes the more energetic σ^* is filled and the transition is then $\sigma^* \rightarrow \pi^*$, which has a much smaller energy gap, causing the redshift of the transition¹⁸². As the platinum atoms are brought closer together, repulsive forces increase and may become dominant; it would appear that emission of red light, peaking at 690 nm for a Pt-Pt distance of 2.8 Å, is seriously approaching this limit¹⁸². At 690 nm, just short of breaching the NIR barrier, emission at even longer wavelengths is likely impossible via MMLCT.

3.2 – Results and discussion

3.2.1 – Ruthenium complexes

Dinuclear ruthenium complexes of selected ligands discussed in Chapter 2, were prepared via a ligand exchange reaction and isolated as PF_6 salts. The complexes were obtained, after purification using neutral alumina, as purple solids which were soluble in alcohol, acetone, acetonitrile, dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF). It should be noted however that, the two latter solvents are generally avoided due to their problematic removal. The increased polarity of the complexes caused by the hydroxyl groups required water-deactivated alumina with water to allow the elution to proceed at a suitable rate. Yields of purified aliphatic DCH and OXA complexes, were generally good.

All the complexes prepared, regardless of functionalization, were redox active and their CVs showed two, reversible, one-electron redox waves representing the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ (ground state), $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ (mixed valence state) and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ states (Figure 3.1). The

redox potentials of the complexes were influenced by the substituents of the bridging ligand; adding electron-withdrawing groups increased the electron ionisation energy of the metal centers, effectively increasing the redox potential while electron-donating groups had the opposite effect. This effect can be further tuned by the number of groups added. Complex **36**, having two extra nitrogens had a lower redox potential than complex **31** (Figure 3.1) which only has one extra nitrogen. This is all relative to complex **30** which does not contain any electron-donating groups and exhibited the highest redox potentials of the trio (see footnote 'a' of Table 3.1 for CV conditions).

Figure 3.1 – CV of **30**, **31** and **36**

The redox potentials of the synthesized complexes are compiled in Table 3.1. When oxygen-based donating groups were involved, such as with **38**, the redox potentials were lowered although the effect was less important than with nitrogen containing complexes. As an electron donor, oxygen is not as effective as nitrogen because of its

higher electronegativity; it retains its valence electrons with a higher affinity translating to higher redox potentials.

Table 3.1 – Electrochemical properties of the ruthenium complexes

$^1E_{1/2}^a$	$^2E_{1/2}^a$	$\Delta E_{1/2}^a$	$^3E_{1/2}$	K_c^d
$R^1 = (CH_2)_3OH$; $R^2 = CH_2CH_3$	30	361	921	560	-	3.0×10^9
$R^1 = (CH_2)_3OH$; $R^2 = NH(CH_2)_2CH_3$	31	279	884	606	-	1.8×10^{10}
$R^1 = (CH_2)_5OH$; $R^2 = NH(CH_2)_2CH_3$	32	281	896	614	-	2.4×10^{10}
$R^1 = R^2 = (CH_2)_5OH$	33	291	870	580	-	6.4×10^9
$R^1 = R^2 = NHCH_2Ph$	34	133	697	564	-	3.5×10^9
$R^1 = R^2 = NHC(CH_3)(CH_2OH)_2$	35	108	646	538	-	1.3×10^9
$R^1 = R^2 = NH(CH_2)_5OH$	36	67	657	590	-	9.5×10^9
$R^1 = R^2 = NHCH_2Ph$ -p-NH ₂	37	134	680	546	1154 ^b	1.7×10^9
$R^1 = R^2 = O(CH_2)_2OH$	38	344	883	539	-	1.3×10^9
$R^1 = R^2 = N$ - -CH ₂ OH	39	278	645	367	149 ^c	2.3×10^6
$R^1 = R^2 = N$ -	40	255	615	361	136 ^c	1.3×10^6
41	424	895	472	-	9.6×10^7
42	234	678	445	-	3.4×10^7
43	383	923	540	-	1.4×10^9

^a electrochemical data (in mV) were recorded in 0.1 M TBAH MeCN solution at 200 mV/s scan rate and are referenced to ferrocene vs SCE;

^b additional redox couple due to aniline oxidation;

^c isomer impurity redox couple;

^d comproportionation constant determined using Equation 3.2

When the carbonyl oxygen was replaced by sulfur, in the cases of **42** and **43**, the redox potentials of the ruthenium complexes decreased. However, the observed effect may be due to the nitrogen donating potential rather than the presence of sulfur.

Chapter 3 – Dinuclear ruthenium and platinum complexes

Sulfurisation of diphenylhydrazide using P_2S_5 , as an attempt to prepare the dithio derivative, which would have provided a reference complex to better evaluate the effect of sulfur, only produced 2,5-diphenyl-1,3,4-thiadiazole by H_2S elimination.

The peak separation, $\Delta E_{1/2}$, of complexes based on the DCH ligands were, on average, 570 mV regardless of the electrodonating potential of the ligand used. A lower $\Delta E_{1/2}$ was observed for the piperidine biureas (**39** and **40**), which did not appear to be significantly different from the other biurea complexes. Disubstituted biureas presented, on average, $^1E_{1/2}$ of 100 mV, while the piperidine biureas (tetrasubstituted biurea) had $^1E_{1/2}$ of 260 mV. On the other hand, the $^2E_{1/2}$ of both groups was of the same order of magnitude, hence the smaller $\Delta E_{1/2}$. To explain this difference, we turn to the mixed valence state which can transfer its electron to a neighbouring molecule, forming Ru^{II}/Ru^{II} and Ru^{III}/Ru^{III} molecules (equation 3.1).

This equilibrium is governed by the comproportionation constant (k_c) and is calculated using $\Delta E_{1/2}$ (equation 3.2)¹⁸³.

$$k_c = 10^{16.91\Delta E_{1/2}} \quad \text{Equation 3.2}$$

When the constant is large, the Ru^{II}/Ru^{III} system coupling is strong, intermolecular electron transfer is no longer dominant, but rather, intramolecular electron transfer between both ruthenium atoms occurs and this charge ‘sharing’ imparts a

stabilizing effect on the system. The comproportionation constant, k_c , can be determined using the free energy of conproportionation, ΔG_c (equation 3.3)¹⁸³.

$$\Delta G_c = -RT(\ln k_c) \quad \text{Equation 3.3}$$

ΔG_c is the sum of many free energy terms, including ΔG_r , the free energy of resonance exchange¹⁸³. Figure 3.2 depicts energy potential curves of a weakly coupling system (a) and a strongly coupling system (b). The free energy of resonance exchange is also shown.

Figure 3.2 – Potential energy curves of a weakly coupled (a) and a strongly coupled (b) mixed valence state

Strong coupling systems, being more stable, will require extra energy to further oxidize the system, thus maintaining the $^2E_{1/2}$ at higher energies. It could be expected that a piperidine, with its nitrogen enriched by the two alkyl groups of the ring, would be a more efficient electron donor thus reducing the redox potentials to a greater degree than the biureas. This, however, does not appear to be the case since the opposite effect was

observed; a lower $\Delta E_{1/2}$ due to weaker coupling, possibly due to orbital misalignment with the carbonyl.

The $\Delta E_{1/2}$ of the thio derivatives (**42** and **43**) behaved similarly to the DCH analogues, becoming lower as the number of sulfur increased. The smaller $\Delta E_{1/2}$ compared to that of the DCH complexes, suggest that they too, have weaker coupling than the biureas.

Each redox state of the complexes was studied by spectroelectrochemistry and their optical properties are compiled in Table 3.2. The ground state ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$) is marked by two MLCTs in the UV-Vis region, resulting in an observed purple coloration, while the mixed valence state ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$) only has one MLCT in the visible region, near 420 nm, giving it a yellow color although a broad absorbance in the NIR is observed due to the IVCT transition. The third oxidation state ($\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$) has a light green tint, almost unperceivable and two MLCTs near 400 nm and 750-950 nm. The NIR transition of the third oxidation state is normally ignored due to complex degradation particularly when high potentials are required to attain this state. The three oxidation states of complex **36**, as well as the NIR region of the mixed valence state of **33** and **38**, are overlaid in Figure 3.3, showing the λ_{max} effect of donating group strength on the mixed valence state.

Table 3.2 – Spectroelectrochemical properties of ruthenium complexes

Ru ^{II} /Ru ^{II} ^a	Ru ^{II} /Ru ^{III} ^a	Ru ^{III} /Ru ^{III} ^a
R ¹ = (CH ₂) ₃ OH; R ² = CH ₂ CH ₃	30		344 (4.56)	426 (4.38)	347 (4.31)
			516 (3.91)	1483 (4.25)	818 (4.42) ^b
R ¹ = (CH ₂) ₃ OH; R ² = NH(CH ₂) ₂ CH ₃	31		342 (4.17)	438 (4.12)	417 (4.19)
			509 (4.09)	1188 (3.66)	915 (3.49)
R ¹ = (CH ₂) ₅ OH; R ² = NH(CH ₂) ₂ CH ₃	32		344 (4.23)	423 (4.03)	367 (3.99)
			514 (4.18)	1184 (3.77)	910 (4.11)
R ¹ = R ² = (CH ₂) ₅ OH	33		345 (4.35)	429 (4.13)	342 (4.07)
			520 (4.31)	1492 (4.12)	818 (4.31) ^b
R ¹ = R ² = NHCH ₂ Ph	34		342 (4.34)	440 (4.19)	392 (4.14)
			502 (4.26)	1162 (3.94)	888 (4.30)
R ¹ = R ² = NHC(CH ₃)(CH ₂ OH) ₂	35		342 (4.38)	448 (4.26)	418 (4.31)
			506 (4.32)	1075 (4.01)	928 (3.52)
R ¹ = R ² = NH(CH ₂) ₅ OH	36		342 (4.40)	437 (4.22)	379 (4.14)
			495 (4.29)	1043 (3.80)	908 (4.27)
R ¹ = R ² = NHCH ₂ Ph-p-NH ₂	37		340 (4.31)	450 (4.12)	385 (4.19)
			502 (4.18)	1115 (3.67)	901 (4.31)
R ¹ = R ² = O(CH ₂) ₂ OH	38		340 (4.30)	444 (4.18)	415 (4.06)
			506 (4.25)	1403 (3.94)	890 (4.11)
R ¹ = R ² = N(CH ₂) ₄ CH ₂ OH	39		362 (4.30)	453 (4.20)	385 (4.13)
			502 (4.16)	1244 (3.85)	904 (4.06)
R ¹ = R ² = N(CH ₂) ₄ CH ₃	40		350 (4.28)	454 (4.19)	386 (4.13)
			506 (4.21)	1192 (3.73)	883 (3.84)
41		372 (4.48)	463 (4.23)	336 (4.18)
			530 (4.38)	1650 (4.17)	637 (3.63)
42		335 (4.30)	410 (4.13)	379 (4.09)
			459 (4.16)	1340 (3.83)	861 (4.01)
43		342 (4.30)	422 (4.09)	342 (4.05)
			488 (4.14)	1578 (4.14)	662 (3.78)
				2500 (3.4) ^c	861 (4.05)

^a λ_{max} in nm (log ε in M⁻¹cm⁻¹);^b this value was estimated based on the slope of the peak on both sides as the Lambda 900 spectrometer does not function between 760 and 860 nm due to mechanical difficulties;^c λ_{max} beyond 2500 nm

Figure 3.3 – Spectroelectrochemistry of **36** and $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ states of **33** and **38**

When semi-biurea and biurea complexes were prepared, excess base was added to compensate for the presence of the extra NH. The expected dinuclear product did form although the yield, after purification, was significantly lower than analogue complexes based on DCH ligands, due to an important formation of a green by-product, **36G**. All attempts to crystallize this green product failed. A single redox wave was observed in its CV, suggesting that it is mononuclear, or perhaps dinuclear with the metal centers far apart, preventing the formation of a mixed valence state. The UV-Vis-NIR of this green compound and corresponding CV (inset) are shown in (Figure 3.4).

Figure 3.4 – Spectroelectrochemistry of **36G** and CV (inset)

Unfortunately, spectroelectrochemistry did not provide additional information as the only change observed is the intensity of the 424 and 794 nm bands. NMR of this green species exhibited a great number of overlapping resonances in both the aromatic and aliphatic regions, suggesting an unsymmetrical dinuclear system, where the ruthenium atoms are not linked through the DCH moiety, or multiple mononuclear isomers (appendix 2). Electrospray ionisation mass spectrometry (ESI-MS) of this complex (Figure 3.5, possible, but unproven structure shown) demonstrated the usual ion patterns as seen in other complexes considered in this study, giving some credibility to the existence of an unsymmetrical dinuclear complex isomer. In addition, the elusive protonated molecular ion was observed ($[M+H]^+$, $m/z = 1405$) as well as the acetonitrile monosolvated specie ($[M+MeCN]^+$, $m/z = 1446$). The fact that there are many ionic

Chapter 3 – Dinuclear ruthenium and platinum complexes

species in the 700-1300 amu range, as opposed to almost none in ‘normal’ complexes (see Figure 3.7 for an example) is yet another puzzle piece pointing towards an unsymmetrical complex. As an effort to find some use for **36G**, its photoluminescence was probed. Excitation at 800 nm did not produce emission in the NIR region. If **36G** is in fact dinuclear, where both ruthenium atoms are chelated differently and are no longer coupled thus behaving as two independent complexes, self-quenching could explain the lack of emission.

Figure 3.5 – ESI-MS of **36G**

The biurea complexes are useful for optical attenuation at the other telecom wavelengths (980 and 1310 nm) but applications may be limited by low yields and the

increasing price of ruthenium(III) chloride. In order to be cost effective, higher yields are needed. Since the exchange reaction requires deprotonation of the hydrazide protons, it seemed likely that the primary amide protons, which can be deprotonated as well, would compete during the complexation reaction.

To validate this hypothesis, biurea analogues, based on piperidines, were prepared using the same azodicarboxylate chemistry used to create secondary amides that are devoid of acidic protons. Indeed, it was found that the amide protons were, at least partially, responsible for the formation of the green complex, since no green species was isolated during the purification of the piperidine complexes. These complexes had similar redox properties as the biureas and had an IVCT centered at 1200 nm. The advantage of a broad absorption makes **39** suitable for the 1310 nm telecommunication band. The $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ state absorption spans past 980 nm, albeit at a lower molar extinction coefficient. Luckily, due to the reduced redox potentials, the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ state is stable enough to be considered for the 980 nm telecommunication band. The yield of **39** was 3 times higher than that of **36** but at 21%, is still quite low. Unfortunately, solving the green complex problem generated another. A third redox wave can be seen, partially overlapping with $^1\text{E}_{1/2}$. The optical properties of the piperidine complex in this form were as expected and it was thought that the ‘impurity’ was a mono-ruthenium specie that did not absorb in the NIR. Mononuclear ruthenium complexes are usually soluble in halogenated solvents such as dichloromethane (DCM), but the diol dinuclear complexes are not. Washing **39** with DCM extracted a brown complex (**39S**, soluble) and left a purple solid behind (**39I**, insoluble). Both were analyzed and surprisingly, both

complexes displayed two redox waves, with the ${}^2E_{1/2}$ overlapping with the other isolated specie (Figure 3.6).

Figure 3.6 – CV of **39S** and **39I**

Spectroelectrochemistry also revealed that both complexes are NIR active; however, the NIR absorption of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ state at 904 nm is not present for **39I**, which is odd, given that the purple complex is usually the ‘expected’ product (Figure 3.7).

Figure 3.7 – Spectroelectrochemistry of **39**, **39S** and **39I**

Crystallography would have unveiled the nature of the two compounds; however, suitable crystals were not obtained. ^1H NMR of **39I** (appendix 1) was well resolved, the only low redox potential complex to be suitable for full resonance assignment, while **39S** was not (appendix 3), proving that **39I** is the expected dinuclear complex even without the usual purple color. The simplified ^1H spectrum of **39I** indicates symmetry and adds additional support that this species is the expected product. Samples of the mixture and both isolated compounds were analyzed by ESI-MS and show the same fragment patterns, with different intensities, again suggesting isomers. Even with a primary amide, there is a competing chelation mode, creating the isomer. It is doubtful that these two complexes are stereoisomers as such compounds are not readily separated by simple chromatography. Since both are NIR active, each ruthenium must be chelated to one atom of the DCH moiety, either O or N. It is feasible that two nitrogens, geminal to a carbonyl carbon could complex the ruthenium but with a four membered ring, the resulting strain would likely promote decomplexation or rearrangement.

Other than CV and spectroelectrochemistry, characterization of the complexes was similar to that of the bridging ligands except for NMR as most complexes, especially the ones having low redox potentials, had an incredibly complex splitting pattern in the aromatic region of both ^1H and ^{13}C experiments which made it impossible to assign resonances. Firstly, unsymmetrical bridging ligands make all four bipyridines unequivalent – that's 32 aromatic protons, just from the bpy moieties. When the ligand is symmetrical, this is halved to 16 signals. Taking advantage of various 2D NMR experiments, the ^1H and ^{13}C resonances of complexes **39I** and **41** have been completely assigned. The reason that the other complexes were not assigned by NMR is that the low redox potential complexes can be oxidized to the mixed valence state by molecular oxygen (especially in solution), albeit at a slow rate, and Ru^{III} is paramagnetic, therefore trace amounts of it is detrimental to NMR data acquisition. Add the potential of stereoisomers, even in regular DCH complexes, and the situation worsens still⁶⁴. The main characterization technique used to analyze the complexes was ESI-MS in positive mode. Since the complex is a salt and therefore positively charged, two main ions, $[\text{M-PF}_6]^+$ and $[\text{M-2PF}_6]^{+2}$ are observed. Ruthenium has seven stable isotopes and the combined isotopic motif of two ruthenium atoms is readily recognizable. Occasionally, the protonated molecular ion is observed but this is rare since the complex is dissolved (Figure 3.8).

Figure 3.8 – ESI-MS of 35

When protonation does occur, it does so at the bridging ligand, destabilizes the complex, forcing the loss of $\text{Ru}(\text{bpy})_2$ and generates another characteristic peak, at $m/z=706$ in the case of 35.

The electrochemical and spectral characteristics of these complexes were considered as complementary techniques to ESI-MS in order to validate the structure of the new dinuclear complexes synthesized.

3.2.2 – Platinum complexes

Platinum complexes of 2-phenylpyridine (ppy) and analogous cyclometallating ligands are well known for their luminescent properties^{155, 158, 160, 161, 181, 184-196}. Three

Chapter 3 – Dinuclear ruthenium and platinum complexes

DCH dinuclear platinum complexes were successfully prepared (Figure 3.9) in high yield using an adapted method based on the ruthenium complex synthesis and the cyclometallated dichlorobridged ppy platinum complex¹⁴⁷. The bridging ligands were chosen to represent electron poor (29) and rich (28) environments as well as a plain aliphatic ligand (16) to serve as a reference point. Unlike bpy, ppy is unsymmetrical and two stereoisomers can be envisaged (cis and trans). However, due to the carbanion generated on the ppy and the negative oxygen of the ligand, same-charge-repulsion should lead to a single isomer. There is also the trans effect that is observed with square planar complexes where certain ligands will tend to promote the formation of trans compounds. The sequence of ligands in increasing order of trans directing effect is: F^- , H_2O , $OH^- < NH_3 < py < Cl^- < Br^- < I^-$, SCN^- , NO_2^- , $SC(NH_2)_2$, $Ph^- < SO_3^{2-} < PR_3$, AsR_3 , SR_2 , $CH_3^- < H^-$, NO , CO , CN^- . While the $C=O$ is trans directing, the two nitrogen chelating sites are cis directing, resulting in both nitrogens being trans to each other. The 1H NMR spectrum of 46 clearly shows the seven aromatic protons on ppy, an indication of symmetry, in addition of aromatics from the bridging ligand (see appendix 1).

Figure 3.9 – Structures of platinum complexes 44-46

ESI-MS of these complexes, being neutral, have different fragmentation patterns than their ionic ruthenium counterparts. The protonated molecular ion is observed as well as acetonitrile mono- and di-solvated species (Figure 3.10). Destabilisation of the complex from the protonation is also observed; however, protonation occurs at the ppy ligand. Proof of this lies in the observed ion corresponding to the $[\text{Pt}(\text{ppy})_2\text{MeCN}]^+$ species. This ion's protonated ppy can be replaced by another acetonitrile molecule, giving the $[\text{Pt}(\text{ppy})(\text{MeCN})_2]^+$ species as seen in Figure 3.9.

Figure 3.10 – ESI-MS of **46**

The photoluminescence (PL) of DCM solutions of the ppy-based complexes, **44** and **45**, when excited at 300 nm, yielded green light (Figure 3.11). This emission results from excitation of the MLCT transition near 400 nm which gives the same PL spectrum when exciting from 250 to 400 nm, except that the PL intensity increases with photon energy. One drawback is that prolong exposure to high energy photons diminishes the intensity of the PL over time, suggesting photodegradation or photobleaching of the complexes. As such, PL studies were performed at a 300 nm excitation wavelength for

optimal signal strength. The complexes should therefore be kept in amber vials, in the dark or both.

Figure 3.11 – Photoluminescence spectra of **44-45** and absorption spectra (inset) of **44-46** (1×10^{-6} M solutions in DCM, not degassed)

One interesting property of these complexes is their ability to produce light in the solid state. Normally, in solution, PL of compounds increases in intensity as the concentration increases; however, at a critical concentration, the intensity begins to fall due to aggregation and the ensuing self-quenching of the excited states¹⁹⁶. This quenching should also be present in solids where energy dissipation through non-radiative pathways can readily occur. The mechanism of self-quenching is thought to proceed by excimer formation between an excited molecule and a ground state molecule and energy transfer to the ground state molecule¹⁹⁵. This self-quenching does not seem to be present in the DCH dinuclear platinum complexes as the amorphous powder is

phosphorescent at room temperature and the same PL features observed in solution are maintained. This could imply that these complexes have high quantum yields. This was investigated for **44** using a comparative method. The reference material should be chosen as such as the absorption and emission of both compounds to be compared have some overlap. Since **44** emits green light, centered at 550 nm, fluorescein, which emits between 500-600 nm and has a quantum yield of 0.79, seemed like a good reference candidate. However, their absorption maxima differs greatly due to the different optical transitions involved. Choosing an excitation wavelength to monitor the PL is problematic. Tris(8-hydroxyquinolato)aluminium (Alq₃), having MLCT optical transitions was deemed a more suitable reference material. Solutions of Alq₃ were prepared in THF while solutions of **44** were in DCM. After searching the literature, the quantum yield of Alq₃ in THF was not found and so only a direct comparison of Φ can be obtained. Linearity must also be maintained for the concentration range considered. The emission was plotted against the absorbance for each compound and the resulting slope or gradient was calculated for both compounds (see appendix 4 for plots). The quantum yield, Φ_X , of the sample to be analyzed, was then calculated using equation 3.4 developed by Williams²⁰²

$$\Phi_X = \Phi_{ST} \left(\frac{Slope_X}{Slope_{ST}} \right) \left(\frac{\eta_{D_X}^2}{\eta_{D_{ST}}^2} \right) \quad \text{Equation 3.4}$$

where Φ_{ST} is the quantum yield of the reference material, and η_D is the refractive index of each solvent used. The calculated quantum yield of **44** was 3 % relative to Alq₃. However, this is only a direct comparison to Alq₃ and a more accurate value of Φ will require the actual quantum yield of Alq₃ in THF. One thing is certain, by assuming that the Φ of Alq₃ is 100 %, the true quantum yield of **44** will be much lower.

Figure 3.12 – ORTEP drawing of 46

Knowing that the dinuclear platinum complexes obtained were indeed chelated by the bridging ligand, their redox properties and ensuing spectral changes were studied. While there is some literature on Pt^{III} complexes^{169, 175, 197-200}, the oxidation state is mostly determined using crystallographic data). The normal oxidation states of platinum are +2 and +4 and oxidation can occur by removal of two valence electrons together or successively. Either way, high redox potentials should be expected due to the combined energy required to remove two valence electrons. Cyclic voltammetry (recorded using the same conditions as described in Table 3.1 except that DCM was used as the solvent) of each complex only displayed one oxidation half wave near 900 mV and an almost unperceivable redox half wave. Both E_{PA} and E_{PC} lose intensity with each consecutive

Chapter 3 – Dinuclear ruthenium and platinum complexes

The effect of the bridging ligand on emission wavelength is quite small, indicating that the orbital energies are not greatly affected. Complex **46** is not phosphorescent, even though the absorbance spectrum showed similar features, albeit redshifted by 70 nm due the nitro groups. The nitro groups quenched any luminescence via dissipation of excitation energies in a non-radiative mechanism, probably by vibrationnal modes. However, **46** did impart valuable structural information as suitable prismatic crystals were obtained by slow diffusion of ethyl ether in a dichloromethane solution of the complex. The ORTEP (Oak Ridge Thermal Ellipsoid Program) drawing of **46** in Figure 3.12 clearly shows the two platinum centers (purple) chelated in the expected dinuclear fashion compared to the ruthenium analogues. A square planar geometry was predicted, however, some deformation is observed due in part to π stacking interactions between neighbouring molecules. The complex takes on a shape that resembles a saddle point where the ppy-Pt-Pt-ppy forms a 'U' shape, while the bridging ligand does the opposite '∩'. The overall appearance is that of an 'X'. The ellipsoids, representing the atoms and their relative positions, are larger for the nitro groups due to their vibrational movement. Bond lengths and angles, along with other pertinent crystallographic data can be found in appendix 5.

cycle (Figure 3.13), suggesting electrodeposition and/or decomposition of the platinum complexes. Unfortunately, it is not clear if this oxidation half wave is the first one-electron oxidation to Pt^{III} or the generation of Pt^{IV} . Kvarn²⁰¹ suggests that electrochemical oxidation of the Pt^{II} state is irreversible due to the rapid solvolysis of Pt^{III} specie generated, effectively degrading the complex. Brooks¹⁴⁷ reported on luminescent platinum complexes having an E_{PC} in the order of -2 V. While we usually focus on the metal redox properties, the ligands can be redox active in the negative potential range and the -2V E_{PC} wave would stem from the cyclometallating ligands employed¹⁹⁵.

Figure 3.13 – CV of **44** in DCM (0.1M TBAH, 200 mV scan rate)

Unfortunately, these dinuclear platinum complexes do not show reversibility in their redox properties; the spectroelectrochemistry was nonetheless verified and as expected, no significant spectral changes were observed. Thermogravimetric analysis (TGA) was performed on complexes **44-46** and it was found that they were quite

thermally stable (Figure 3.14). A 5% weight loss temperature of 306, 338 and 364°C was recorded for **44**, **45** and **46** respectively.

Figure 3.14 – TGA of **44-46**

Undeterred by the lack of electrochromism of the ppy-based platinum complexes and wanting to achieve NIR phosphorescence, we proceeded to study the effect of the peripheral ligand and prepared three new complexes, **47**, **48** and **49** (Figure 3.15). As with ppy, dichlorobridged platinum dimers of each peripheral ligand were prepared using a previously described procedure¹⁴⁷. The DCH ligand, diacetyl hydrazine, was utilized in order to simplify the NMR of the resulting complexes and increase the chances of obtaining crystallographic-grade crystals. These complexes were also characterized by NMR and ESI-MS.

Figure 3.15 – Structure of **47-49** and stereoisomers

Following a simple purification through a silica gel plug, proton NMR of **47** showed multiple methyl groups as well as two doublets near 9.6 ppm. This suggested two isomers and from the peak integration, one isomer is present in 14 % relative to the other. Since isomerization was not observed for ppy-based complexes, it was expected that a single isomer would also form for **47-49**. The product was further purified on preparative chromatography 2 mm plates, using ethyl ether as the eluent. Two phosphorescent fractions were collected at $R_f = 0.3-0.8$ and $R_f = 0$ (R_f = retention factor). It was initially thought that the compound that did not elute was the starting dichlorobridged dimer as the ppy-based dimers hardly eluted on a TLC plate. NMR of the eluted fraction did show an enrichment of one isomer over the other but still, a significant intensity of the second methyl was observed. In fact, recording the ^1H NMR of the same solution of **47** four days later showed an enrichment of the minor isomer. This phenomenon is linked to fluxionality, that is, there is an equilibrium that exists between both isomers, preventing the isolation of one pure isomer. Full resonance assignment of **47** was not achievable.

Chapter 3 – Dinuclear ruthenium and platinum complexes

ESI-MS of both fractions of **47** (Figure 3.16) have the same spectrum, albeit with different intensities due to concentration variations, proving that they are in fact, isomers. It is very strange that one isomer hardly elutes while the other migrates at a higher rate. This dilemma can be explained using dipolar moments: the symmetric isomer of **47** (Figure 3.16) will have a nullified dipolar moment while the unsymmetrical isomer will have a net dipolar moment, increasing its overall polarity, hence the lower R_f . With the 2-phenylquinoline peripheral ligand, being sufficiently bulky to allow isomers to form, it was expected that similar isomers would be observed for both **48** and **49** as well. Surprisingly, the fraction of **48** having an $R_f = 0.3-0.8$, chromatographed using the same conditions as with **47**, did not possess an NMR corresponding to the expected product. However, the fraction at $R_f = 0$ proved to be pure **48**, devoid of a second isomer, which enforces the golden law – never throw out unanalyzed compounds! Using the dipolar moment analogy, the unsymmetrical isomer should have a lower R_f than the symmetrical one. However, the proton NMR signals add up to a symmetrical environment. Perhaps this is due to the extra nitrogen, which increases the overall polarity of the molecule and limits elution.

Figure 3.16 – ESI-MS of isolated fractions of **47**

In the case of **49**, none of the fractions collected showed a clean NMR spectra and it was not possible to determine if the dinuclear complex did in fact form. In addition, preparative chromatography of the crude compound yielded a yellow fraction having an $R_f = 0.85-1.0$ which turned out to be the bare ligand, 2-Methyl-3-phenylbenzo[g]quinoxaline (mpbq), uncomplexed to platinum. Either the isolated dichlorobridged dimer still contained the excess ligand, which was carried over between reactions, or some decomposition occurred during the synthesis of the dinuclear complex. While NMR failed to elucidate the structure of **49**, ESI-MS of both fractions ($R_f = 0.4-0.8$ and $R_f = 0$) confirm the presence of the **49**, although probably two isomers as with **47**.

The absorption spectrum of **47-49** (Figure 3.17) is quite similar to that of ppy series of dinuclear complexes although the MLCT band is highly affected: 430 nm for **47**, 490 nm for **48**, and 540 nm for **49**.

Figure 3.17 – Absorption spectra of **47-49** in DCM (inset: spectra expansion)

The bathochromic effect of the quinoline moiety on emissive properties in **47** was impressive, whereas yellow-orange light was observed (Figure 3.18), using a simple UV light (365 nm) compared to the green emission of **44**, a bathochromic shift of 65 nm. However, in the case of **48**, where the extra heteroatomic nitrogen's donating potential was expected to induce a hypsochromic shift, the opposite effect was observed and a bathochromic shift of 105 nm was induced compared to **44**, 40 nm more than in **47**, resulting in the emission of a deep red color. No visible emission was observed for **49** when exposed to the same UV light source which could implicate NIR emission.

Figure 3.18 – Visible PL of **47-49** (excited at 365 nm)

Since excitation at 365 nm was sufficient to observe a strong emission of the solid state, the PL of **47-48** was also recorded, in DCM, at 360 nm excitation wavelength (Figure 3.19), even though each complex MLCT wavelength differed (Figure 3.17). Higher PL intensities can be achieved by using higher energy photons but the cost is high as the PL diminishes with time, suggesting degradation or photobleaching. The excitation wavelength was scanned from 250-500 nm for PL and as expected, only the intensity varied.

Figure 3.19 – PL spectra of **47-48** in DCM (excited at 360 nm)

Complex **49**, which did not produce visible light in the solid state, emitted intense blue light in DCM. The blue emission at 478 nm is confirmed to belong to a $\pi \rightarrow \pi^*$ transition originating from the peripheral ligand, by comparing it to the PL of the free ligand (mpbq). Some NIR emission beginning at 840 nm can be observed (Figure 3.20) but it is an artefact from the double emission of the ligand emission.

Figure 3.20 – Visible PL of **49** and ligand mpbq (350 nm excitation)

3.3 – Conclusion

A new series of hydroxyl-containing dinuclear ruthenium complexes were prepared and characterized. These will be used in various polymerization schemes, discussed in the next chapter. The redox and optical properties varied with the donor strength of the bridging ligand and this tuneability increases the versatility of the complexes and the possibility of studying their attenuation properties at all three telecommunication wavelengths. Some challenges still remain concerning the biureas such as elucidating the structure of the isomers observed. The thio derivatives could provide a solution to this problem, if hydroxyl groups can be introduced, by using 3,5-

Chapter 3 – Dinuclear ruthenium and platinum complexes

dihydroxybenzoic hydrazide for example or some other diol hydrazide. The thio derivatives were obtained in much higher yields and without impurities as encountered with the biureas. Thiocarbonyls appear to be stronger chelates and promote the formation of the desired dinuclear system.

Dinuclear platinum analogues were successfully prepared and fully characterized, with one structure resolved by x-ray crystallography. Even though they are not redox active and by definition, not electrochromic, they are phosphorescent, emitting visible light, regardless of the nature of the DCH bridging ligand. Varying the peripheral ligand showed potential in obtaining NIR phosphorescence by systematically increasing the conjugate π system, which had a bathochromic effect on luminescence. Red emission was achieved with potential room for improvement since many peripheral ligand systems can be imagined. Broad NIR emission from 900 to 1700 nm was demonstrated for the mpbq peripheral ligand. However, it is not clear how this NIR PL is allowed, especially at a 400 nm excitation wavelength. Nevertheless, this ground work laid out the foundation to study dinuclear DCH platinum complexes as potential NIR light sources. With strong phosphorescence in the solid state, as well as good thermostability, these materials might even demonstrate potential as luminous sources.

3.4 – Experimental

NMR characterization was performed on a Bruker AMX 400 MHz or Advance 300 MHz spectrometer in CDCl_3 , $\text{DMSO}-d_6$ or CD_3CN and is reported in ppm (multiplicity, integration, assignment, coupling constants). Coupling constants are given

Chapter 3 – Dinuclear ruthenium and platinum complexes

in Hertz and multiplicity terms used are: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and combinations such as dd (doublet of doublet). 2D NMR (COSY, HSQC, HMBS and NOESY) experiments were recorded when required. Infrared (IR) spectra were recorded on a Varian Scimitar 1000 series FT-IR spectrometer using an attenuated total reflectance (ATR) accessory or by NaCl plate. Mass spectra of the ligands were acquired at the University of Ottawa Regional Mass Spectrometry Center on a Micromass Quattro LC Electrospray Mass Spectrometer (needle at 3.9-4.1 kV, methanol:MeCN 1:1 used as solvent) and peaks are reported as m/z (ion fragment, % intensity relative to the base peak). Voltammetric-related experiments were conducted on a Bioanalytical Systems BAS-100 potentiostat. Visible absorption spectra were recorded on a Varian Cary 3 spectrometer while UV-Vis-NIR absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer. The OTTLE cell utilized was composed of quartz plates and the WE was a manually fashioned platinum wire linear mesh (see Figure 1.3a), with the RE and CE being silver and platinum wires respectively. Visible PL was obtained using a Shimadzu RF-1501 spectrofluorometer while NIR PL was obtained using a Photon Technology International QuantaMaster UV-Vis-NIR spectrofluorometer. Thermogravimetric analysis (TGA) was performed on a TA Instrument Hi-Res TGA2950 instrument using a 20°C/minute temperature ramp. Ruthenium(III) chloride trihydrate was purchased from Pressure Chemicals Co, potassium tetrachloroplatinate was purchased from TCI America, 2,2'-bipyridine, 2-phenylpyridine, 2-phenylquinoline (pq) and 1-phenyl-1,2-propanedione were obtained from Aldrich Canada. All reagents and solvents were used as received.

General procedure for the synthesis of the dinuclear ruthenium complexes²⁰³

cis-Ru(bpy)₂Cl₂ (1.04g, 2 mmol), prepared according to Sullivan²⁰⁴, bridging ligand (1 mmol), NaOH (0.08g, 2 mmol) and 50 mL of 5:1 H₂O:EtOH are placed in a 100 mL RBF and refluxed under argon for 16 hours. The purple solution was concentrated to half volume using a rotoevaporator and NH₄PF₆ (650 mg, 4 mmol) in 15 mL of water was added to the solution. The resulting precipitate was filtered and air dried. The crude complex was purified by column chromatography on neutral alumina, conditioned with 3% water by weight. The eluent system varied from acetone, acetonitrile, wet acetonitrile or acetonitrile:Toluene, depending on the overall polarity of the complex. The purple fraction was collected, concentrated to dryness and redissolved in a minimum acetone or acetonitrile and precipitated in 500 mL ethyl ether. The fine purple powder was filtered and air dried under vacuum.

In the case where biurea bridging ligands were utilized, an extra equivalent of base was added to compensate for each additional NH present. Prior to the addition of NH₄PF₆, the excess base was neutralized using a 2M HPF₆ solution.

[{Ru(bpy)₂}₂μ-CH₂CH₃, (CH₂)₃OH-dicarbonyl hydrazine](PF₆)₂ (**30**). Yield: 74 %. ESI-MS: 1143 ([M-PF₆]⁺, 1.0 %), 587 ([M-Ru(bpy)₂-2PF₆]⁺, 5.7) and 500 ([M-2PF₆]²⁺, 100).

[{Ru(bpy)₂}₂μ-NH(CH₂)₂CH₃, (CH₂)₃OH-dicarbonyl hydrazine](PF₆)₂ (**31**). Yield: 58 %. ESI-MS: 1202 ([M-PF₆]⁺, 0.7 %), 1055 ([M+H-2PF₆]⁺, 0.2), 643 ([M-Ru(bpy)₂-2PF₆]⁺, 0.1) and 528 ([M-2PF₆]²⁺, 100).

$[\{Ru(bpy)_2\}_2\mu-NH(CH_2)_2CH_3, (CH_2)_5OH\text{-dicarbonyl hydrazine}](PF_6)_2$ (**32**). Yield: 62 %. ESI-MS: 1174 ($[M-PF_6]^+$, 0.8 %), 1028 ($[M+H-2PF_6]^+$, 0.1), 615 ($[M-Ru(bpy)_2-2PF_6]^+$, <0.1) and 514 ($[M-2PF_6]^{2+}$, 100).

$[\{Ru(bpy)_2\}_2\mu-((CH_2)_5OH)_2\text{-dicarbonyl hydrazine}](PF_6)_2$ (**33**). Yield: 80 %. ESI-MS: 1231 ($[M-PF_6]^+$, 2.3 %), 673 ($[M-Ru(bpy)_2-2PF_6]^+$, 1.5) and 544 ($[M-2PF_6]^{2+}$, 100).

$[\{Ru(bpy)_2\}_2\mu-(NHCH_2Ph)_2\text{-dicarbonyl hydrazine}](PF_6)_2$ (**34**). Yield: 16 %. ESI-MS: 1414 (M^+ , <0.1 %), 1269 ($[M-PF_6]^+$, 0.9), 1123 ($[M+H-2PF_6]^+$, 0.4), 710 ($[M-Ru(bpy)_2-2PF_6]^+$, 0.2) and 562 ($[M-2PF_6]^{2+}$, 100).

$[\{Ru(bpy)_2\}_2\mu-(NHC(CH_3)(CH_2OH)_2)\text{-dicarbonyl hydrazine}](PF_6)_2$ (**35**). Yield: 65 %. ESI-MS: 1411 (M^+ , <0.1 %), 1265 ($[M-PF_6]^+$, 0.9), 706 ($[M-Ru(bpy)_2-2PF_6]^+$, 0.2) and 560 ($[M-2PF_6]^{2+}$, 24).

$[\{Ru(bpy)_2\}_2\mu-(NH(CH_2)_5OH)_2\text{-dicarbonyl hydrazine}](PF_6)_2$ (**36**). Yield: 6 %. ESI-MS: 1406 (M^+ , <0.1 %), 1261 ($[M-PF_6]^+$, 1.1) and 558 ($[M-2PF_6]^{2+}$, 25).

$[\{Ru(bpy)_2\}_2\mu-(NHCH_2Ph\text{-}p\text{-}NH_2)_2\text{-dicarbonyl hydrazine}](PF_6)_2$ (**37**). Yield: 7 %. ESI-MS: 1299 ($[M-PF_6]^+$, 1.0 %), 1198 ($[M+H-2PF_6]^+$, 0.4) and 577 ($[M-2PF_6]^{2+}$, 57).

Chapter 3 – Dinuclear ruthenium and platinum complexes

[{Ru(bpy)}₂]₂μ-(O(CH₂)₂OH)₂-dicarbonyl hydrazine](PF₆)₂ (38). Yield: 19 %. ESI-MS: 1178 ([M-PF₆]⁺, 1.6 %), 715 ([M+MeCN+3H₂O-Ru(bpy)₂-2PF₆]⁺, 0.4) and 517 ([M-2PF₆]²⁺, 29).

[{Ru(bpy)}₂]₂μ-(4-hydroxymethyl piperidine)₂-dicarbonyl hydrazine](PF₆)₂ (39). Yield: 21 %. ¹H NMR (300MHz, CD₃CN): 9.07 (d, 2H, H6, ³J = 5Hz); 8.71 (d, 2H, H15, ³J = 5Hz); 8.50 (d, 2H, H9, ³J = 8Hz); 8.35 (d, 2H, H12, ³J = 5Hz); 8.32 (d, 2H, H22, ³J = 5Hz); 8.26 (d, 2H, H19, ³J = 8Hz); 8.16 (dd, 2H, H24, ³J = 8Hz); 7.96 (dd, 2H, H13, ³J = 8Hz); 7.91 (dd, 2H, H7, ³J = 8Hz); 7.80 (d, 2H, H25, ³J = 5Hz); 7.76 (dd, 2H, H18, ³J = 8Hz); 7.68 (dd, 2H, H23, ³J = 8Hz); 7.45 (dd, 2H, H14, ³J = 5Hz); 7.39 (dd, 2H, H16, ³J = 5Hz); 7.10 (dd, 2H, H17, ³J = 8Hz); 7.04 (dd, 2H, H24, ³J = 8Hz); 2.91 (dd, 4H, H5, ³J = 6Hz); 2.49 (d, 2H, H2a', ³J = 10Hz); 2.32 (t, 2H, OH, ³J = 6Hz); 2.03 (dd, 2H, H2b', ³J = 11Hz); 1.60 (dd, 2H, H2a, ³J = 11Hz); 1.37 (d, 2H, H2b, ³J = 10Hz); 0.99 (d, 2H, H3b, ³J = 12Hz); 0.87 (s, 4H, H3b' and H4), -0.02 (ddd, 2H, H3a, ³J = 10Hz) and -0.44 (ddd, 2H, H3a', ³J = 10Hz). ¹³C NMR (75MHz, CD₃CN): 177.3 (C1); 160.3 (C21); 159.7 (C10); 159.5 (C20); 159.0 (C11); 153.9 (C25); 152.6 (C15); 152.3 (C16); 151.1 (C6); 136.8 (C13); 136.6 (C8); 136.3 (C18); 134.8 (C23); 127.1 (C7); 127.0 (C14); 126.7 (C17); 126.4 (C24); 124.4 (C22); 124.0 (C12); 123.9 (C9); 123.8 (C19); 67.4 (C5); 51.0 (C2'); 50.8 (C2); 38.3 (C4) and 27.8 (C3). ESI-MS: 1285 ([M-PF₆]⁺, 0.9 %), 726 ([M-Ru(bpy)₂-2PF₆]⁺, 0.3) and 570 ([M-2PF₆]²⁺, 100).

[{Ru(bpy)}₂]₂μ-(4-methyl piperidine)₂-dicarbonyl hydrazine](PF₆)₂ (40). Yield: 56 %. ESI-MS: 1253 ([M-PF₆]⁺, 6.8 %), 1107 ([M+H-2PF₆]⁺, 0.4), 694 ([M-Ru(bpy)₂-2PF₆]⁺, 4.4) and 554 ([M-2PF₆]²⁺, 91).

$[\{ Ru(bpy)_2 \}_2 \mu - ((CH_2)_5OH)_2\text{-oxamide}] (PF_6)_2$ (41). Yield: 43 %. 1H NMR (300MHz, CD_3CN): 8.98 (d, 1H, H26, $^3J = 5Hz$); 8.94 (d, 1H, H7, $^3J = 5Hz$); 8.47 (d, 1H, H23, $^3J = 8Hz$); 8.41 (d, 1H, H10, $^3J = 8Hz$); 8.32 (d, 1H, H20, $^3J = 6Hz$); 8.30 (d, 1H, H13, $^3J = 4Hz$); 8.10 (ddd, 1H, H24, $^3J = 6Hz$, $^4J = 1Hz$); 8.06 (ddd, 1H, H9, $^3J = 7Hz$, $^4J = 1Hz$); 7.89 (d, 1H, H17, $^3J = 6Hz$); 7.88, 7.79 (m, 2H, H8 and H25); 7.79 (ddd, 1H, H14, $^3J = 8Hz$, $^4J = 1Hz$); 7.73 (ddd, 1H, H19, $^3J = 8Hz$, $^4J = 1Hz$); 7.43 (d, 1H, H16, $^3J = 5Hz$); 7.16 (ddd, 1H, H15, $^3J = 7Hz$, $^3J = 6Hz$, $^4J = 1Hz$); 7.11 (ddd, 1H, H18, $^3J = 7Hz$, $^3J = 6Hz$, $^4J = 1Hz$); 3.49 (m, 1H, H2); 2.88 (s, 2H, H6); 2.27 (m, 1H, H2'); 0.65 (tt, 2H, H5, $^3J = 7Hz$); 0.35 (m, 1H, H3), 0.13 (m, 1H, H4), 0.04 (m, 1H, H3') and -0.01 (m, 1H, H4'). ^{13}C NMR (75MHz, CD_3CN): 172.7 (C1); 160.4 (C21); 159.6 (C12); 159.2 (C11); 158.9 (C22); 154.2 (C17); 153.2 (C7); 152.4 (C16); 151.4 (C26); 136.8 (C9); 136.4 (C14); 136.1 (C24); 135.1 (C19); 127.7, 127.4 (C8 and C25); 127.0 (C15 and C18); 124.2 (C20); 124.0 (C10, C13 and C23); 62.0 (C6); 47.6 (C2); 33.0 (C5); 29.9 (C3) and 23.1 (C4). ESI-MS: 1231 ($[M-PF_6]^+$, 2.5 %), 1085 ($[M+H-2PF_6]^+$, 0.1), 673 ($[M-Ru(bpy)_2-2PF_6]^+$, 3.1) and 543 ($[M-2PF_6]^{2+}$, 100).

$[\{ Ru(bpy)_2 \}_2 \mu - (NH(CH_2)_3CH_3)_2\text{-dithiocarbonyl hydrazine}] (PF_6)_2$ (42). Yield: 81 %. ESI-MS: 1233 ($[M-PF_6]^+$, 1.7 %), 1088 ($[M+H-2PF_6]^+$, 0.4), 472 (34), 414 (17), 367 (53), 330 (75) and 290 (36).

Chapter 3 – Dinuclear ruthenium and platinum complexes

$[\{Ru(bpy)_2\}_2\mu-NH(CH_2)_3CH_3, Ph-thiocarbonylcarbony-hydrazine](PF_6)_2$ (43). Yield: 91 %. ESI-MS: 1221 ($[M-PF_6]^+$, 2.5 %), 1076 ($[M+H-2PF_6]^+$, 0.8), 664 ($[M-Ru(bpy)_2-2PF_6]^+$, 0.5), 495 (8.1), 454 (5.4), 433 (9.6), 413 (10), 391 (69), 373 (39) and 359 (26).

General procedure for the synthesis of the peripheral ligands¹³⁰

o-Phenylene diamine (0.22 g, 2 mmol) and 1-phenyl-1,2-propanedione (0.29 g, 2 mmol) were dissolved in 1 mL of MeCN. I_2 (0.01 g, 10% mol) was added to the stirring solution. An exotherm was observed and the mixture turns dark orange. The stirring was maintained for 15 minutes. The crude mixture was filtered through a small plug of silica gel and an orange fraction was eluted using MeCN. The solvent was rotoevaporated and an orange solid was obtained. Yield: 95 %. NMR and ESI-MS agree with literature data¹³⁰.

General procedure for the synthesis of dichlorobridged platinum dimers¹⁴⁷

Potassium tetrachloroplatinate (0.4g, mmol) and 2-phenylpyridine (0.38g, mmol) were heated to 80°C in 80 mL of 3:1 methoxyethanol:deionized water, under argon for 16 hours. The lime green mixture was cooled to room temperature, poured in 160 mL of deionized water and kept in a refrigerator for 3 hours. The solid was filtered, air dried, dissolved in DCM and filtered through a small plug of silica gel to remove metallic platinum that may have formed. When the dichlorobridged platinum dimer of mpbq was prepared, the aqueous filtrate was still orange and slightly opaque. Solids eventually began to form after three weeks, which were recovered and worked up as described above. The products were used, as-is, in the preparation of dinuclear platinum complexes.

General procedure for the synthesis of dinuclear platinum complexes¹⁴⁷

2-Phenylpyridine dichlorobridged platinum dimer (0.1 g, 0.13 mmol) dissolved in 5 mL 4:1 methoxyethanol:deionized water was added to a solution of **16** (0.037 g, 0.13 mmol) and Na₂CO₃ (0.35 mL of 1M solution) in 5 mL of 4:1 methoxyethanol:deionized water contained in a modified 10 cm test tube (size 14 ground joint added). The mixture was heated to 80°C for 4 hours (or until no further precipitate forms; overnight for **45** and **46**) under argon.

The workup from this point could be done in two ways: the ppy-based complex precipitates were simply filtered, washed with fresh solvent (4:1 methoxyethanol:deionized water) followed by deionized water and air dried; or, in the case of the larger peripheral ligands, the solvent was completely removed under vacuum. Regardless of the method employed, the resulting solids were dissolved in DCM and filtered through a small silica gel column (DCM as eluent). This gave a satisfactory purity level for the ppy complexes; however, this was not the case with **47-49**. These were purified by preparative chromatography on 20 x 20 x 0.02 cm silica gel plates using ethyl ether for **47-48** and 2:1 ethyl ether:DCM for **49**. The phosphorescent fractions were isolated in each case (scraping the silica with a razor blade, grounding it into a powder, packing it in a small column and eluting the complex using ethyl ether, chloroform or a mixture of both). ¹H NMR and ESI-MS assisted in identifying the fraction containing the desired product.

[{Pt(ppy)}₂]₂μ-(heptyl)₂-dicarbonyl hydrazine] (44). Yield: 72 %. ¹H NMR (300 MHz, CDCl₃): 9.01 (d, 2H, H₉, ³J = 5Hz); 7.86 (dd, 2H, H₁₁, ³J = 7Hz); 7.67 (d, 2H, H₁₂, ³J = 8Hz); 7.48 (dd, 2H, H₁₆, ³J = 5Hz); 7.46 (dd, 2H, H₁₇, ³J = 5Hz); 7.14 (dd, 2H, H₁₀, ³J = 6Hz); 7.10 (d, 2H, H₁₅, ³J = 4Hz); 7.08 (d, 2H, H₁₈, ³J = 4Hz); 2.98 (t, 4H, H₂, ³J = 8Hz); 1.85 (s, 4H, H₃); 1.30 (s, 8H, H₅ and H₆); 1.25 (s, 8H, H₄ and H₇) and 0.84 (t, 6H, H₈, ³J = 6Hz). ¹³C NMR (75 MHz, CDCl₃): 178.2 (C₁); 166.7 (C₁₃); 148.7 (C₉); 145.0 (C₁₄); 140.1 (C₁₉); 138.1 (C₁₁); 136.7 (C₁₆); 129.9 (C₁₅); 123.1 (C₁₇); 122.9 (C₁₈); 121.7 (C₁₀); 118.3 (C₁₂); 34.3 (C₂); 31.8 (C₃); 29.1 (C₅ and C₆); 27.4 (C₃); 22.7 (C₇) and 14.1 (C₈). ESI-MS: 981 ([M+H]⁺, 0.01 %), 432 ([Pt(ppy)(MeCN)₂]⁺, 0.05), 214 ([Pt(Hppy)(MeCN)₂]⁺, 1.4) and 156 (Hppy, 1.0).

[{Pt(ppy)}₂]₂μ-(4-methoxyphenyl)₂-dicarbonyl hydrazine] (45). Yield: 70 %. ¹H NMR (300 MHz, CDCl₃): 9.23 (d, 2H, H₇, ³J = 5Hz); 8.52 (d, 4H, H₃, ³J = 9Hz); 7.64 (dd, 2H, H₉, ³J = 8Hz); 7.63 (d, 2H, H₁₀, ³J = 8Hz); 7.29 (d, 2H, H₁₃, ³J = 8Hz); 7.18 (dd, 2H, H₈, ³J = 5Hz); 6.82 (dd, 2H, H₁₄, ³J = 7Hz); 6.72 (d, 4H, H₄, ³J = 9Hz); 6.51 (dd, 2H, H₁₅, ³J = 7Hz); 6.40 (d, 2H, H₁₆, ³J = 7Hz) and 3.73 (s, 6H, H₆). ¹³C NMR (75 MHz, CDCl₃): 173.3 (C₁); 167.1 (C₁₁); 162.0 (C₅); 148.7 (C₇); 143.7 (C₁₂); 138.0 (C₉); 136.0 (C₁₆); 133.3 (C₃); 132.3 (C₁₇); 128.5 (C₁₅); 125.7 (C₂); 122.2 (C₁₃); 121.9 (C₁₄); 121.4 (C₈); 118.3 (C₁₀); 112.5 (C₄) and 55.4 (C₆). ESI-MS: 1089 ([M+H+MeCN+MeOH]⁺, 0.01 %), 648 ([M+H-Pt(ppy)]⁺, 0.03), 432 ([Pt(ppy)(MeCN)₂]⁺, 0.3), 214 ([Pt(Hppy)(MeCN)₂]⁺, 5.2) and 156 (ppy, 1.4).

[{Pt(ppy)}₂]₂μ-(4-nitrophenyl)₂-dicarbonyl hydrazine] (46). Yield: 67 %. ¹H NMR (300 MHz, CDCl₃): 9.13 (d, 2H, H6, ³J = 5Hz); 8.75 (d, 4H, H3, ³J = 9Hz); 8.05 (d, 4H, H4, ³J = 9Hz); 7.94 (ddd, 2H, H8, ³J = 8Hz, ⁴J = 1.2Hz); 7.68 (d, 2H, H9, ³J = 8Hz); 7.31 (d, 2H, H12, ³J = 8Hz); 7.25 (dd, 2H, H7, ³J = 6Hz); 6.81 (dd, 2H, H13, ³J = 7Hz); 6.45 (ddd, 2H, H14, ³J = 7Hz, ⁴J = 1.2Hz) and 6.28 (s, 2H, H15). ¹³C NMR (75 MHz, CDCl₃): 172.3 (C1); 166.9 (C10); 149.1 (C5); 148.7 (C6); 143.8 (C11); 139.2 (C2); 138.7 (C8); 137.5 (C16); 135.4 (C15); 132.6 (C3); 128.4 (C14); 122.8 (C12 and C13); 122.2 (C4); 121.8 (C7) and 118.6 (C9). ESI-MS: 1105 ([M+H+2MeCN]⁺, 0.04 %), 1068 ([M+H+MeCN]⁺, 0.04), 1027 ([M+H]⁺, 0.04), 545 ([Pt(ppy)₂+H+MeCN]⁺, 0.4), 431 ([Pt(ppy)(MeCN)₂]⁺, 3.2), 214 ([Pt(ppy)(MeCN)₂+H]²⁺, 14) and 156 (ppy, 7.8).

[{Pt(2-Phenyl-quinoline)}₂]₂μ-(methyl)₂-dicarbonyl hydrazine] (47). Crude yield: 58 %. ESI-MS: 996 ([M+H+DCM]⁺, 0.1 %), 953 ([M+H+MeCN]⁺, 0.3), 928 ([M+H+MeCN-CH₃]⁺, 0.2), 913 ([M+H]⁺, 0.2), 645 ([Pt(pq)₂+H+MeCN], 0.1), 482 (0.9) and 214 (18).

[{Pt(2-Methyl-3-phenyl-quinoxaline)}₂]₂μ-(methyl)₂-dicarbonyl hydrazine] (48). Yield: 28 %. ¹H NMR (300 MHz, CDCl₃): 9.56 (d, 2H, H4, ³J = 9Hz); 8.05 (d, 2H, H7, ³J = 8Hz); 8.00 (dd, 2H, H12, ³J = 7Hz, ⁴J = 2Hz); 7.88 (ddd, 2H, H5, ³J = 9Hz, ³J = 7Hz, ⁴J = 2Hz); 7.79 (d, 2H, H15, ³J = 7Hz); 7.77 (dd, 2H, H6, ³J = 7Hz); 7.20 (m, 4H, H13 and H14); 3.14 (s, 6H, H2) and 2.66 (s, 6H, H17). ¹³C NMR (75 MHz, CDCl₃): 176.0 (C1); 161.3 (C10); 151.6 (C9); 144.9 (C11); 142.4 (C16); 141.2 (C3 and C8); 136.6 (C15); 131.0 (C5); 130.0 (C6); 129.8 (C13); 128.2 (C7); 128.0 (C12); 126.4 (C4); 123.4 (C14);

27.1 (C2) and 23.3 (C17). ESI-MS: 1076 ($[M+H+MeCN]^+$, <0.1 %), 994 (<0.1), 943 ($[M+H]^+$, 0.1), 675 (0.1), 496 (0.3); 265 (1.2) and 214 (97).

[{Pt(2-Methyl-3-phenyl-benzo[g]quinoxaline)₂}₂μ-(methyl)₂-dicarbonyl hydrazine] (49).

Crude yield: 38 %. ESI-MS: 1082 ($[M+H+MeCN]^+$, <0.1 %), 1044 ($[M+H]^+$, <0.1), 775 (0.4), 542 (0.1), 454 (1.7); 271 (22) and 214 (73).

Quantum yield determination procedure

Solutions of the reference material (Alq₃) and **44** were prepared at concentrations that gave a satisfactory linear absorbance (high correlation coefficients). The solution concentrations used were 0.004 mM, 0.006 mM, 0.008 mM, 0.01 mM and 0.015 mM. The excitation wavelength was set to 494 nm. The phosphorescence was measured for each solution and it was plotted against the absorbance data. The slopes of the linear curves were obtained and used in equation 3.4 (see appendix 4 for plots). The quantum yield was 3 % by comparison to Alq₃.

Chapter 4 – Macromolecular materials of ruthenium complexes

4.1 – Introduction

Once a suitable electrochrome is designed and characterized, it is preferable to study its properties in solid form since devices based on solids tend to have a longer duty lifetime instead of encapsulated liquid-based design. While many techniques can be used to create homogeneous thin films on a substrate, casting, dip-coating and spin-coating are usually employed as they are readily accessible. Other techniques include screen printing and R_f sputtering that require more elaborate instrumentation and stringent work conditions. Normally small molecules tend to create films of poor quality and usually require mixing into an inert polymeric matrix (doping). Since the dopant is not chemically bound to the matrix, aggregation can occur during and after solvent evaporation, where the dopant(s) still retains some mobility, creating heterogenous areas within the film. Another issue is the potential leaching of the dopant.

Incorporating the electrochromic moiety into a polymeric system through chemical bonding is a more reasonable choice since the gain in molecular weight and viscosity will result in better film forming ability. Also, leaching and aggregation will be avoided since the electrochrome can neither be moved nor removed. The easiest method to incorporate the ruthenium complex electrochrome into a polymer network is to prepare a polymer ligand followed by complexation. This method has been explored within our group previously. However, the monomeric diacyl hydrazides, oxamides and biureas all possess limited solubility, even in very polar solvents and the resulting polymers would

also inherit this property and only oligomers would be obtained instead of high molecular weight polymers. Unfortunately, the complexation step of even oligomers can be problematic – will each and every ligand site host be fully complexed? This situation can be avoided altogether by polymerizing purified functionalized complexes thus ensuring that all ligand sites are complexed, and controlling the electrochrome content with a higher degree of certainty. Many polymeric systems were explored during this project and a very brief description of each is given below.

Linear polymers, the simplest polymers, are prepared by the reaction of difunctionalized monomers. This can be achieved by the reaction of an AB monomer containing both functional groups or by two monomers, AA and BB. Factors to consider are regioregularity and connectivity of the resulting polymer as unsymmetrical monomers can undergo head-to-head, head-to-tail or tail-to-tail polymerization which affects the physical properties of the material²⁰⁵. The AB monomers, sometimes more difficult to prepare, are another route in obtaining regioregular polymers. Most AA + BB polymerizations are of the condensation type, where the molecular weight obtained is highly dependant on the ratio of monomers utilized, which must be 1:1, otherwise, the excess of one monomer will cause chain termination, limiting the molecular weight²⁰⁵.

Another class of polymers is hyperbranched polymers which are formed when an A₃ monomer reacts with a BB monomer, resulting in randomly branched macromolecules. Reaction time and temperature are key parameters to control in order to avoid insoluble matter which cannot be processed into films.

Other types of polymers include dendrimers, which are tree-like molecules, similar to hyperbranched polymers with the exception that they are grown in orderly

fashion, created from dendrons (such as AB_2 monomers), branching out symmetrically and forming globular networks (Figure 4.1). Two synthetic approaches are recognized: the divergent method, where the molecule is grown from the inside-out and conversely the convergent method²⁰⁶. The divergent method can be more problematic when a multifunctionalized core reacts with a dendron, creating the first level of branching or first generation dendrimer (G1). If a trifunctionalized core is employed, the reaction must be performed at three sites and multiple products are often observed; this is even more troublesome as the generation increases since more reactive sites are added to the dendritic core. Fortunately, this can be simplified through the convergent method, where the terminal groups are formed first, leaving a single free group (R_2B) that can be attached to a compatible A_2D dendron (where D is a protected form of B) to increase the dendron generation, repeating at will to achieve the desired G-n dendrimer.

Figure 4.1 – Dendrimer depiction showing generation levels (C = core)

Hydrogels, as the name implies, are water-soaked hyperbranched polymers which can be obtained by polymerization of acrylate and diacrylate (crosslinker) monomers in water. The resulting 'wet' solid acts as a water permeable membrane and is ubiquitously employed by biochemists for chromatography of proteins, DNA and other large molecular weight biomolecules.

Finally, sol-gels are high surface area, porous solids and tend to form good quality films. Silica sol-gels, for example, are produced by base hydrolysis of tetra-alkoxysilanes, which condense into a polymeric network and dry into solid films. Surfactants are often added to the reaction mix to minimize shrinking and cracking.

4.2 – Results and discussion

4.2.1 – Dendrimers

AB₂ monomers, also called dendrons, were devised to incorporate the DCH moiety. The first target dendron was a diester hydroxyl ligand (**50**) which was readily prepared by condensing dimethyl 5-(chlorocarbonyl)isophthalate to 6-hydroxyhexanoic hydrazide. The free OH group could then be coupled to an aromatic core, creating a simple G1 dendrimer. Previous members of our group had already achieved this generation level. Hydrazinolysis of **50** and subsequent condensation with an acid chloride should yield **51**, a G2 dendron (Figure 4.2). However, the nucleophilicity of hydrazine was underestimated and while hydrazinolysis of both esters was achieved, hydrazinolysis of the DCH moiety also occurred, forming the tri-hydrazide **52** and the starting 6-hydroxyhexanoic hydrazide. It was conceded that any other synthetic route requiring

hydrazinolysis would not allow access to higher generation dendrimers than G1 and thus a different approach was required.

Figure 4.2 – G2 dendron **51** reaction scheme

Next, a synthetic route based on Suzuki coupling was explored. Isophthalic acid was selectively brominated at the 5 position using silver sulfate and bromine in concentrated sulfuric acid, as described by Rau²⁰⁷ (Figure 4.3). The acid chloride was then prepared and reacted with benzoic hydrazide, generating the G1 dendron **53**. The boronic acid **55**, prepared in 3 steps starting with 4-bromotoluene, was reacted with **52** to obtain a G1 dendrimer core **56**. Suzuki coupling of **53** to **56** was attempted, but the G2 dendrimer **57** (Figure 4.3) was not obtained, as evidenced by ESI-MS analysis. It was thought that the free DCH ligand moieties were poisoning or inhibiting the catalyst and so the ruthenium complexes of both **53** and **56** were prepared to repeat the coupling (Figure 4.4).

Figure 4.3 – G2 dendrimer **57** pathway via Suzuki coupling

It was thought unlikely that steric hindrance due to the $\text{Ru}(\text{bpy})_2$ moieties was responsible in preventing the coupling to occur; however, molecular modeling of the complex showed π stacking from two nearby bpy with the bromophenyl moiety as well as two other bpy covering the two other sides, effectively guarding the C-Br moiety against any approaching molecule (Figure 4.4), especially the bulky catalyst, $\text{Pd}(\text{PPh}_3)_4$.

Figure 4.4 – Stick (top) and 3-D model (bottom) of ruthenium complex of **53** (hydrogens omitted for clarity)

Since G2 dendrimers seemed so elusive and G1 dendrimers containing six ruthenium atoms had already been synthesized, routes to make larger G1 dendrimers were explored. After consulting the literature, it was found that the double Micheal addition of acrylates to primary aliphatic amines was an elegant method for creating branched esters. 1,2-diaminobutane was added to excess methyl acrylate and the resulting tetra ester was subjected to hydrazinolysis to obtain a tetra hydrazide²⁰⁸ which could be capped with any acid chloride to give a tetra DCH dendridic ligand (Figure 4.5). Cinnamyl chloride was chosen for its ability to cyclize with other nearby cinnamyl

groups when irradiated with UV^{209, 210}. Through this effort, the dendrimer ligand **58** was successfully prepared, as well as the octanuclear ruthenium complex **59**, which was confirmed by ESI-MS (m/z peaks arising from the successive removal of 8 PF₆ counterions). CV and spectroelectrochemistry also confirm that **59** was obtained (Figure 4.6). Good quality films were obtained by spin coating and these were subjected to UV curing at 250 nm, based on a method by Ito²⁰⁹. IR of the film was taken after each irradiation period to monitor the intensity of the conjugated C=C band and to determine the reaction endpoint. According to the procedure, cyclizing should be complete after a few minutes but even after 15 minutes of irradiation, no crosslinking was observed. It would appear that the bpy moieties, outnumbering the cinnamyl groups four to one, are absorbing the bulk of the energy and even at slow rates of cyclization, that no change was observed in the IR spectrum. Given the globular nature of the complex, the cinnamyl groups are perhaps too far apart to react, or masked by the bpy. It is also likely that the bpy moieties, which outnumber the cinnamyl groups 4-to-1, would absorb the bulk of the available photons, preventing the curing to proceed. This could be overcome by using a photoinitiator or a thermal initiator such as AIBN or APS to initiate the crosslinking.

Figure 4.5 – Tetra DCH G1 dendrimer synthesis

Figure 4.6 – Spectroelectrochemical properties of **59** (CV in inset)

4.2.2 – Linear polymers

Using the newly prepared hydroxyl-containing complexes, linear polymers were then considered. To avoid steric hindrance issues from the bpys as encountered in the previous section, the longest ligands (C_5 chain) were chosen. Using a diacid chloride (AA), such as adipoyl chloride or terephthaloyl chloride, equimolar amounts of diol complex (BB) and triethylamine were reacted in a small testtube using distilled MeCN under inert atmosphere to obtain polyesters (Figure 4.7). The reaction was quenched after 12 hours of stirring at room temperature, despite the low viscosity appearance (a sign of a low molecular weight polymer). The product was then precipitated in ethyl ether. IR of the resulting crude complex did show a new C=O ester peak, but its intensity was only a fifth of the O-C=N band of the complex, confirming that either only a mixture of

oligomers or a low molecular weight polymer and monomer was obtained. Repeating the reaction at higher temperatures did not improve the quality of the product.

Figure 4.7 – Polyester and polyurethane synthesis (bpy omitted for clarity)

An investigation of polyurethanes (Figure 4.7) was also attempted using the same procedure without the use of a base and exchanging the diacid chloride for hexamethylenediisocyanate (HMDI). This time, an increase in viscosity was observed. Pouring the reaction mixture into MeOH did not produce a precipitate, suggesting that the molecular weight, while higher than that obtained via ester methodology, is still too low for practical use in devices.

Monomer ratio control is thought to be the main reason that high molecular weights were not achieved. Condensation polymerization requires a perfect 1:1 ratio in order to obtain high molecular weight. For example, if one monomer is only 95% pure, the theoretical repeat unit in the average polymer chain is 20. The diol complex has a molecular weight in the 1200-1400 g/mol range and are, as is the case with most research materials, precious. The reaction was thus performed on a 100 mg scale of the complex, which translates to less than 0.1 mmol. The other monomers (acid chloride or isocyanate)

have a much lower molecular weight and accurately adding both reagents in equimolar amounts is challenging on its own. This issue is further compounded by trace humidity that consumes some of the monomer. This is more problematic with polyesters since formation of carboxylic acid, through reaction with water, will terminate the chain, preventing further growth on one end. With isocyanates, the hydrolysis product is an amine, which can still react with another isocyanate, ensuring the chain growth. The only problem is that irregularities are introduced which create areas of lower electrochromic ruthenium density.

One possible solution to the molecular weight difference is to create an AB monomer. Following the synthetic approach depicted in Figure 4.2, hydroxyacid complex **60** was prepared (Figure 4.8). *In-situ* polymerization via acid chloride generation seemed like an attractive method for polymerization, but it was eliminated due to the competing chlorination of the OH group by thionyl chloride²¹¹.

Figure 4.8 – Hydroxyacid complex synthesis

To polymerize **60**, 1,1'-carbonyldiimidazole (CDI) assisted esterification was considered. The CDI activates the carboxylic acid by the formation of an initial ester which is readily displaced by weaker nucleophilic species. Dicyclohexylcarbodiimide (DCC), and p-toluenesulfonic acid catalyzed esterification are other methods. Water was removed from the reaction medium via freshly activated molecular sieves or by a Dean-

Stark trap. Even with all these refinements, high molecular weight was not achieved, regardless of the conditions utilized.

Recent dendrimer advances by Fréchet used the triazole moiety to prepare high generation dendrimers. The reaction is clean, requiring only an azide, a terminal acetylene and a copper(I) catalyst, generated from CuSO_4 and sodium ascorbate (Figure 4.9). Utilizing propargyl amine, the diacetylene oxamide ligand **61** was prepared readily and α,α' -p-xylene diazide was easily obtained from the dichloro precursor²¹². The polymerization was performed on the bare ligand to assess its potential. Some methanol-insoluble solid was obtained following workup and NMR did confirm the triazole moiety. NMR also showed that the reaction, as expected, is not regioregular as the acetylene can be turned 180° and still react with the azide, although there is surely a degree of steric control.

Figure 4.9 – Ligand **61** and triazole ‘click’ chemistry (showing possible isomers)

The complexation reaction on ligand **61** did not produce the expected dinuclear complex **62**. ESI-MS did not show the expected peaks (Figure 4.10), which should have been at 1279 (M^+), 1134 ($[\text{M-PF}_6]^+$) and 495 ($[\text{M-2PF}_6]^{+2}$). Instead, a m/z peak at 1670 is observed, 391 amu higher than the expected molecular ion. After consulting the

literature, it was found in a few papers that non-terminated acetylenes, deprotonated by base, can also complex to ruthenium^{213, 214}, which could be competing with the oxamide site, preventing the formation of the desired dinuclear complex. However, a molecular species corresponding to the 1670 peak could not be deduced. Peaks at 1836, 1693 and 774 m/z would be observed if a third ruthenium atom complexed to the ligand, which is not the case. The situation where four ruthenium atoms are complexed, does not fit either.

Figure 4.10 – ESI-MS of the attempted complexation of **61**

A last effort to obtain a diacetylene ruthenium complex was made via an indirect route, by reacting an excess of propargyl chloroformate with **33**. Surprisingly, ESI-MS did not confirm the diacetylene complex although a portion was converted to the monoacetylene. Longer reaction times, higher temperatures, larger excess of

chloroformate, repurifying the complex or additional complex drying time failed to produce the desired diacetylene in high yield. The complexes are normally stable in basic conditions, but not necessarily so in acidic conditions. TEA was added to the reaction to neutralize the formed acid. Perhaps the acetylene is a stronger ligand, compared to the DCH moiety which resulted in a rearrangement of the DCH complex.

4.2.3 – Hydrogels and sol-gels

When considering options in designing a biosensor, aqueous chemistry is necessary in order to preserve the activity of the enzymatic system employed. Immobilizing both the ruthenium complex and an enzyme within a porous, polymeric network called for hydrogels or sol-gels.

Polyacrylamide hydrogels were first considered because of their easy preparation. This process requires water soluble ruthenium complexes which is unfortunately not the case with PF_6 salts. Fortunately, the PF_6 counterion can be exchanged to chlorine by addition of excess tetrabutylammonium chloride to an acetone solution of the complex. As the dichloro complex is insoluble in acetone, a simple workup ensues and the complex can be doped into the reaction medium uniformly. A solution of each reagent, acrylamide (AM), methylene bisacrylamide (MBA), tetramethylene ethylene diamine (TMED) and water-soluble complex **35** was prepared. The radical initiator, ammonium persulfate (APS), was added last. Instead of obtaining a gel, the solution, originally purple, turned green. Furthermore, within an hour, the solution had become yellow. This was an interesting result and the discovery of an unexplored property of the biurea ruthenium complexes; they are strong radical quenchers, or antioxidants, owing to their low redox

potentials. The initial addition of APS was sufficient to fully oxidize **35** to its Ru^{III}/Ru^{III} state which was then reduced to the Ru^{II}/Ru^{III} state. There may be some degree of cycling available as the mixed valence state could be re-oxidized again. Adding 1.2 equivalents of APS, based on the quantity of **35**, yielded gels where the complex oxidized to its mixed valence state. Since the complex is water soluble and not covalently bound to the polymer network, some leaching occurred by diffusion through the pores of the gel. This should have been easily remediated by acrylating the hydroxyl groups of the complex but, as it was with the similar case of propargyl chloride, acryloyl chloride only decomposed the complex (deduced by the ESI-MS spectra of the recovered product) was obtained. The dinuclear ruthenium complexes are base stable but even with the addition of triethylamine (quantity based on molar equivalent of complex), the excess acid chloride employed could have reduced the pH to a level that caused degradation. Further discussion regarding the incorporation of the enzyme into the gel and biosensor scheme will be detailed in Chapter 5.

Next, sol-gels containing **35** which were prepared using an oxidized complex were explored. Tetraethoxysilane was hydrolyzed to a gel using a common procedure²¹⁵ by casting the fluid solution onto glass plates. Cetyltrimethylammonium bromide (CTAB) was added as a surfactant to minimize shrinkage and cracking of the gel. Two DCH-Ru complexe concentrations were prepared: 1.2 mg (A series) and 2.4 mg (B series) per 0.4 mL of sol solution. Unfortunately, the resulting gel films did crack and did not adhere strongly to the glass substrate. The films were prepared in triplicate and UV-Vis-NIR of these, were surprisingly reproducible, considering the randomness of the cracks observed (Figure 4.11).

Figure 4.11 – Absorption spectra of solgel films containing **35** (inset: picture of ‘A’ films)

4.2.4 – Hyperbranched polymers

Following these obstacles, hyperbranched systems, which have been previously employed in our group⁷³ were considered. Conditions, such as reagent concentration, reaction time, spin coating speed and curing temperature were optimized in order to obtain the thinnest film possible containing a maximum amount of ruthenium complex.

A triisocyanate, derived from trimethylolpropane and xylene diisocyanate was mixed with trimethylolpropane to produce urethane hyperbranched polymers. Initially, a monomer concentration of 50% by weight in 1:1 MeCN:THF was utilized, maintaining a 50% excess of isocyanato group over the hydroxyl group. Once mixed, the solutions gelled within a few minutes when at 50°C. The gellation time increased to 10 minutes without heating, for a longer working window. Spin coating at 1000 rpm for 30 seconds and curing at 150°C resulted in films on the order of 10-15 microns in thickness. Increasing the spin speed gradually decreased the thickness to 4-6 microns, which was

higher still than the sub-micron goal that we had established. Diluting the monomers to 5 % by weight, increasing the spin coating speed to 3000 rpm and curing at 150°C were required to obtain high-quality, transparent thin films on the order of 400 nm in thickness (Figure 4.12).

Figure 4.12 – Sample spin-coated crosslinked films containing **41**

With the model system now optimized, the diol complex concentration was gradually increased, while decreasing the trimethylolpropane concentration by the same hydroxyl equivalent, to maintain the 50% excess isocyanato group. It was found that 48% by weight of complex was the highest concentration possible that produced clear films as phase separation occurred, during spin coating, at concentrations exceeding this value.

4.3 – Conclusion

A few synthetic pathways to dendrimers were considered and it was found that hydrazinolysis of ester groups, in the presence of already-formed DCH sites, is not selective to only ester groups. Hydrazine is such a strong nucleophile that it also hydrolyzes the existing DCH ligands, preventing the formation of higher generation dendrons. Suzuki coupling methodology applied to a G2 dendrimer scheme also failed due to the lack of coupling between a triboronic acid G1 DCH dendrimer core and a di-

DCH bromo dendron. A potentially photocrosslinkable tetra-DCH G1 dendrimer was readily obtained; however, UV irradiation failed to produce crosslinking. This might be due to steric repulsions and the globular nature of the nearby complex sites, preventing two cinnamyl groups from interacting and photodimerizing. Redesigning this route with an extended chain separating the cinnamyl group from the complexation site might enable photocrosslinking. This is also dependant on the effect of UV absorbance of the bpy moieties, as they outnumber the cinnamyl groups 4 to 1 and can absorb the bulk of the UV radiation.

Many polymerization methods were considered to prepare macromolecular materials containing the dinuclear ruthenium complex moiety. As unfortunate as it is, most of them only produced low molecular weight materials, unsuitable for application purposes. High molecular weights play an important role for good film-forming properties and having reliable, stable physical and optical properties. The conducting element that ensures uniform conductivity across the film is normally an electrolyte, such as an ionic liquid, or a polyelectrolyte based on dissolved lithium perchlorate. The latter is able to dissolve low molecular weight ruthenium complex polymers, as they are essentially ionic compounds as well. Only hyperbranched polyurethanes produced adequate materials and a procedure to prepare high-quality thin films containing up to 48 % by weight of ruthenium complex was devised and optimized. Their optical and electrochemical properties will be discussed in chapter 5.

4.4 – Experimental

Polymerization reactions were performed under inert atmosphere, usually argon, using in-house Shlenk lines, having screw caps on both ends, permitting the use of septa. A small side hole was blown on small test tubes with threaded top and a standard GC vial, its bottom cut out, was fused to the side opening, facilitating the use of needles to supply the inert gas. Acetonitrile was distilled over CaH_2 and kept in a bottle which was placed in a dessicator. N,N-Dimethylformamide (DMF) was distilled over CaH_2 and stored over 4Å molecular sieves. Reagents such as trimethylolpropane, carbamate with xylene diisocyanate (TMP-NCO), trimethylolpropane (TMP), and DCC were purchased from Aldrich and used as received. The complexes were prepared, isolated, purified and analyzed as described in Chapter 3. NMR characterization of the organic synthons was achieved as described in Chapter 2. Spin-coated films were prepared using a Chemat Technology Spin Coater, model KW-4B. UV irradiation was done using an EFOS N2001-A1 Novacure spot curing light source.

Dendrimer related synthesis

Dimethyl 5-[N'-(6-Hydroxy-hexanoyl)-hydrazinocarbonyl]isophthalate (50). Trimethyl 1,3,5-benzenetricarboxylate (5.05 g, 20 mmol), dissolved in 200 mL of methanol was partially hydrolyzed by adding 0.9 equivalent of NaOH (18 mL, 1 M) and stirred overnight at room temperature. The solution was rotoevaporated to dryness. The resulting salt was dissolved in 50 mL of distilled water (DW) and the solution was acidified to pH = 3 using concentrated HCl. The white precipitate was filtered, washed with DW and dried

in a vacuum oven at 50°C overnight. This monoacid was converted to an acid chloride in refluxing thionyl chloride (1 g of monoacid in 10 mL SOCl₂) for 4 hours. The excess thionyl chloride was rotoevaporated and 0.924 g of the formyl chloride (3.6 mmol) is dissolved in 25 mL of DCM and added dropwise to a solution of 6-hydroxyhexanoic hydrazide¹³⁴ (3.4 mmol) and TEA (0.38 g, 3.8 mmol) in THF. After stirring for 3 hours, the TEA-HCl salt was filtered off and the filtrate was concentrated to dryness. The solid was triturated with DCM (**50** is soluble in THF) to remove impurities and air dried. The overall yield of **50** (three steps) was 82%. ¹H NMR (400 MHz, DMSO-*d*₆): 10.79 (s, 1H, H8); 10.00 (s, 1H, H9); 8.70 (d, 2H, H2, ⁴J = 1.5Hz); 8.62 (t, 1H, H4, ⁴J = 1.5Hz); 4.37 (t, 1H, OH, ³J = 5Hz); 3.94 (s, 6H, H6); 3.40 (td, 2H, H15, ³J = 5Hz); 2.20 (t, 2H, H11, ³J = 5Hz); 1.57 (tt, 2H, H14, ³J = 7Hz); 1.44 (tt, 2H, H12, ³J = 7Hz, ³J = 6.5Hz) and 1.34 (tt, 2H, H13, ³J = 7Hz, ³J = 6.5Hz). MP: 182-184 °C.

3,5-Bis(phenylhydrazido)bromobenzene (**53**). Isophthalic acid (12.17 g, 73 mmol), silver sulphate (13.32 g, 43 mmol) and bromine (5 mL, 97 mmol) were stirred in concentrated sulfuric acid (60 mL) at 100 °C for 32 hours. The remaining bromine was distilled out and the mixture was poured in 500 mL of cold water (ice bath). The white solid and silver bromide were collected transferred into 700 mL of DW to which NaHCO₃ was added until only lime green AgBr remains suspended. AgBr was filtered off and kept (AgSO₄ can be regenerated). The aqueous phase was concentrated to 250 mL and concentrated sulfuric acid was added until pH = 3 was reached. The white precipitate was filtered, rinsed with cold DW and dried overnight under vacuum at 70°C (15.7 g obtained). 5-bromoisophthaloyl dichloride was prepared by treatment with SOCl₂ as previously

described for **50**, and was dissolved in 50 mL of THF. A solution of benzoic hydrazide (2.2 molar equivalents and TEA 2.2 molar equivalents) in 50 mL of THF was added dropwise to the acid chloride solution. The reaction was poured in water and **53** was filtered, washed with DW, cold acetone and air dried under vacuum. Overall yield (three steps) was 63%. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): 10.83 (s, 1H, H6); 10.66 (s, 1H, H7); 8.49 (s, 1H, H4); 8.32 (d, 2H, H2, $^4J = 1.2\text{Hz}$); 7.94 (d, 4H, H10, $^3J = 7\text{Hz}$); 7.66 (t, 2H, H12, $^3J = 7\text{Hz}$) and 7.54 (dd, 4H, H11, $^3J = 7\text{Hz}$). MP: 266-268 °C. EI-MS: 482 (M^+ , 1.7 %); 446 ($[\text{M}-2\text{H}_2\text{O}]^+$, 3.2); 406 ($[\text{M}-\text{C}_6\text{H}_5]^+$, 0.4); 327 ($[\text{M}-\text{C}_6\text{H}_5-\text{Br}]^+$, 2.4); 256 (2.5); 224 (1.6); 192 (2.1); 160 (5.0); 122 (22); 105 (100) and 77 (39).

Tri-boronic acid G1 dendrimer core (56). Boronic acid **54** was prepared as described by Chen²¹⁶. **54** was refluxed in SOCl_2 for 4 hours and **55** was isolated after rotoevaporating the excess thionyl chloride and used without further purification. **55** (1.71 g, 9.3 mmol), diluted in 15 mL of THF, was added dropwise to a 1,2-dimethoxyethane (DME):DMF (60 mL 1:1) solution of trihydrazide **52** (0.76 g, 3 mmol) and TEA (0.94 g, 3 mmol) under inert atmosphere. The mixture was heated to maintain a gentle reflux for 16 hours. The cooled reaction mixture was poured in to 150 mL DW and the resulting pale yellow solid washed with DW and air dried under vacuum. 0.68 g was recovered. Yield: 32%. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): 10.95 (s, 3H, H4); 10.65 (s, 3H, H5); 8.72 (s, 3H, H4); 8.29 (s, 6H, H11); 7.92 (d, 6H, H8, $^3J = 8\text{Hz}$) and 7.89 (d, 6H, H9, $^3J = 8\text{Hz}$).

Cinnamoyl-terminated G1 dendrimer (58). The starting tetrahydrazide was prepared according to a procedure published by Vercruysse²⁰⁸. This hydrazide (0.43 g, 1 mmol)

and TEA (0.41 g, 4 mmol) were placed in a 50 mL RBF containing dry DMF (25 mL) under inert atmosphere. A solution of cinnamoyl chloride (0.75 g, 4.5 mmol) in dry DMF (5 mL) was added dropwise to the flask at room temperature. Once the addition is complete, the mixture was heated to 80°C and stirred overnight. The mixture was rotoevaporated to half volume and, once cooled, was poured in 150 mL acetone. The resulting slurry was cooled to -20 °C for 1 hour before collecting the white solid, washing it with small portions of acetone. The solid was dried in a vacuum oven overnight at room temperature. 0.83 g of a white powdery **58** was obtained. Yield: 87 %. ¹H NMR (300 MHz, DMSO-*d*₆): 10.37 (s, 4H, H7); 10.26 (s, 4H, H6); 7.57 (s, 8H, H12); 7.54 (d, 4H, H10, ³J = 15Hz); 7.39 (s, 12H, H13 and H14); 6.74 (d, 4H, H9, ³J = 15Hz); 3.30 (s, 8H, H4); 3.08 (s, 4H, H2); 2.77 (s, 8H, H3) and 1.75 (s, 4H, H1). ¹³C NMR (75 MHz, DMSO-*d*₆): 168.3 (C5); 164.2 (C8); 140.7 (C10); 135.0 (C14); 130.3 (C11); 129.4 (C12); 128.2 (C13); 119.8 (C9); 48.8 (C4); 45.8 (C3); 31.2 (C2) and 8.9 (C1).

Octanuclear ruthenium complex of 58 (59). The same procedure as described in Chapter 3 was used to prepare the complex. Yield: 72%. ESI-MS: 1662 ([M-3PF₆]⁺³, 0.7 %); 1210 ([M-4PF₆]⁺⁴, 4.4); 939 ([M-5PF₆]⁺⁵, 43); 758 ([M-6PF₆]⁺⁶, 100); 629 ([M-7PF₆]⁺⁷, 16), 535 ([M-8PF₆+H₂O]⁺⁸, 46) and 533 ([M-8PF₆]⁺⁸, 6.6).

Linear polymerization procedures

Polyesters: Equimolar amounts of monomers (diol, diacid chloride and TEA) were charged in a small custom schlenk line and dissolved in 1 mL dry MeCN. Reactions were normally performed at either 5% m/v (diol complex: 50 mg, 0.04 mmol) or 10% (diol

complex: 100 mg, 0.08 mmol) and under inert atmosphere. Due to the small volume of solvent, the temperatures never exceeded 60°C. The reactions were monitored by IR (ester C=O band) periodically during 24-72 hour periods. Viscosity was not measured since no appreciable increase was noted. Gel permeation chromatography (GPC) was not performed neither for fear to permanently contaminate the column based on the low-but-permanent adsorption of ruthenium complex on alumina.

In the case of AB monomers, the polymerization reaction was done using a coupling agent such as DCC or CDI. Essentially, **60** (100 mg, 0.08 mmol) was dissolved in 2 mL of 1:1 THF:MeCN with DCC or CDI (0.21 mmol). 4-Dimethylaminopyridine (DMAP) was added as a catalyst (5 mg). The mixture was stirred at room temperature overnight.

p-Toluenesulfonic acid catalyzed esterification of **60** (100 mg), in refluxing 2.5 mL of 1:1 toluene: dimethylacetamide (DMAc) showed some success.

Synthesis of AB ruthenium complex monomer **60**

Dimethyl terephthalate was partially hydrolyzed to the monoacid using the saponification procedure described in preparing **50**. The monoacid (1 g, 5.6 mmol) was refluxed in 15 mL of SOCl₂ and 20 mL of THF overnight. The excess solvent was rotoevaporated and the acide choride was dissolved in 10 mL of THF which was then added dropwize to a 20 mL solution of 6-hydroxyhexanoic hydrazide (0.85 g, 5.8 mmol) and equimolar amount of TEA. The reaction was stirred at 50 °C for 3 hours. The ligand was significantly water soluble. The reaction solvent was removed and the solid was washed with hot acetone. The filtrate was poured in ethyl ether and the resulting white precipitate was collected,

washed with ethyl ether and air dried. 0.94 g of the hydroxyester ligand **60pre** (see appendix 1 for structure) was obtained. Yield: 55 %. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 10.52 (s, 1H, H7); 9.94 (s, 1H, H8); 8.07 (dd, 2H, H3, $^3J = 8\text{Hz}$, $^4J = 1.4\text{Hz}$); 8.01 (dd, 2H, H4, $^3J = 8\text{Hz}$, $^4J = 1.4\text{Hz}$); 3.89 (s, 3H, H15); 3.77 (s, 1H, OH); 3.41 (t, 2H, H14, $^3J = 6\text{Hz}$); 2.20 (t, 2H, H10, $^3J = 7\text{Hz}$); 1.57 (tt, 2H, H11, $^3J = 7\text{Hz}$); 1.45 (tt, 2H, H13, $^3J = 6\text{Hz}$, $^3J = 7\text{Hz}$) and 1.35 (m, 2H, H12). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): 171.5 (C1); 165.6 (C6); 164.6 (C9); 136.6 (C2); 132.2 (C5); 129.2 (C3); 127.8 (C4); 160.5 (C14); 52.3 (C15); 33.3 (C10); 32.2 (C13); 25.1 (C11) and 24.9 (C10). EI-MS: 308 (M^+ , 0.3%); 290 ($[\text{M}-\text{H}_2\text{O}]^+$, 1.3); 259 (1.1); 230 (7.7); 194 (34); 181 (2.0); 163 (100); 149 (3.2); 135 (13); 115 (27); 97 (13) and 69 (31). MP: 149-150 °C.

The ligand was complexed in the usual manner, with the exception that excess base was utilized to ensure hydrolysis of the ester group and perchloric acid was used as the precipitating and neutralizing agent. Complex **60** was obtained, after purification on deactivated neutral alumina (adding 3 % by weight of water, MeCN used for eluent), in 82 % yield. ESI-MS: 1318 (M^+ , <0.1 %); 1219 ($[\text{M}-\text{ClO}_4]^+$, 2.2); 1119 ($[\text{M}+\text{H}-2\text{ClO}_4]^+$, 0.7); 706 ($[\text{M}-\text{Ru}(\text{bpy})_2-2\text{ClO}_4]^+$, 1.2) and 560 ($[\text{M}-2\text{ClO}_4]^{+2}$, 100).

Polyurethanes: Same as described for the polyesters except that no base was added. Higher viscosity was obtained however, only a small fraction of the polymer would be soluble in DMF – any polymer soluble in MeCN was deemed as too low molecular weight to be considered for device applications. In addition, only film casting is possible when using DMF due to its low volatility, which produces thicker films, often of lesser quality than with spin coating.

Polytriazoles: The diacetylene oxamide ligand **61** was prepared following a previously described method¹³². Equimolar parts of propargyl amine and diethyl oxalate were added to 20 mL THF and stirred under inert atmosphere for two hours at room temperature. 50 mL ethyl ether was added to the mixture. The white solid was filtered and air dried. ¹H NMR (300 MHz, DMSO-*d*₆): 9.22 (t, 2H, H₂, ³J = 6Hz); 3.90 (d, 4H, H₃, ³J = 6Hz) and 3.10 (s, 2H, H₅). ¹³C NMR (75 MHz, DMSO-*d*₆): 160.0 (C₁); 80.8 (C₄); 73.4 (C₅) and 28.8 (C₃).

Procedure for hydrogel formation

The procedure is based on J. Franklyn's²¹⁷ PhD thesis with the exception that a 1.2 molar excess of APS, based on the quantity of ruthenium complex, was required to obtain suitable gels.

Exchanging the counterion of ruthenium complexes from PF₆ to Cl was relatively simple. Dissolving the PF₆ complex in acetone and adding excess tetrabutyl ammonium chloride permitted the exchange. The dichloro ruthenium complex precipitated out of the acetone solution and simply filtering and washing it with acetone produced the complex in a water soluble form.

Procedure for sol-gel formation

Tetraethoxysilane (1 g), concentrated HCl (0.05 g), 3.85 % cetyl trimethylammonium bromide (CTAB) in ethanol 95% (0.25 g), and H₂O (0.04 g) were mixed in a small Erlenmeyer and vortexed at low speed for one hour. This solution was used to cast blank sol-gels on glass slides (four drops of solution per 1 x 1 cm slides).

Chapter 4 – Macromolecular materials of ruthenium complexes

Water soluble ruthenium complex (chloride counter anion) in the mixed valence state was added at 1.2 mg and 2.4 mg per 0.4 mL of blank solution. Once the solution was deposited on the glass slides, they were placed in a refrigerator at 5°C until the solgel film formation was complete. The remaining, unused solution completely gelled up, with no cracks or defects, within a few days. Unfortunately, the cast films were always cracked and did not adhere strongly to the substrate.

Preparation of the crosslinked films of ruthenium complex

Indium-doped tin oxide (ITO) coated glass strips (0.9 x 4.0 cm) were cut from 15 x 15 cm sheets using a diamond glass cutter and washed, with gloved hands, using 10% wt K₃PO₄ solution, rinsed with hot water followed by distilled water. The strips were 'toweled' off using Kimwipe® tissues and air dried. The procedure was repeated if smudges were still present. The clean strips were kept in a Petri dish.

Ruthenium complex **41** (7 mg), tetrabutylammonium hexafluorophosphate (TBAH, 2 mg), 0.018 mL of 5% wt TMP solution (250 mg in 4.75 g THF:MeCN 1:1) and 1 mg of 1,2-diazabicyclo[2,2,2]octane (DABCO) were added to a 1.5 mL screw cap vial. Lastly, 0.125 mL of 5% wt TMP-NCO solution (333 mg in 3.92 g THF:MeCN 1:1) was added to the vial and the mixture was vortexed at high speed for 10 seconds. The mixture was immediately spin coated into films (3000 rpm for 30 seconds) on the ITO strips. The solution was deposited on one side of the strip only, as to obtain a film that is about 2 cm in length. Duplicate films of each batch were prepared. Any solution that did spread over to the other half of the ITO strip was rubbed off with an acetone-soaked

cotton swab to ensure that this section of ITO was bare. The films were then cured on a digital hotplate at 150 °C for two hours.

Using less of the ruthenium complex or higher organic monomer concentrations, no leaching occurred when washing the film with acetone, confirming that the crosslinking was complete; however, the best results were obtained with the above mentioned quantity of ruthenium, even though a small amount of surface complex did leach out when washed with acetone. In the case of biureas such as **39**, a significant portion of the ruthenium complex leached out of the cured film. Increasing the isocyanate concentration or curing time did not prevent leaching.

Chapter 5 – Device applications based on dinuclear ruthenium complexes

5.1 – Introduction

In the scope of this project, biosensor and VOA applications were developed. Based on the action of the glucose oxidase (GOX) enzyme (Figure 5.1), the glucose biosensor scheme is able to evaluate the glucose content of various matrices. This well-known scheme has been tested against many sensing materials in optical²¹⁸⁻²³² and in amperometric configurations^{39, 233-244}. This particular enzyme, along with many others (cholesterol oxidase²⁴⁵, alcohol oxidase²⁴⁶, amine oxidase²⁴⁷ and cocaine oxidase²⁴⁸), produces hydrogen peroxide as a byproduct, at the expense of an equimolar amount of substrate, rendering the concentration correlation process simple. The active site of the enzyme contains a flavenoid core (FAD, Flavin-Adenine Dinucleotide) which is oxidized by molecular oxygen, generating the active form of the enzyme GOX and producing hydrogen peroxide. With molecular oxygen being plentiful, the oxidized form of the enzyme is dominant. When the substrate, glucose, reaches the FAD core, it is oxidized to gluconic acid while the enzyme is reduced to its non-active GOX-H₂ form.

Figure 5.1 – Glucose oxidase sensing scheme considered

Figure 5.2 – GOX active site mechanism

The chemical sensing materials are normally redox active and it is the current change from their oxidation by H_2O_2 that is monitored through amperometric means, which is the working principle of current human blood sugar apparatus. This redox titration can also be used to determine the concentration of glucose in various matrices, as long as the conditions are sufficient to ensure proper enzyme activity. Since redox materials usually change color, the monitoring can also be achieved via optical means.

Variable optical attenuators (VOA) are devices that can affect the amount of light that reaches its intended target. Electrochromic VOAs vary their attenuation capability through an applied potential. The optical attenuation can be achieved by micromechanical means, where a slit or other moving parts physically block the incident beam²⁴⁹⁻²⁵¹. Unfortunately, the moving parts tend to be bulky and make the devices noisy²⁵². In comparison, a VOA device using an EC material to absorb the light does not require the use of any moving parts and can be operated or switched on and off by applying a low voltage. The dinuclear ruthenium complexes are suitable materials for NIR VOA applications with further potential in controlling and processing light signals in linear and nonlinear optics^{70, 253-256}. McDonagh and coworkers have studied the NIR electrochromism of dinuclear molybdenum complexes in a 6-mm-thick liquid cell design

for their VOA properties at 1300 nm and achieved high attenuation⁷⁰. Optical attenuation can also be achieved by thermo-optic-based planar lightwave circuits²⁵⁷⁻²⁶², where an applied voltage generates heat that induces a drop in the refractive index of a fiber optic cable cladding, allowing light to ‘escape’ the fiber, weakening the signal strength and through the use of liquid crystals which also relies on refractive index manipulation via an applied voltage to the liquid crystal.

Two optical configurations can be considered. The first is a transmission-based design where the incident beam passes through a clear EC material film sandwiched between two ITO plates. The second is a reflection-based design where the incident beam passes through the EC film and is reflected back through the same film, theoretically doubling the attenuation efficiency per thickness unit compared to transmissive configurations. A conducting element, such as a polymer electrolyte gel, completes the circuit in both cases.

Figure 5.3 – a) transmissive and b) reflective VOA constructs

A reflective design may offer higher attenuation but requires more space to accommodate the incident and reflected beams particularly when compared to transmissive designs, which can be placed in line with the incident beam source.

While ITO is employed as a colorless electrode in visible applications, it starts reflecting NIR light from 1000 nm (Figure 5.4). Furthermore, transmissive designed VOAs, will lose signal strength each time an ITO layer is encountered. This property can be harnessed when operating in a reflective mode. However, double reflection can occur since ITO will partially reflect the incident beam, potentially reducing the overall signal strength. These and other optical losses were not considered when evaluating the VOA properties of the films in this study.

Figure 5.4 – ITO NIR reflectance (100 nm thick coating)

5.2 – Results and discussion

5.2.1 – Glucose biosensor

The first sensing tests were performed using hydrogen peroxide (concentration range reflecting the normal blood sugar levels) and complex **34**, to evaluate the oxidation potential of the complex in 0.1 M Tris (2-Amino-2-(hydroxymethyl)-1,3-propanediol) buffered at pH = 7.4 and containing 10 % v/v MeCN. The solution absorbance was monitored at 1200 nm in real time for a period of 10 minutes at various peroxide concentrations. A good calibration curve was observed at different reaction times (Figure 5.5). Note that the trend line did not pass through the zero intercept. The solution, minus the hydrogen peroxide, was used as the baseline. As discussed in Chapter 3, the low redox potential biureas, such as **34**, can be oxidized by oxygen. Therefore, any NIR absorbance observed at 0 mM concentration is due to the complex oxidation by dissolved oxygen.

Figure 5.5 – Oxidation of **34** with hydrogen peroxide

With the NIR monitoring conditions set, the biosensing scheme was evaluated by adding glucose and GOX into the equation. Solutions of glucose and GOX enzyme were prepared in the same solvent system and incubated at 37°C for 30 minutes to generate the hydrogen peroxide. An aliquot of a 10^{-4} M solution of **34** was then added to the incubated solutions and the absorbance was monitored at 1200 nm in real time (Figure 5.6).

Figure 5.6 – Enzymatic oxidation of **34** by GOX at various glucose concentrations

The resulting calibration curve, using a linear regression, was not as good as previously. However, using a second order polynomial regression, very good fits were obtained. One feature of Figure 5.6 is that the absorbance peaks and begins decreasing with time for the higher glucose concentrations. This is due to the excess of hydrogen peroxide being produced, compared to the amount of complex present, which oxidized the complex to the non NIR active $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ state.

It was also found that the current system had poor reproducibility from one preparation to another. This can be justified by the lack of sample mixing during the measurement. Even though the solutions were mixed a few seconds prior to absorbance monitoring, diffusion, which is totally random, governs the rate of oxidation as a molecule must first dock with the enzyme active site. The produced peroxide must then also diffuse towards a DCH-Ru complex to oxidize it. Using a small electrical motor, magnets were mounted on the rotor shaft using plexiglass disks. The motor was mounted under the cuvette holder and mixing of sample was enabled. Given the size of the cuvette, we were limited to micro stir bars. Also, the spinning speed was kept low enough to prevent air bubbles or a vortex to perturb the optical path. Although the oxidation rate did increase with stirring, it was not sufficient to obtain reproducible results. Incubating the solutions at 37 °C for a period of time prior to measuring the final absorbance did speed up the oxidation process, but did not significantly improve the reproducibility.

Expecting to obtain better results in a solid state configuration, hydrogels containing the enzyme and DCH-Ru complex were prepared as described in Chapter 4. Even if the initiator used in acrylamide crosslinking reaction oxidized the complex to its NIR active redox state, it could be electrochemically reduced to the ground state. With diffusion being the limiting factor to our sensor sensitivity, preparation of a hydrogel, within a plastic 1 x 1 cm cuvette was attempted and modified to obtain a crude flowcell. It was found that the porosity of the gel was not sufficient to enable a reasonable amount of glucose solution to be filtered through. Increasing the pressure only compressed the gel against the opposite opening of the cell.

Sol-gels, which are known to be porous, could have been tested as a solid sensor matrix if a solution to the cracking and low adhesion to glass substrates would have been established. Crosslinked polyurethane thin films of **41**, prepared as described in Chapter 4, were submerged in dilute acidified hydrogen peroxide. Although the films switched rapidly to the mixed-valence state by electrochemical means, the hydrophobicity of the film hindered the migration of the peroxide into the film. Only when using 30 % hydrogen peroxide was the desired oxidative effect achieved. Given that the time scale and harsh conditions required to effectively oxidize the complex to its NIR active state were more demanding than current commercialized glucose sensors, it became apparent that a glucose optical biosensor using dinuclear ruthenium complexes would not create interest for commercialization.

5.2.2 – Reflective NIR variable optical attenuator

Transmissive VOAs, thin films and solution configurations, have been employed by previous members of our group^{263, 264}. Designing a reflective film and evaluating its attenuation properties would shed some light on the optical losses stemming from the dual layers of ITO. The crosslinked complex films, prepared as described in Chapter 4, retained their electrochemical properties relative to the complex monomer itself (Figure 5.7).

Figure 5.7 – CV of crosslinked polyurethane film of **41**

As expected, the redox couples (E_{PA} and E_{PC}) of the crosslinked complex film show a larger separation than of those of the monomer due to slow counter ion diffusion through the polymer network. This effect is expected to lessen with each cycle as the counter ion, once within the polymer network, will tend to remain within this network and will be 'available' for the next cycle. Swelling with the electrolyte solution (e.g., acetonitrile) may also be playing a role in diffusion, since a fresh film is dry and has a slower diffusion rate than the wet film. A 65-fold increase in peak current generated from the films was also noted which can easily be explained from the much larger working electrode surface area available (1.5 cm^2) compared to a 1.5-mm-diameter platinum disk electrode used for CV measurements.

Chronoamperometry of the films was monitored at the 1550 nm wavelength by cycling the potential from -0.5 V to 0.8 V. Silvered films based on **41** showed about 80% optical contrast (recorded in a static mode), which is defined as the difference in

transmission between the two redox states considered at a particular wavelength. The absorbance of the ground state was set as the baseline (100% transmission, without consideration of any optical loss due to absorption and/or scattering). Since the intensity of the reflected light depends on the angle of incident light, the signal strength was probed within a range of incident angles from 30° to 70°. The highest signal strength was attained with an incident angle of 56°. Thus, the reflectance was measured at this incident angle. Prolonged switching between the two states showed that the polymeric films possessed good cycling stability. In fact, the attenuation improved slightly with time, due to swelling of the film from being submerged in an electrolytic solution as well as the migration of the counter anion factor.

The attenuation of an EC material can be evaluated using the following equation:

$$Attenuation = 10 \log \left(\frac{T_b}{T_c} \right) \quad \text{Equation 5.1}$$

where T_b is the transmission of the bleached state ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ state, approximately 100%) and T_c is the transmission of the colored state. For example, an 80% optical contrast would translate into an attenuation of 7 dB. The attenuation is dependent on film thickness and taking the 400 nm thickness into consideration, the intrinsic attenuation is 17.5 dB/ μm . When the film is rapidly switched between redox states, the attenuation range obtained is dynamic and normally lower since the oxidation is incomplete due to the time limitations. Using a 5 second stepping time, a dynamic range attenuation of 14.5 dB/ μm was achieved (Figure 5.8), 15 % lower than in the static mode, meaning that 85 %

of the EC is oxidized in 5 seconds. As expected, similar films that were not silvered only displayed an attenuation of 1.6 dB, due to partial NIR reflection from the ITO WE.

Figure 5.8 – Chronoamperometry of a crosslinked polyurethane film of **41** using a 5 second stepping time

In comparison with the transmissive device, the similar ruthenium complex gave attenuation values of 0.05 dB/ μm in a 100- μm (path length) solution-based device assembly²⁶⁴ and 4.9–5.4 dB/ μm in a film-based device¹³⁴. Also, optical attenuation of the dinuclear molybdenum complex, when thickness is taken into consideration, becomes 0.01 dB/ μm ⁷⁰. While some variation can be accounted by the differences in molar extinction coefficients of the complexes used, it is clear that the device configuration also plays a role in performance. When the stepping time was reduced to 2.5 seconds, a drop in dynamic attenuation range of 10.9 dB/ μm was observed (Figure 5.9).

Figure 5.9 - Chronoamperometry of a crosslinked polyurethane film of **41** using a 2.5 second stepping time

A common practice is to use higher potentials in order to reduce the response time²⁶⁵, but biurea-based dinuclear ruthenium complexes can be further oxidized to the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ specie which, in this case, forms at potentials above 850 mV (based on Figure 5.7) and does not express NIR activity. Since the redox process must pass through the mixed-valence state, it is probable that faster stepping time and higher potentials could generate the NIR active state exclusively. Improving the conductivity within the film should yield faster switching times.

The wavelength of 1550 nm is a major telecommunication band. Using the biurea complex **39**, similar crosslinked films were prepared on silvered ITO. Strangely, a significant portion of the EC material leached from the film when being washed with MeCN, indicating an incomplete curing. Increasing the temperature resulted in the initially brown-purple films to turn green which were no longer electrochromic. Having lost so much EC component, it was no surprise that the intrinsic dynamic attenuation of the resulting films, using a 5 second stepping time, was only 5.1 (Figure 5.10) and 3.9

dB/ μm (Figure 5.11) at the 1310 and 980 nm bands respectively. In the case of the 980 nm band, the MLCT of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ was utilized and the redox cycling was done between -0.5 V to 0.9 V.

Figure 5.10 – Chronoamperometry at 1310 nm of a crosslinked polyurethane film of **39** using a 5 second stepping time

Figure 5.11 – Chronoamperometry at 980 nm of a crosslinked polyurethane film of **39** using a 5 second stepping time

5.3 – Conclusion

The working concept of a glucose biosensor by monitoring the NIR absorbance at 1200 nm of a biurea DCH-Ru complex was demonstrated. The results point to a viable system; however the slow response time and reproducibility issues could not be overcome by increasing the temperature, the enzyme concentration, the incubation time or agitation.

Thin films of **41** prepared in Chapter 4 displayed a dynamic range of 14.7 dB/ μm at 1550 nm while similar films of **39** only offered a dynamic range of 5.1 and 3.9 dB/ μm at the 1310 and 980 nm telecommunication bands due to low EC content (incomplete crosslinking).

It was shown that a three-fold increase in optical attenuation was achieved for ruthenium complex polymer films when operating in a reflective mode and cycling from -0.5 to 0.8 V compared to a transmissive device based on similar EC materials. Faster response time could be expected if higher oxidation potentials were used, but only if the mixed-valence state ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$) can be generated selectively. It is expected that resolving the crosslinking issue with complex **39** will result in superior attenuation at both 1310 and 980 nm telecommunication wavelengths. Larger dynamic range in optical attenuation and faster switching can be expected for an electrochromic VOA with a well-designed reflective configuration.

5.4 – Experimental

Materials

Tris base, β -D-glucose, glucose oxidase (type VII from *Aspergillus niger*, 192,000-217,000 units/g), silver nitrate and potassium sodium tartrate (Rochelle salt) were purchased from Aldrich and used as received. The enzyme was stored at -20°C. The two-part conductive silver epoxy paste was purchased from a local electronics shop.

Sample preparations for glucose sensing

Tris base buffer pH 7.4 was prepared by dissolving 0.01 mole of base in 90 mL of DW, adjusting the pH with concentrated HCl, transferring the solution to a 100 mL volumetric flask and completing the volume with DW. The enzyme was dissolved in Tris buffer (5 mg/mL) to create a stock solution containing 960-1085 units/mL of enzyme.

The stock solution of enzyme (0.3 mL), MeCN (0.1 mL) and a known concentration of glucose were adjusted to 1 mL using Tris buffer and incubated at 37 °C for 30 minutes and degassed with nitrogen gas for one minute. A ruthenium complex aliquot was added so that the concentration of the complex is 10^{-4} M. The solution was mixed a few seconds, transferred to a quartz cuvette, the absorbance zeroed at 1200 nm and monitored for 10 minutes. This was repeated for various glucose concentrations.

Optical attenuation setup and measurement

The electrochromic films were prepared as described in Chapter 4 and their thickness was measured with a Tencor Instruments Alpha-step 200 profiler. The

electrochemical and spectroelectrochemical properties of the films were investigated using a Bioanalytical SystemsTM BAS100 potentiostat coupled to a Perkin Elmer Lambda 900 spectrophotometer. Reflectance measurements were done using a Harrick ScientificTM variable angle specular reflectance module and an in-house cuvette holder (see Appendix 6).

To measure the CV of the thin but long films, a specialized glass tube with inward blown spikes to hold the glass slide in place as well as two downward open spikes as ports for the other two electrodes (CE and RE). The working electrode lead was attached either by using an alligator clip directly to the ITO or by attaching a section of copper wire to the bare ITO using conductive silver epoxy paste, which was cured at 60°C for two hours and left to harden overnight at room temperature.

For silvering of the glass side of ITO glass strips, the Rochelle Salts process was used²⁶⁶. The ITO layer was first masked using clear adhesive tape and then placed, taped side facing down, in a glass Petri dish. A mixture of equal parts of a silver nitrate/ammonium hydroxide aqueous solution and a silver nitrate/potassium sodium tartrate aqueous solution was poured over the exposed slides to completely cover them. The silver deposition proceeded at 38 °C. Once completed, the ITO strips were taken out and washed off using distilled water. The silvering process could be repeated to obtain a thicker layer of silver but it must be done while the silver layer is still damp. Since only the ITO surface was masked, silver was also deposited on the cross-section side of the ITO glass strips. It was necessary to remove this extra silver (using a rotary tool and polishing head) as it became apparent that an electrical contact with the ITO existed.

Failure to break the contact while applying a positive potential resulted in oxidation of the silver, effectively destroying the mirror finish.

The optical contrast of the films (ITO and silvered ITO) was measured using a Harrick Scientific™ variable angle specular reflectance module and an hand built in-house plexiglass cuvette holder (see appendix 6). The coated ITO strip (8×40 mm) was submerged in a four-sided 1-cm quartz cuvette containing 0.1 M TBAH in acetonitrile as supporting electrolyte solution. Silver and platinum wires were used as pseudo reference and counter electrodes, respectively. The $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ state of the complex in the polymer film (electrochemically reduced at -0.5 V) was used as the background correction. Since the intensity of the reflected light depends on the angle of incident light, the signal strength was probed within a range of incident angles from 30° to 70° . The highest signal strength was attained with an incident angle of 56° . Thus, the reflectance was measured at this incident angle, while the polymer film was electrochemically oxidized and reduced between the two oxidation states ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ states).

Claim to original research

NIR active dinuclear ruthenium complexes have been known for many years and some success has been demonstrated towards making film-forming macromolecules containing this moiety, by complexing ligand oligomers. In considering functional groups for use in polymerization, long chain aliphatic hydroxyl ligands were chosen to ensure that the hydroxyl group would not be hindered by the bulky Ru(bpy)₂ groups. Various classes of polymerizations were explored, but only crosslinked polymers gave satisfactory films that could be used in devices.

The variable optical attenuator device application is the usual end point of optoelectronic research and such was the case in the scope of this project. The common transmissive configuration was replaced with a reflective one and a three fold increase in intrinsic attenuation was achieved compared to similar transmissive devices. These results were published in the Journal of Solid State Electrochemistry²⁶⁷.

The preparation of low redox potential complexes resulted in readily oxidizable materials which are adequate in optical biosensing schemes. The working concept of a glucose biosensor, based on the enzyme glucose oxidase, was demonstrated. Even though the response time was somewhat slow, this scheme could be adapted to other substrates, based on other peroxide-forming oxidases. These results were published in Organic Letters²⁶⁸.

The IVTC transition observed in DCH-Ru complexes should theoretically be present in other dinuclear metal complexes based on the DCH bridging ligand, more so if the metal considered has two redox states that are linked through a one-electron redox process. Dinuclear complexes of platinum were successfully prepared and their phosphorescent properties studied. However, variations of the bridging ligand had little effect on the emission wavelength, but modifying the peripheral ligand had a significant impact on the emission color. Unfortunately, the second goal to achieve NIR emission was not reached, although deep red emission was observed from one complex. With many peripheral ligands accessible via simple synthetic routes, the potential of breaching the NIR emission barrier, at 700 nm, is tangible.

References

1. Platt, J. R., *Journal of Chemical Physics* **1961**, 34, 862-3.
2. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R., *Electrochromism: Fundamentals and Applications*. VCH, Weinheim, **1995**, p 217.
3. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R., *Electrochromism and Electrochromic Devices*. Cambridge University Press, New York, **2007**, p 483.
4. Izutsu, K., *Electrochemistry in Nonaqueous Solutions*. Wiley-VCH, Weinheim, **2002**, p 330.
5. Gritzner, G.; Kuta, J., *Pure and Applied Chemistry* **1984**, 56, 461-466.
6. Connelly, N. G.; Geiger, W. E., *Chemical Reviews* **1996**, 96, 877-910.
7. Dautremont-Smith, W. C., *Displays* **1982**, 3, 3-22.
8. Dautremont-Smith, W. C., *Displays* **1982**, 3, 67-80.
9. Baucke, F. G. K.; Bange, K.; Gambke, T., *Displays* **1988**, 9, 179-87.
10. Kang, K. S.; Shay, J. L., *Journal of the Electrochemical Society* **1983**, 130, 766-9.
11. Hiruta, Y.; Kitao, M.; Yamada, S., *Japanese Journal of Applied Physics, Part 1* **1984**, 23, 1624-7.
12. Talledo, A.; Andersson, A. M.; Granqvist, C. G., *Journal of Applied Physics* **1991**, 69, 3261-5.
13. Fu, Z.; Kong, J.; Qin, Q.; Tian, Z., *Science in China, Series B* **1999**, 42, 493-500.
14. Lee, G. R.; Crayston, J. A., *Journal of Materials Chemistry* **1991**, 1, 381-6.
15. Polo da Fonseca, C. N.; De Paoli, M. A.; Gorenstein, A., *Advanced Materials* **1991**, 3, 553-5.
16. Isidorsson, J.; Granqvist, C. G., *Solar Energy Materials and Solar Cells* **1996**, 44, 375-381.
17. Richardson, T. J.; Slack, J. L.; Rubin, M. D., *Electrochimica Acta* **2001**, 46, 2281-2284.
18. Ozer, N.; Tepehan, F., *Solar Energy Materials and Solar Cells* **1999**, 56, 141-152.
19. Pifer, J. H.; Sichel, E. K., *Journal of Electronic Materials* **1979**, 9, 129-40.
20. Owen, J. F.; Teegarden, K. J.; Shanks, H. R., *Physical Review B: Condensed Matter and Materials Physics* **1978**, 18, 3827-37.
21. Deneuville, A.; Gerard, P., *Journal of Electronic Materials* **1978**, 7, 559-88.
22. Taylor, D. J.; Cronin, J. P.; Allard, L. F. J.; Birnie III, D. P., *Chemistry of Materials* **1996**, 8, 1396-1401.
23. Deepa, M.; Srivastava, A. K.; Singh, S.; Agnihotry, S. A., *Journal of Materials Research* **2004**, 19, 2576-2585.
24. Bange, K.; Gambke, T., *Advanced Materials (Weinheim, Germany)* **1990**, 2, 10-16.
25. Goettsche, J.; Hinsch, A.; Wittwer, V., *Solar Energy Materials and Solar Cells* **1993**, 31, 415-28.
26. Ohtani, B.; Masuoka, M.; Atsumi, T.; Nishimoto, S.; Kagiya, T., *Chemistry Express* **1988**, 3, 319-22.
27. Ozkan, E.; Lee, S.-H.; Liu, P.; Tracy, C. E.; Tepehan, F. Z.; Pitts, J. R.; Deb, S. K., *Solid State Ionics* **2002**, 149, 139-146.
28. Neff, V. D., *Journal of the Electrochemical Society* **1978**, 125, 886-7.
29. Yano, Y.; Kinugasa, N.; Yoshida, H.; Fujino, K.; Kawahara, H., *Proceedings - Electrochemical Society* **1990**, 90-2, 125-36.

30. Ellis, D.; Eckhoff, M.; Neff, V. D., *Journal of Physical Chemistry* **1981**, 85, 1225-31.
31. Ho, K.-C., *Proceedings - Electrochemical Society* **1994**, 94-2, 170-84.
32. Gomathi, H.; Rao, G. P., *Journal of Applied Electrochemistry* **1990**, 20, 454-6.
33. Kellawi, H.; Rosseinsky, D. R., *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1982**, 131, 373-6.
34. Miller, L. L.; Duan, R. G.; Hong, Y.; Tabakovic, I., *Chemistry of Materials* **1995**, 7, 1552-7.
35. Almlof, J. E.; Feyereisen, M. W.; Jozefiak, T. H.; Miller, L. L., *Journal of the American Chemical Society* **1990**, 112, 1206-1214.
36. Hu, Y.-z.; Chiang, L.-j. J., *Journal of Photochemistry and Photobiology, A: Chemistry* **1996**, 94, 37-41.
37. Qiao, W.; Zheng, J.; Wang, Y.; Zheng, Y.; Song, N.; Wan, X.; Wang, Z. Y., *Organic Letters* **2008**, 10, 641-644.
38. Moskalev, P. N.; Kirin, I. S., *Optika i Spektroskopiya* **1970**, 29, 414-15.
39. Zhang, J.; Lu, F.; Huang, H.; Wang, J.; Yu, H. a.; Jiang, J.; Yan, D.; Wang, Z., *Synthetic Metals* **2005**, 148, 123-126.
40. Kim, Y. H.; Jeong, D. H.; Kim, D.; Jeoung, S. C.; Cho, H. S.; Kim, S. K.; Aratani, N.; Osuka, A., *Journal of the American Chemical Society* **2001**, 123, 76-86.
41. Miyahara, T.; Nakatsuji, H.; Hasegawa, J.; Osuka, A.; Aratani, N.; Tsuda, A., *Journal of Chemical Physics* **2002**, 117, 11196-11207.
42. Tsuda, A.; Furuta, H.; Osuka, A., *Journal of the American Chemical Society* **2001**, 123, 10304-21.
43. Tsuda, A.; Osuka, A., *Science* **2001**, 293, 79-82.
44. Cho, H. S.; Jeong, D. H.; Cho, S.; Kim, D.; Matsuzaki, Y.; Tanaka, K.; Tsuda, A.; Osuka, A., *Journal of the American Chemical Society* **2002**, 124, 14642-14654.
45. Ou, Z.; E, W.; Shao, J.; Burn, P. L.; Sheehan, C. S.; Walton, R.; Kadish, K. M.; Crossley, M. J., *Journal of Porphyrins and Phthalocyanines* **2005**, 9, 142-151.
46. Kobayashi, N.; Numao, M.; Kondo, R.; Nakajima, S.; Osa, T., *Inorganic Chemistry* **1991**, 30, 2241-4.
47. Paolesse, R.; Jaquinod, L.; Della Sala, F.; Nurco, D. J.; Prodi, L.; Montalti, M.; Di Natale, C.; D'Amico, A.; Di Carlo, A.; Lugli, P.; Smith, K. M., *Journal of the American Chemical Society* **2000**, 122, 11295-11302.
48. Silverstein, R. M.; Webster, F. X.; Kiemle, D. J., *Spectrometric Identification of Organic Compounds*. John Wiley & Sons, Hoboken, **2005**, p 512.
49. Chiang, C. K.; Drury, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H., *Journal of the American Chemical Society* **1978**, 100, 1013-1015.
50. Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R., *Synthetic Metals* **1986**, 15, 169-74.
51. Mastragostino, M., *Applications of Electroactive Polymers*. Chapman and Hall, London, **1993**, p 354.
52. Cotton, F. A.; Wilkinson, G., *Advanced Inorganic Chemistry: A Comprehensive Text*. John Wiley & Sons, New York, **1980**, p 1396.
53. Laporte, O.; Meggers, W. F., *Journal of the Optical Society of America* **1925**, 11, 459-64.

54. McCleverty, J. A., *Metal 1,2-dithiolene and related complexes in Progress in Inorganic Chemistry*. John Wiley & Sons, New York, **1968**, Vol. 10, p 49-221.
55. Schrauzer, G. N.; Mayweg, V. P., *Journal of the American Chemical Society* **1965**, 87, 3585-92.
56. Baker-Hawkes, M. J.; Billig, E.; Gray, H. B., *Journal of the American Chemical Society* **1966**, 88, 4870-5.
57. Williams, R.; Billig, E.; Waters, J. H.; Gray, H. B., *Journal of the American Chemical Society* **1966**, 88, 43-50.
58. Shupack, S. I.; Billig, E.; Clark, R. J. H.; Williams, R.; Gray, H. B., *Journal of the American Chemical Society* **1964**, 86, 4594-602.
59. Creutz, C.; Taube, H., *Journal of the American Chemical Society* **1973**, 95, 1086-94.
60. Laye, R. H.; Couchman, S. M.; Ward, M. D., *Inorganic chemistry* **2001**, 40, 4089-92.
61. Kasack, V.; Kaim, W.; Binder, H.; Jordanov, J.; Roth, E., *Inorganic Chemistry* **1995**, 34, 1924-33.
62. Rocha, R. C.; Toma, H. E., *Canadian Journal of Chemistry* **2001**, 79, 145-156.
63. Mosher, P. J.; Yap, G. P.; Crutchley, R. J., *Inorganic chemistry* **2001**, 40, 1189-95.
64. Rastegar, M. F.; Todd, E. K.; Tang, H.; Wang, Z. Y., *Organic Letters* **2004**, 6, 4519-4522.
65. Haga, M.; Dodsworth, E. S.; Lever, A. B. P., *Inorganic Chemistry* **1986**, 25, 447-53.
66. Lee, S.-M.; Marcaccio, M.; McCleverty, J. A.; Ward, M. D., *Chemistry of Materials* **1998**, 10, 3272-3274.
67. Harden, N. C.; Humphrey, E. R.; Jeffery, J. C.; Lee, S.-M.; Marcaccio, M.; McCleverty, J. A.; Rees, L. H.; Ward, M. D., *Journal of the Chemical Society, Dalton Transactions* **1999**, 2417-2426.
68. Bayly, S. R.; Humphrey, E. R.; de Chair, H.; Paredes, C. G.; Bell, Z. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D.; Totti, F.; Gatteschi, D.; Courric, S.; Steele, B. R.; Screttas, C. G., *Journal of the Chemical Society, Dalton Transactions* **2001**, 1401-1414.
69. McDonagh, A. M.; Ward, M. D.; McCleverty, J. A., *New Journal of Chemistry* **2001**, 25, 1236-1243.
70. McDonagh, A. M.; Bayly, S. R.; Riley, D. J.; Ward, M. D.; McCleverty, J. A.; Cowin, M. A.; Morgan, C. N.; Varrazza, R.; Penty, R. V.; White, I. H., *Chemistry of Materials* **2000**, 12, 2523-2524.
71. Kowallick, R.; Jones, A. N.; Reeves, Z. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D., *New Journal of Chemistry* **1999**, 23, 915-921.
72. Barthram, A. M.; Cleary, R. L.; Kowallick, R.; Ward, M. D., *Chemical Communications* **1998**, 2695-2696.
73. Qi, Y.; Desjardins, P.; Wang, Z. Y., *Journal of Optics A: Pure and Applied Optics* **2002**, 4, S273-S277.
74. Azens, A.; Granqvist, C. G., *Journal of Solid State Electrochemistry* **2003**, 7, 64-68.
75. Lampert, C. M., *Solar Energy Materials and Solar Cells* **1998**, 52, 207-221.
76. Rosseinsky, D. R.; Mortimer, R. J., *Advanced Materials* **2001**, 13, 783-793.

77. Inaba, H.; Iwaku, M.; Nakase, K.; Yasukawa, H.; Seo, I.; Oyama, N., *Electrochimica Acta* **1995**, 40, 227-32.
78. Leventis, N.; Chen, M.; Liapis, A. I.; Johnson, J. W.; Jain, A., *Journal of the Electrochemical Society* **1998**, 145, L55-L58.
79. Yasuda, A.; Seto, J., *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1988**, 247, 193-202.
80. Panero, S.; Scrosati, B.; Baret, M.; Cecchini, B.; Masetti, E., *Solar Energy Materials and Solar Cells* **1995**, 39, 239-46.
81. Passerini, S.; Scrosati, B.; Hermann, V.; Holmblad, C.; Bartlett, T., *Journal of the Electrochemical Society* **1994**, 141, 1025-8.
82. Jelle, B. P.; Hagen, G.; Sunde, S.; Oedegaard, R., *Synthetic Metals* **1993**, 54, 315-20.
83. Takeyasu, T.; Takase, S.; Shimizu, Y., *Chemical Sensors* **2006**, 22, 97-99.
84. Apetrei, C.; Casilli, S.; De Luca, M.; Valli, L.; Jiang, J.; Rodriguez-Mendez, M. L.; De Saja, J. A., *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* **2006**, 284+285, 574-582.
85. Walczak, R. M.; Reynolds, J. R., *Advanced Materials* **2006**, 18, 1121-1131.
86. de Saja, J. A.; Rodriguez-Mendez, M. L., *Advances in Colloid and Interface Science* **2005**, 116, 1-11.
87. Demiryont, H., *Proceedings of SPIE-The International Society for Optical Engineering* **1991**, 1536, 2-28.
88. Buyan, M.; Brühwiler, P. A.; Azens, A.; Gustavsson, G.; Karmhag, R.; Granqvist, C. G., *International Journal of Industrial Ergonomics* **2006**, 36, 11-16.
89. Heckner, K.-H.; Kraft, A., *Solid State Ionics* **2002**, 152-153, 899-905.
90. Sapers, S. P.; Cumbo, M. J.; Sargent, R. B.; Raksha, V. P.; Wang, L. S.; Lahaderne, R. B.; Hichwa, B. P., *Annual Technical Conference Proceedings - Society of Vacuum Coaters* **1996**, 39th, 248-255.
91. Nazeeruddin, M. K.; Grätzel, M., *Conversion and storage of solar energy using dye-sensitized nanocrystalline TiO₂ cells. In Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*. Elsevier, Oxford, **2003**, Vol. 9, p 719-758.
92. Dai, J.; Jiang, X.; Wang, H.; Yan, D., *Applied Physics Letters* **2007**, 91, 253503/1-253503/3.
93. DeBreuil, R.; Nord, S. P.; Cavinato, A. G.; Mayes, D. M.; Lin, M.; Rasco, B. A., *Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002* **2002**, CHED-264.
94. Bonnett, R., *Metal complexes for photodynamic therapy. In Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*. Elsevier, Oxford, **2003**, Vol. 9, p 945-1003.
95. Barone Paul, W.; Baik, S.; Heller Daniel, A.; Strano Michael, S., *Nature materials* **2005**, 4, 86-92.
96. Costello, K. A. GaAs photocathode wavelength extension for back-thinned silicon CMOS OR CCD image array sensors. 2004-7640492005161703, 20040123., 2005.
97. Siddiqi, M. A.; Kilduff, G. M.; Gearhart, J. D., *J Microsc FIELD Full Journal Title:Journal of microscopy* **2003**, 212, 132-43.
98. Norton, P., *Opto-Electronics Review* **2006**, 14, 1-10.

99. Chandrasekhar, P.; Zay, B. J.; Ross, D.; McQueeney, T.; Birur, G. C.; Swanson, T.; Kauder, L.; Douglas, D., *Far-IR-through-Visible Electrochromics Based on Conducting Polymers for Spacecraft Thermal Control and Military Uses. In Chromogenic Phenomena in Polymers: Tunable Optical Properties*. Oxford University Press, Washington DC, **2005**, p 434 pp.
100. Ward, M. D., *Journal of Solid State Electrochemistry* **2005**, 9, 778-787.
101. Wang, Z. Y.; Zhang, J.; Wu, X.; Birau, M.; Yu, G.; Yu, H.; Qi, Y.; Desjardins, P.; Meng, X.; Gao, J. P.; Todd, E.; Song, N.; Bai, Y.; Beaudin, A. M. R.; LeClair, G., *Pure and Applied Chemistry* **2004**, 76, 1435-1443.
102. Card, R. J.; Neckers, D. C., *Journal of the American Chemical Society* **1977**, 99, 7733-4.
103. Muehlebach, A.; Bernhard, P.; Buehler, N.; Karlen, T.; Ludi, A., *Journal of Molecular Catalysis* **1994**, 90, 143-56.
104. Cheng, K. W.; Mak, C. S. C.; Chan, W. K.; Ng, A. M. C.; Djuricic, A. B., *Journal of Polymer Science, Part A: Polymer Chemistry* **2008**, 46, 1305-1317.
105. Desjardins, P. Synthesis and characterization of novel organometallic and organic electrochromic materials. PhD Dissertation, Carleton University, Ottawa, 2001.
106. Xun, S.; LeClair, G.; Zhang, J.; Chen, X.; Gao, J. P.; Wang, Z. Y., *Organic Letters* **2006**, 8, 1697-1700.
107. Wu, D.-Y.; Herbst, R. M., *Journal of Organic Chemistry* **1952**, 17, 1216-27.
108. Lee, K.; Kim, H.-J.; Cho, J. C.; Kim, J., *Macromolecules* **2007**, 40, 6457-6463.
109. Yeh, K.-M.; Chen, Y., *Journal of Polymer Science, Part A: Polymer Chemistry* **2007**, 45, 2259-2272.
110. Li, X.-C.; Spencer, G. C. W.; Holmes, A. B.; Moratti, S. C.; Cacialli, F.; Friend, R. H., *Synthetic Metals* **1996**, 76, 153-6.
111. Ye, X.-Y.; Robl, J. A.; Hanson, R. L.; Guo, Z.; Patel, R. N. Cyclic compounds as 11 β -hydroxysteroid dehydrogenase type 1 inhibitors and their preparation, pharmaceutical compositions and use in the treatment of diseases. 2007-US76593 2008024892, 20070823., 2008.
112. Planken, S. P.; Sutton, S. C.; Chen, R. Preparation of pyrazole derivatives as cytochrome P450 inhibitors. 2007-IB18782008004096, 20070625., 2008.
113. Myers, M. C.; Shah, P. P.; Diamond, S. L.; Huryn, D. M.; Smith, A. B., *Bioorganic & Medicinal Chemistry Letters* **2008**, 18, 210-214.
114. Boschelli, D. H.; Connor, D. T.; Bornemeier, D. A.; Dyer, R. D.; Kennedy, J. A.; Kuipers, P. J.; Okonkwo, G. C.; Schrier, D. J.; Wright, C. D., *Journal of Medicinal Chemistry* **1993**, 36, 1802-10.
115. Khau, V. V.; Martinelli, M. J., *Tetrahedron Letters* **1996**, 37, 4323-4326.
116. Kraebel, C. M.; Davis, S. M., *Journal of Chemical and Engineering Data* **1969**, 14, 133-5.
117. Lisitsyn, V. N.; Bolkvadze, L. I., *Khimiya i Tekhnologiya Krasheniya, Sintez Krasitelei i Polimernykh Materialov* **1981**, 36-41.
118. Kulkarni, P. P.; Kadam, A. J.; Desai, U. V.; Mane, R. B.; Wadgaonkar, P. P., *Journal of Chemical Research, Synopses* **2000**, 184-185.
119. Marcotullio, M. C.; Epifano, F.; Curini, M., *Trends in Organic Chemistry* **2003**, 10, 21-34.

120. Tamhankar, B. V.; Desai, U. V.; Mane, R. B.; Kulkarni, P. P.; Wadgaonkar, P. P., *Synthetic Communications* **2002**, 32, 3643-3646.
121. Jadhav, V. K.; Wadagaonkar, P. P.; Salunkhe, M. M., *Journal of the Chinese Chemical Society* **1998**, 45, 831-833.
122. Hoffman, R. V.; Kumar, A., *Journal of Organic Chemistry* **1984**, 49, 4014-17.
123. Hacking, M. A. P. J.; van Rantwijk, F.; Sheldon, R. A., *Journal of Molecular Catalysis B: Enzymatic* **2000**, 9, 183-191.
124. Liu, Y.; Bei, M.; Zhou, Z.; Takaki, K.; Fujiwara, Y., *Chemistry Letters* **1992**, 1143-4.
125. Neveux, M.; Bruneau, C.; Lecolier, S.; Dixneuf, P. H., *Tetrahedron* **1993**, 49, 2629-40.
126. Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J., *Inorganic Chemistry* **2005**, 44, 6802-6827.
127. Eskelinen, E.; Luukkanen, S.; Haukka, M.; Ahlgren, M.; Pakkanen, T. A., *Dalton* **2000**, 2745-2752.
128. Belser, P.; Von Zelewsky, A. Synthese, spektroskopische Eigenschaften und elektrochemisches Verhalten von Ruthenium(II)-Komplexen mit zweizähligen Stickstoffliganden. 1980.
129. Thimmaiah, M.; Fang, S., *Tetrahedron* **2007**, 63, 6879-6886.
130. More, S. V.; Sastry, M. N. V.; Wang, C.-C.; Yao, C.-F., *Tetrahedron Letters* **2005**, 46, 6345-6348.
131. Koenig, E.; Thoma, W.; Pedain, J.; Koenig, K. Thermosetting reactive polyurethane coating composition poor in solvent and its use in a direct or conversion coating process. 82-10403465688, 19820510., 1982.
132. Wolfs, I.; Desseyn, H. O.; Perlepes, S. P., *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* **1994**, 50A, 1141-52.
133. Gojon-Zorrilla, G. A preparation of amides via amidation of esters. 2004-858057 2005027120, 20040602., 2005.
134. Qi, Y.; Wang, Z. Y., *Macromolecules* **2003**, 36, 3146-3151.
135. Broussard, F.; Neri, C.; Somenzi, F. Process for the manufacture of symmetrical diacylhydrazines. WO 2000034227, 1999/12/03., 2000.
136. Broussard, F.; Neri, C.; Somenzi, F. Process for the preparation of symmetrical diacylhydrazines. US 6,444,848 B1, 1999/12/03, 2002.
137. Wu, D.-Y.; Herbst, R. M., *Journal of Organic Chemistry* **1952**, 17, 1216-27.
138. Cariati, F.; Caruso, U.; Centore, R.; De Maria, A.; Fusco, M.; Panunzi, B.; Roviello, A.; Tuzi, A., *Optical Materials (Amsterdam, Netherlands)* **2004**, 27, 91-97.
139. Hou, J.-L.; Shao, X.-B.; Chen, G.-J.; Zhou, Y.-X.; Jiang, X.-K.; Li, Z.-T., *Journal of the American Chemical Society* **2004**, 126, 12386-12394.
140. Furdik, M.; Mikulasek, S.; Livar, M.; Priehradny, S., *Chemicke Zvesti* **1967**, 21, 427-42.
141. Hammami, A.; Cavalie-Kosheiry, H.; Armand, M., *Bulletin of the Chemical Society of Japan* **2004**, 77, 165-167.
142. Shah, M. H.; Mhasalkar, M. Y.; Patki, V. M.; Deliwala, C. V.; Sheth, U. K., *Journal of Pharmaceutical Sciences* **1969**, 58, 1398-401.
143. Rice, L. M.; Grogan, C. H.; Reid, E. E., *Journal of the American Chemical Society* **1953**, 75, 242-3.

144. Trout, G. E.; Levy, P. R., *Recueil des Travaux Chimiques des Pays-Bas* **1966**, 85, 765-73.
145. Wen, Y. H.; Shen, X.; Bi, S.; Zhang, S. S., *Acta Crystallographica, Section E: Structure Reports Online* **2006**, E62, o3780-o3781.
146. Stylianides, N.; Danopoulos, A. A.; Pugh, D.; Hancock, F.; Zanotti-Gerosa, A., *Organometallics* **2007**, 26, 5627-5635.
147. Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E., *Inorganic Chemistry* **2002**, 41, 3055-3066.
148. Keus, D.; Kaminski, M.; Warkentin, J., *Journal of Organic Chemistry* **1984**, 49, 343-7.
149. Xun, S.; LeClair, G.; Zhang, J.; Xin, C.; Gao, J. P.; Wang Zhi, Y., *Organic Letters* **2006**, 8, 1697-1700.
150. Borek, C.; Hanson, K.; Djurovich, P. I.; Thompson, M. E.; Aznavour, K.; Bau, R.; Sun, Y.; Forrest, S. R.; Brooks, J.; Michalski, L.; Brown, J., *Angewandte Chemie, International Edition* **2007**, 46, 1109-1112.
151. Brinas, R. P.; Troxler, T.; Hochstrasser, R. M.; Vinogradov, S. A., *Journal of the American Chemical Society* **2005**, 127, 11851-11862.
152. Cocchi, M.; Virgili, D.; Fattori, V.; Williams, J. A. G.; Kalinowski, J., *Applied Physics Letters* **2007**, 90, 023506/1-023506/3.
153. Dienel, T.; Proehl, H.; Fritz, T.; Leo, K., *Journal of Luminescence* **2004**, 110, 253-257.
154. O'Riordan, T. C.; Fitzgerald, K.; Ponomarev, G. V.; Mackrill, J.; Hynes, J.; Taylor, C.; Papkovsky, D. B., *American Journal of Physiology* **2007**, 292, R1613-R1620.
155. Kim, D. U.; Paik, S.-H.; Kim, S.-H.; Tak, Y.-H.; Kim, S.-D.; Han, Y.-S.; Kim, T.-J.; Ko, T.-H.; Yoon, U.-C.; Mariano, P. S., *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* **2008**, 313+314, 444-447.
156. Cardolaccia, T.; Li, Y.; Schanze, K. S., *Journal of the American Chemical Society* **2008**, 130, 2535-2545.
157. Zhou, G.-J.; Wang, X.-Z.; Wong, W.-Y.; Yu, X.-M.; Kwok, H.-S.; Lin, Z., *Journal of Organometallic Chemistry* **2007**, 692, 3461-3473.
158. Yan, B.-P.; Cheung, C. C. C.; Kui, S. C. F.; Xiang, H.-F.; Roy, V. A. L.; Xu, S.-J.; Che, C.-M., *Advanced Materials* **2007**, 19, 3599-3603.
159. Saito, T.; Asakura, N.; Kamachi, T.; Okura, I., *Journal of Porphyrins and Phthalocyanines* **2007**, 11, 160-164.
160. Niedermair, F.; Waich, K.; Kappaun, S.; Mayr, T.; Trimmel, G.; Mereiter, K.; Slugovc, C., *Inorganica Chimica Acta* **2007**, 360, 2767-2777.
161. Wong, W.-Y.; Poon, S.-Y.; Shi, J.-X.; Cheah, K.-W., *Journal of Polymer Science, Part A: Polymer Chemistry* **2006**, 44, 4804-4824.
162. Scriban, C.; Wicht, D. K.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L., *Organometallics* **2006**, 25, 3370-3378.
163. Jain, V. K.; Jain, L., *Coordination Chemistry Reviews* **2005**, 249, 3075-3197.
164. Klein, A., *Reviews in Inorganic Chemistry* **2000**, 20, 283-303.
165. Anderson, G. K.; Nair, P.; Rath, N. P., *Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000* **2000**, INOR-151.
166. Steenwinkel, P.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Van Koten, G., *Organometallics* **1998**, 17, 5411-5426.

167. Jain, N.; Mittal, R.; Srivastava, T. S.; Satyamoorthy, K.; Chitnis, M. P., *Journal of Inorganic Biochemistry* **1994**, 53, 79-94.
168. Mansuri-Torshizi, H.; Srivastava, T. S.; Parekh, H. K.; Chitnis, M. P., *Journal of Inorganic Biochemistry* **1992**, 45, 135-48.
169. Gokagac, G.; Isci, H.; Mason, W. R., *Inorganic Chemistry* **1992**, 31, 2184-91.
170. Gruff, E. S.; Orgel, L. E., *Nucleic Acids Research* **1991**, 19, 6849-54.
171. Harvey, P. D.; Gray, H. B., *Polyhedron* **1990**, 9, 1949-53.
172. Pelova, R.; Wolowiec, S.; Spasovska, N.; Ivin, A., *Nauchni Trudove - Plovdivski Universitet Paisii Khilendarski* **1987**, 25, 11-20.
173. Whangbo, M. H.; Canadell, E., *Inorganic Chemistry* **1986**, 25, 1726-8.
174. Vlasov, V. V.; Kazakov, S. A., *Bioorganicheskaya Khimiya* **1983**, 9, 530-8.
175. Muraveiskaya, G. S.; Orlova, V. S.; Golovaneva, I. F.; Shchelokov, R. N., *Zhurnal Neorganicheskoi Khimii* **1981**, 26, 3300-7.
176. Bancroft, G. M.; Chan, T.; Puddenphatt, R. J.; Brown, M. P., *Inorganica Chimica Acta* **1981**, 53, L119-L120.
177. Abel, E. W.; Khan, A. R.; Kite, K.; Orrell, K. G.; Sik, V., *Journal of the Chemical Society, Dalton Transactions* **1980**, 2208-19.
178. Kuehn, A.; Werner, H., *Journal of Organometallic Chemistry* **1979**, 179, 421-38.
179. Balch, A. L.; Benner, L. S.; Olmstead, M. M., *Inorganic Chemistry* **1979**, 18, 2996-3003.
180. Takeda, A.; Igarashi, T. Organic electroluminescent device and complex compound. 2006-5183552007059552, 20060911., 2007.
181. Ma, B.; Djurovich, P. I.; Garon, S.; Alleyne, B.; Thompson, M. E., *Advanced Functional Materials* **2006**, 16, 2438-2446.
182. Ma, B.; Li, J.; Djurovich Peter, I.; Yousufuddin, M.; Bau, R.; Thompson Mark, E., *Journal of the American Chemical Society* **2005**, 127, 28-9.
183. Crutchley, R. J., *Electrochemistry: mixed valence systems. In Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*. Elsevier, Oxford, **2003**, Vol. 2, p 235-244.
184. Ren, X.; Huo, S. Light-emitting devices containing cyclometallated phosphorescent platinum or iridium complexes. 2007-US154402008010915, 20070705., 2008.
185. Yasukawa, N.; Oshiyama, T.; Kato, E. Organic electroluminescent devices having regulated emission wavelength, their materials, displays, and illumination apparatuses therewith. 2005-1896572007009009, 20050629., 2007.
186. Yang, C.-H. Organic light-emitting materials based on transition metal complexes having five-five-membered rings in ligand and organic light-emitting devices employing the materials. 2006-4099342007054150, 20060424., 2007.
187. Ren, X. Blue-emitting organic electroluminescent devices based on a phosphorescent transition metal complex. 2005-216948 2007048546, 20050831., 2007.188. Cocchi, M.; Virgili, D.; Fattori, V.; Rochester, D. L.; Williams, J. A. G., *Advanced Functional Materials* **2007**, 17, 285-289.
189. Chou, P.-T.; Chi, Y., *Chemistry--A European Journal* **2007**, 13, 380-395.
190. Cho, J.-Y.; Domercq, B.; Barlow, S.; Saponitsky, K. Y.; Li, J.; Timofeeva, T. V.; Jones, S. C.; Hayden, L. E.; Kimyonok, A.; South, C. R.; Weck, M.; Kippelen, B.; Marder, S. R., *Organometallics* **2007**, 26, 4816-4829.

191. Camerel, F.; Ziessel, R.; Donnio, B.; Bourgogne, C.; Guillon, D.; Schmutz, M.; Iacovita, C.; Bucher, J.-P., *Angewandte Chemie, International Edition* **2007**, 46, 2659-2662.
192. He, Z.; Wong, W.-Y.; Yu, X.; Kwok, H.-S.; Lin, Z., *Inorganic Chemistry* **2006**, 45, 10922-10937.
193. Liu, Q.-D.; Wang, R.; Wang, S., *Dalton Transactions* **2004**, 2073-2079.
194. Thompson, M. E.; Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Forrest, S. R.; Baldo, M.; Burrows, P. E., *Polymeric Materials Science and Engineering* **2000**, 83, 202-203.
195. Ma, B.; Djurovich, P. I.; Thompson, M. E., *Coordination Chemistry Reviews* **2005**, 249, 1501-1510.
196. Che, C. M.; Wan, K. T.; He, L. Y.; Poon, C. K.; Yam, V. W. W., *Journal of the Chemical Society, Chemical Communications* **1989**, 943-4.
197. Bancroft, D. P. The synthesis and characterization of binuclear complexes of platinum(III). 1986.
198. Lamansky, S.; Kwong, R. C.; Nugent, M.; Djurovich, P. I.; Thompson, M. E., *Organic Electronics* **2001**, 2, 53-62.
199. Hollis, L. S.; Lippard, S. J., *Journal of the American Chemical Society* **1981**, 103, 6761-3.
200. Bryan, S. A. Thermal, photochemical and electrochemical reactions of dinuclear platinum(III) complexes. 1985.
201. Kvam, P.-I.; Puzyk, M. V.; Balashev, K. P.; Songstad, J., *Acta Chemica Scandinavica* **1995**, 49, 335-43.
202. Williams, A. T. R.; Sinfield, S. A.; Miller, J. N., *Analyst* **1983**, 108, 1067-1071.
203. Kaim, W.; Kasack, V., *Inorganic Chemistry* **1990**, 29, 4696-9.
204. Sullivan, B. P.; Salmon, D. J.; Meyer, T. J., *Inorganic Chemistry* **1978**, 17, 3334-41.
205. Cowie, J. M. G., *Polymers: chemistry and physics of modern materials*. Chapman & Hall, Cheltenham, **2001**, p 436.
206. Newkome, G. R.; Moorefield, C. N.; Vogtle, F., *Dendrimers and Dendrons: Concepts, Syntheses, Applications*. John Wiley & Sons, Weinheim, **2001**, p 635.
207. Rau, H.; Waldner, I., *Physical Chemistry Chemical Physics* **2002**, 4, 1776-1780.
208. Vercruysse, K. P.; Marecak, D. M.; Marecek, J. F.; Prestwich, G. D., *Bioconjugate Chemistry* **1997**, 8, 686-694.
209. Ito, Y.; Matsuura, T., *Journal of Photochemistry and Photobiology, A: Chemistry* **1989**, 50, 141-6.
210. Ito, Y.; Kajita, T.; Kunitomo, K.; Matsuura, T., *Journal of Organic Chemistry* **1989**, 54, 587-91.
211. Szilagy, L.; Kasa, I.; Bitter, I., *Periodica Polytechnica, Chemical Engineering* **1973**, 17, 125-33.
212. Zhang, G.; Fang, L.; Zhu, L.; Sun, D.; Wang, P. G., *Bioorganic & Medicinal Chemistry* **2006**, 14, 426-434.
213. Adams, C. J.; Bowen, L. E.; Humphrey, M. G.; Morrall, J. P. L.; Samoc, M.; Yellowlees, L. J., *Dalton Transactions* **2004**, 4130-4138.
214. Wong, C.-Y.; Chan, M. C. W.; Zhu, N.; Che, C.-M., *Organometallics* **2004**, 23, 2263-2272.

215. Brinker, C. J.; Scherer, G. W., *Sol-gel science : the physics and chemistry of sol-gel processing*. Academic Press, Inc., Boston, **1990**, p 908.
216. Chen, S.-l.; Xu, C.-g.; Zhao, K.-q.; Hu, P., *Sichuan Shifan Daxue Xuebao, Ziran Kexueban* **2000**, 23, 511-512.
217. Franklin, J. D. Development and optimisation of polymeric matrices for use in biomolecular devices. Dissertation, Carleton University, Ottawa, 2003.
218. Azarnia, R.; Fuentes, S.; Russel, T. Apparatus for measuring analytes in a fluid sample. 96-US41139630751, 19960326., 1996.
219. Barie, N. *Development of a universal process for biofunctionalization of surfaces to be used in sensor technology by surface acoustic wave (SAW) devices*; Inst. Instrumentelle Analytik, Germany.: 2000; pp i-xvi, 1-171, A1-A34.
220. Bharathi, S.; Lev, O., *Applied Biochemistry and Biotechnology* **2000**, 89, 209-216.
221. de Marcos, S.; Galindo, J.; Sierra, J. F.; Galban, J.; Castillo, J. R., *Sensors and Actuators, B: Chemical* **1999**, B57, 227-232.
222. Desprez, V.; Oranth, N.; Spinke, J.; Tusa, J. K. Nanoparticles for optical sensors. 2004-161511496126, 20040708., 2005.
223. Endo, H. Biosensor oxygen-sensitive optical fiber and oxidase, and its production method. 2006-JP3023532006090596, 20060210., 2006.
224. Jiang, D.; Liu, E.; Chen, X.; Huang, J., *Chinese Optics Letters* **2003**, 1, 108-110.
225. Kuenzelmann, U.; Boettcher, H., *Sensors and Actuators, B: Chemical* **1997**, B39, 222-228.
226. McCurley, M. F.; Seitz, W. R., *ACS Symposium Series* **1992**, 487, 301-9.
227. Osada, T. Optical enzyme biosensor. 92-20304006027023, 19920707., 1994.
228. Saito, A.; Shionoya, K. Microscopic system for evaluating defect of biosensor membrane. 91-35078305196578, 19911212., 1993.
229. Schueler, R.; Wittkamp, M.; Chemnitius, G. C.; Sperveslage, G.; Grobe, J. Biosensor consisting of a membrane-coated transducer and an immobilized biological component. 97-1971187919711879, 19970321., 1998.
230. Shah, R.; Margerum, S. C.; Gold, M., *Proceedings of SPIE-The International Society for Optical Engineering* **1988**, 906, 65-73.
231. Trettnak, W.; Wolfbeis, O. S., *Analytica Chimica Acta* **1989**, 221, 195-203.
232. Turner, R. F. B.; Kilburn, D. G.; Phelps, M. R. Biosensor and interface membrane. 94-3093385624537, 19940920., 1997.
233. Olea, D.; Viratelle, O.; Faure, C., *Biosensors & Bioelectronics* **2008**, 23, 788-794.
234. Xu, L.; Zhu, Y.; Tang, L.; Yang, X.; Li, C., *Electroanalysis* **2007**, 19, 717-722.
235. Reyes-De-Corcuera, J. I.; Cavalieri, R. P.; Powers, J. R.; Tang, J.; Kang, D. H., *Journal of Agricultural and Food Chemistry* **2005**, 53, 8866-8873.
236. Alonso Lomillo, M. A.; Ruiz, J. G.; Pascual, F. J. M., *Analytica Chimica Acta* **2005**, 547, 209-214.
237. Mailley, P.; Cummings, E. A.; Mailley, S.; Cosnier, S.; Eggins, B. R.; McAdams, E., *Bioelectrochemistry* **2004**, 63, 291-296.
238. Guemas, Y.; Boujtita, M.; El Murr, N., *Applied Biochemistry and Biotechnology* **2000**, 89, 171-181.
239. Guiomar, A. J.; Evans, S. D.; Guthrie, J. T., *Supramolecular Science* **1997**, 4, 279-291.
240. Varadi, M.; Adanyi, N.; Szabo, E. E., *Acta Alimentaria* **1995**, 24, 365-377.

241. Bilitewski, U.; Chemnitius, G. C.; Rueger, P.; Schmid, R. D., *Sensors and Actuators, B: Chemical* **1992**, B7, 351-5.
242. Fortier, G.; Brassard, E.; Belanger, D., *Biosensors & Bioelectronics* **1990**, 5, 473-90.
243. Lomen, C. E.; De Alwis, U.; Wilson, G. S., *Journal of the Chemical Society, Faraday Transactions 1* **1986**, 82, 1265-70.
244. Reyes-De-Corcuera Jose, I.; Cavalieri Ralph, P.; Powers Joseph, R.; Tang, J.; Kang Dong, H., *Journal of agricultural and food chemistry* **2005**, 53, 8866-73.
245. Deacon, A. C.; Dawson, P. J., *Clinical chemistry* **1979**, 25, 976-84.
246. Ozimek, P.; Veenhuis, M.; van der Klei, I. J., *FEMS Yeast Research* **2005**, 5, 975-983.
247. Ralph, E. C.; Hirschi, J. S.; Anderson, M. A.; Cleland, W. W.; Singleton, D. A.; Fitzpatrick, P. F., *Biochemistry* **2007**, 46, 7655-7664.
248. Rahman, M. A.; Kwon, N.-H.; Won, M.-S.; Choe, E. S.; Shim, Y.-B., *Analytical Chemistry* **2005**, 77, 4854-4860.
249. Cai, H.; Zhang, X. M.; Lu, C.; Liu, A. Q., *IEEE Sensors 2005, 4th IEEE Conference on Sensors, Irvine, CA, United States, Oct. 30-Nov. 3, 2005* **2005**, 1, 508-511.
250. Lee, C., *Sensors and Actuators, A: Physical* **2005**, A123-A124, 596-601.
251. Wu, Y.-H.; Lin, Y.-H.; Lu, Y.-Q.; Ren, H.; Fan, Y.-H.; Wu, J. R.; Wu, S.-T., *Proceedings of SPIE-The International Society for Optical Engineering* **2005**, 5936, 59360J/1-59360J/8.
252. O'Brien, N. A.; Mathew, J. G. H.; Hichwa, B. P., *OFC Proceedings, Optical Fiber Communication Conference* **1999**, Supplement, PD26/21-PD26/23.
253. Cifuentes, M. P.; Powell, C. E.; Morrall, J. P.; McDonagh, A. M.; Lucas, N. T.; Humphrey, M. G.; Samoc, M.; Houbrechts, S.; Asselberghs, I.; Clays, K.; Persoons, A.; Isoshima, T., *Journal of the American Chemical Society* **2006**, 128, 10819-10832.
254. McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Houbrechts, S.; Wada, T.; Sasabe, H.; Persoons, A., *Journal of the American Chemical Society* **1999**, 121, 1405-1406.
255. Powell, C. E.; Cifuentes, M. P.; Morrall, J. P.; Stranger, R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Heath, G. A., *Journal of the American Chemical Society* **2003**, 125, 602-610.
256. Powell, C. E.; Morrall, J. P.; Ward, S. A.; Cifuentes, M. P.; Notaras, E. G. A.; Samoc, M.; Humphrey, M. G., *Journal of the American Chemical Society* **2004**, 126, 12234-12235.
257. Jin, Y.-S.; Lee, S.-S.; Son, Y.-S., *Electronics Letters* **1999**, 35, 916-917.
258. Kawai, T.; Koga, M.; Okuno, M.; Kitoh, T., *Electronics Letters* **1998**, 34, 264-265.
259. Kim, S.; Hung, Y.-C.; Geary, K.; Yuan, W.; Fetterman, H. R.; Jin, D.; Dinu, R.; Steier, W. H., *IEEE Photonics Technology Letters* **2006**, 18, 1055-1057.
260. Ma, H.; Jen, A. K. Y.; Dalton, L. R., *Advanced Materials* **2002**, 14, 1339-1365.
261. Uetsuka, H., *IEEE Journal of Selected Topics in Quantum Electronics* **2004**, 10, 393-402.
262. Wolfs, I.; Desseyn, H. O.; Perlepes, S. P., *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* **1994**, 50A, 1141-52.

- 263. Qi, Y. H.; Desjardins, P.; Meng, X. S.; Wang, Z. Y., *Optical Materials* **2003**, 21, 255-263.
- 264. Zhang, J.; Wu, X.; Yu, H.; Yan, D.; Wang, Z., *Chinese Science Bulletin* **2005**, 50, 2688-2690.
- 265. Deng, X.; Zheng, X.; Cao, Z.; Shen, Q.; Li, H., *Applied Physics Letters* **2007**, 90, 151124/1-151124/3.
- 266. Curtis, H. D., *Publications of the Astronomical Society of the Pacific* **1911**, 23, 13-32.
- 267. LeClair, G; Wang, Z.Y., *Journal of Solid State Electrochemistry* published online May 6th 2008 (DOI: 10.1007/s10008-008-0562-y)
- 268. Xun, S.; LeClair, G.; Zhang, J.; Chen, X.; Gao, J. P.; Wang, Z. Y., *Organic Letters* **2006**, 8, 1697-1700.

Appendices

Appendix 1 – ^1H and ^{13}C NMR spectra of ligands

4-hydroxy-N'-propionylbutanehydrazide (1)

Current Data Parameters
NAME G148
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080416
Time 14.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 64
DW 80.800 usec
DE 6.00 usec
TE 295.9 K
D1 1.00000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME G148
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080416
Time 15.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 192
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DW 27.733 usec
DE 6.00 usec
TE 296.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TDO 1

----- CHANNEL f1 -----
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727780 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

6-hydroxy-N'-propionylhexanehydrazide (2)

2-(4-hydroxybutanoyl)-N-propylhydrazinecarboxamide (3)

Current Data Parameters
 NAME G144
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080416
 Time 14.40
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6188.119 Hz
 FIDRES 0.188846 Hz
 AQ 2.6477044 sec
 RG 64
 DW 80.800 usec
 DE 6.00 usec
 TE 295.8 K
 D1 1.00000000 sec
 TDO 1

----- CHANNEL f1 -----
 NUC1 1H
 PL1 12.00 usec
 PL1 0.00 dB
 SFO1 300.1518535 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1500000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Current Data Parameters
 NAME G144
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080416
 Time 14.50
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg
 TD 32768
 SOLVENT DMSO
 NS 204
 DS 4
 SWH 18028.846 Hz
 FIDRES 0.550197 Hz
 AQ 0.9088159 sec
 RG 181
 DW 27.733 usec
 DE 6.00 usec
 TE 296.3 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TDO 1

----- CHANNEL f1 -----
 NUC1 13C
 PL1 9.50 usec
 PL1 -1.00 dB
 SFO1 75.4803248 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 0.00 dB
 PL12 18.42 dB
 PL13 21.34 dB
 SFO2 300.1512006 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4727780 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

2-(6-hydroxyhexanoyl)-N-propylhydrazinecarboxamide (4)

Current Data Parameters
NAME G143
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20051219
Time 10.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.647704 sec
RG 32
DW 80.800 usec
DE 6.00 usec
TE 299.0 K
D1 1.00000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1499984 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Current Data Parameters
NAME G143
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 20051219
Time 10.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 128
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DW 27.733 usec
DE 6.00 usec
TE 299.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TDO 1

----- CHANNEL f1 -----
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727780 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

6-hydroxy-N'-(6-hydroxyhexanoyl)hexanehydrazide (5)

*N*¹,*N*²-bis(3-hydroxypropyl)hydrazine-1,2-dicarboxamide (6)

*N*¹,*N*²-bis(5-hydroxypentyl)hydrazine-1,2-dicarboxamide (**7**)

*N*¹,*N*²-bis(1,3-dihydroxy-2-methylpropan-2-yl)hydrazine-1,2-dicarboxamide (**8**)

4-hydroxy-N'-(4-hydroxypiperidine-1-carbonyl)piperidine-1-carbohydrazide (10)

4-(hydroxymethyl)-N'-(4-(hydroxymethyl)piperidine-1-carbonyl)piperidine-1-carbohydrazide (11)

*N*¹-(5-hydroxypentyl)-*N*²-propyloxalamide (12)

*N*¹,*N*²-bis(4-aminobenzyl)hydrazine-1,2-dicarboxamide (**21**)

Current Data Parameters
NAME G153
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060316
Time 10.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 181
DW 80.800 usec
DE 6.00 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME G153
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060316
Time 10.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DW 27.733 usec
DE 6.00 usec
TE 296.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4728131 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,3'-(hydrazine-1,2-diylbis(oxomethylene))bis(azanediy) dipropionic acid (22)

4-methyl-N'-(4-methylpiperidine-1-carbonyl)piperidine-1-carbohydrazide (23)

[{Ru(bpy)₂}₂μ-(4-hydroxymethyl piperidine)₂-dicarbonyl hydrazine](PF₆)₂ (39I)

$[\{Ru(bpy)_2\}_2\mu-(4\text{-hydroxymethyl piperidine})_2\text{-dicarbonyl hydrazine}](PF_6)_2$ (**39I**)

Structure model with atom numbering for resonance assignments (half the molecule is masked for clarity)

3-D model of **39** showing spacial interactions as seen from NOESY

$[\{Ru(bpy)_2\}_2\mu-((CH_2)_5OH)_2\text{-oxamide}](PF_6)_2$ (41)

Structure model with atom numbering for resonance assignments (half the molecule is masked for clarity)

3-D model of **41** showing spacial interactions as seen from NOESY

[{Pt(ppy)₂}₂μ-(heptyl)₂-dicarbonyl hydrazine] (44)

Current Data Parameters
NAME G237
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080220
Time 19.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 71.8
DW 80.800 usec
DE 6.00 usec
TE 295.1 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518935 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME G237
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080220
Time 22.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4000
DS 2
SWH 18028.845 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 19.1
DW 27.733 usec
DE 6.00 usec
TE 295.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 -1.80 dB
SFO1 75.4603140 MHz

===== CHANNEL f2 =====
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727788 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

[{Pt(ppy)₂}₂μ-(4-methoxyphenyl)₂-dicarbonyl hydrazine] (45)

Current Data Parameters
NAME g239
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071127
Time 16.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 114
DW 80.800 usec
DE 6.00 usec
TE 295.5 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME g239
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071127
Time 16.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DW 27.733 usec
DE 6.00 usec
TE 296.0 K
D1 2.0000000 sec
d11 0.0300000 sec
DELTA 1.8999999 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727780 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

[{Pt(ppy)}₂μ-(4-nitrophenyl)₂-dicarbonyl hydrazine] (46)

Current Data Parameters
NAME G240
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20071128
Time 8.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 181
DW 80.800 usec
DE 6.00 usec
TE 295.3 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME G240
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date 20071128
Time 22.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 6000
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 2050
DW 27.733 usec
DE 6.00 usec
TE 296.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727780 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

[{Pt(2-Phenyl-quinoline)₂}₂μ-(methyl)₂-dicarbonyl hydrazine] (47)

Current Data Parameters
NAME G260
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080504
Time 20.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 114
DW 80.800 usec
DE 6.00 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz
F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME G260
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080504
Time 20.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 6000
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DW 27.733 usec
DE 6.00 usec
TE 296.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz
F2 - Processing parameters
SI 32768
SF 75.4727780 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

[{Pt(2-Methyl-3-phenyl-quinoxaline)₂}₂μ-(methyl)₂-dicarbonyl hydrazine] (48)

$[\{ \text{Pt}(2\text{-Methyl-3-phenyl-benzo}[g]\text{quinoxaline})_2 \}_2 \mu\text{-(methyl)}_2\text{-dicarbonyl hydrazine}]$ (49)

Current Data Parameters
NAME G262 F2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080512
Time_ 11.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 181
DW 80.800 usec
DE 6.00 usec
TE 296.0 K
D1 1.0000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

5-[N'-(6-Hydroxy-hexanoyl)-hydrazinocarbonyl]-isophthalic acid dimethyl ester (**50**)

3,5-bis(phenylhydrazido) bromobenzene (53)

Tri-boronic acid G1 dendrimer core (56)

Cinnamoyl-terminated tetraDCH G1 dendrimer (58)

Current Data Parameters
NAME G171
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060725
Time 10.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 90.3
DW 80.800 usec
DE 6.00 usec
TE 296.4 K
D1 1.0000000 sec
TDO 1

***** CHANNEL f1 *****
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME G171
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060725
Time 12.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT DMSO
NS 2000
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 144
DW 27.733 usec
DE 6.00 usec
TE 296.4 K
D1 2.0000000 sec
d11 0.0300000 sec
DELTA 1.8999999 sec
TDO 1

***** CHANNEL f1 *****
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727780 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

4-[N'-(6-Hydroxy-hexanoyl)-hydrazinocarbonyl]-benzoic acid methyl ester (60pre)

Propargyl oxamide (61)

Current Data Parameters
NAME diacetylene oxamide
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080511
Time 21.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 101
DW 80.400 usec
DE 6.00 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.1518535 MHz

F2 - Processing parameters
SI 32768
SF 300.1500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME diacetylene oxamide
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080511
Time 21.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT DMSO
NS 215
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 181
DW 27.733 usec
DE 6.00 usec
TE 296.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TD0 1

----- CHANNEL f1 -----
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
SFO1 75.4803248 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.42 dB
PL13 21.34 dB
SFO2 300.1512006 MHz

F2 - Processing parameters
SI 32768
SF 75.4727780 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Appendix 2 – NMR of green impurity from biurea complex

NMR of 36G

Appendix 3 – NMR of piperidine biurea complex soluble in DCM

NMR of 39S

Appendix 4 – Quantum yield determination of 44

Alq ₃			44		
Concentration (μM)	Absorbance	PL (494 nm)	Concentration (μM)	Absorbance	PL (494 nm)
0.4	0.02358	18.417	0.4	0.05425006	1.674
0.6	0.02997	25.436	0.6	0.07502662	2.024
0.8	0.04419	35.264	0.8	0.10391437	2.435
1	0.05442	42.344	1	0.12449421	2.855
1.5	0.08317	61.229	1.5	0.18461071	3.788

refractive index of DCM = 1.4241

refractive index of THF = 1.4072

Appendix 5 – Crystallography data of 46

Table 1. Crystal data and structure refinement for **46**.

Identification code	46	
Empirical formula	C ₇₄ H ₅₂ Cl ₄ N ₁₂ O ₁₂ Pt ₄	
Formula weight	2223.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5869(7) Å	α = 112.5950(10)°.
	b = 14.8974(14) Å	β = 91.5210(10)°.
	c = 17.0460(16) Å	γ = 90.1320(10)°.
Volume	1778.0(3) Å ³	
Z	1	
Density (calculated)	2.077 Mg/m ³	
Absorption coefficient	8.067 mm ⁻¹	
F(000)	1056	
Crystal size	0.21 x 0.08 x 0.08 mm ³	
Theta range for data collection	1.48 to 26.07°.	
Index ranges	-9 ≤ h ≤ 8, -15 ≤ k ≤ 18, -21 ≤ l ≤ 19	
Reflections collected	9936	
Independent reflections	6846 [R(int) = 0.0221]	
Completeness to theta = 26.07°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5829 and 0.2860	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6846 / 0 / 475	
Goodness-of-fit on F ²	1.005	
Final R indices [I > 2σ(I)]	R1 = 0.0339, wR2 = 0.0924	
R indices (all data)	R1 = 0.0388, wR2 = 0.0968	
Largest diff. peak and hole	1.645 and -2.190 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 46. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	2597(1)	-5175(1)	3977(1)	35(1)
Pt(2)	3457(1)	-8185(1)	1782(1)	34(1)
N(1)	7336(8)	-9833(4)	4795(4)	65(2)
N(2)	3699(6)	-7124(3)	2960(3)	36(1)
N(3)	3501(6)	-6189(3)	2898(3)	35(1)
N(4)	5360(11)	-2705(5)	1627(5)	85(2)
N(5)	1857(6)	-4240(3)	5114(3)	39(1)
N(6)	3180(6)	-9075(3)	556(3)	38(1)
O(1)	7186(9)	-9741(4)	5535(4)	92(2)
O(2)	8141(11)	-10486(5)	4280(4)	111(2)
O(3)	3776(5)	-6206(2)	4384(2)	40(1)
O(4)	4480(5)	-6991(3)	1555(2)	43(1)
O(5)	5871(12)	-1982(4)	2222(5)	124(3)
O(6)	5044(14)	-2746(5)	901(5)	138(3)
C(1)	6448(8)	-9122(4)	4518(4)	48(1)
C(2)	5590(10)	-8373(5)	5098(4)	60(2)
C(3)	4739(8)	-7695(4)	4840(3)	46(1)
C(4)	4777(7)	-7806(4)	3989(3)	37(1)
C(5)	5663(7)	-8581(4)	3416(3)	42(1)
C(6)	6497(8)	-9238(4)	3669(4)	49(1)
C(7)	3994(7)	-7013(4)	3763(3)	36(1)
C(8)	4121(7)	-6200(4)	2181(3)	37(1)
C(9)	4423(7)	-5280(4)	2057(3)	41(1)
C(10)	5120(8)	-4452(4)	2716(4)	45(1)
C(11)	5418(8)	-3605(4)	2571(4)	52(2)
C(12)	5020(10)	-3615(5)	1773(4)	60(2)
C(13)	4391(10)	-4425(5)	1123(4)	62(2)
C(14)	4127(9)	-5264(4)	1253(4)	53(2)
C(15)	1289(7)	-4226(4)	3622(3)	41(1)
C(16)	861(8)	-4283(4)	2808(4)	50(1)
C(17)	51(9)	-3520(5)	2658(5)	63(2)

C(18)	-392(10)	-2681(5)	3337(5)	70(2)
C(19)	-98(9)	-2626(4)	4163(4)	57(2)
C(20)	727(7)	-3412(4)	4300(4)	47(1)
C(21)	1007(7)	-3425(4)	5131(4)	44(1)
C(22)	486(8)	-2743(5)	5910(4)	58(2)
C(23)	833(9)	-2890(5)	6652(4)	62(2)
C(24)	1689(8)	-3720(5)	6611(4)	57(2)
C(25)	2188(8)	-4385(5)	5832(4)	50(1)
C(26)	2319(7)	-9317(4)	1926(3)	37(1)
C(27)	1827(7)	-9435(4)	2663(3)	45(1)
C(28)	1067(8)	-10283(5)	2641(4)	56(2)
C(29)	794(10)	-11082(5)	1879(4)	64(2)
C(30)	1241(10)	-10974(5)	1144(4)	60(2)
C(31)	1975(8)	-10117(4)	1145(3)	43(1)
C(32)	2420(7)	-9957(4)	378(3)	41(1)
C(33)	2099(8)	-10584(4)	-458(4)	52(2)
C(34)	2540(8)	-10303(5)	-1099(4)	54(2)
C(35)	3351(8)	-9414(5)	-916(4)	52(2)
C(36)	3631(8)	-8811(4)	-81(3)	45(1)
C(37)	1605(15)	-3627(7)	-880(6)	104(3)
Cl(1)	17(4)	-3033(2)	-1244(2)	67(1)
Cl(2)	-282(11)	-3068(6)	-1035(5)	72(2)
Cl(3)	1001(12)	-4492(7)	-529(6)	95(2)
Cl(4)	141(19)	-3619(10)	268(9)	144(4)
Cl(5)	877(12)	-4000(7)	-142(6)	118(2)

Table 3. Bond lengths [Å] and angles [°] for 46.

Pt(1)-C(15)	1.995(6)	C(11)-C(12)	1.380(9)	N(5)-Pt(1)-N(3)	173.81(17)
Pt(1)-N(5)	2.000(4)	C(12)-C(13)	1.361(10)	C(15)-Pt(1)-O(3)	175.24(18)
Pt(1)-N(3)	2.018(4)	C(13)-C(14)	1.367(9)	N(5)-Pt(1)-O(3)	97.70(16)
Pt(1)-O(3)	2.106(4)	C(15)-C(16)	1.386(8)	N(3)-Pt(1)-O(3)	76.25(15)
Pt(2)-C(26)	1.993(5)	C(15)-C(20)	1.393(8)	C(26)-Pt(2)-N(6)	80.99(19)
Pt(2)-N(6)	2.003(4)	C(16)-C(17)	1.397(9)	C(26)-Pt(2)-N(2)	106.25(19)
Pt(2)-N(2)	2.027(4)	C(17)-C(18)	1.387(9)	N(6)-Pt(2)-N(2)	171.57(17)
Pt(2)-O(4)	2.111(4)	C(18)-C(19)	1.391(10)	C(26)-Pt(2)-O(4)	175.03(18)
N(1)-O(2)	1.210(8)	C(19)-C(20)	1.422(8)	N(6)-Pt(2)-O(4)	95.96(15)
N(1)-O(1)	1.224(7)	C(20)-C(21)	1.434(8)	N(2)-Pt(2)-O(4)	76.50(15)
N(1)-C(1)	1.473(8)	C(21)-C(22)	1.395(8)	O(2)-N(1)-O(1)	123.4(6)
N(2)-C(7)	1.326(6)	C(22)-C(23)	1.381(10)	O(2)-N(1)-C(1)	118.8(6)
N(2)-N(3)	1.445(6)	C(23)-C(24)	1.377(10)	O(1)-N(1)-C(1)	117.8(6)
N(3)-C(8)	1.314(7)	C(24)-C(25)	1.381(8)	C(7)-N(2)-N(3)	110.4(4)
N(4)-O(5)	1.216(8)	C(26)-C(27)	1.394(7)	C(7)-N(2)-Pt(2)	140.4(4)
N(4)-O(6)	1.233(9)	C(26)-C(31)	1.422(7)	N(3)-N(2)-Pt(2)	109.1(3)
N(4)-C(12)	1.492(8)	C(27)-C(28)	1.374(8)	C(8)-N(3)-N(2)	111.1(4)
N(5)-C(25)	1.339(7)	C(28)-C(29)	1.394(9)	C(8)-N(3)-Pt(1)	136.4(4)
N(5)-C(21)	1.368(7)	C(29)-C(30)	1.373(9)	N(2)-N(3)-Pt(1)	112.1(3)
N(6)-C(36)	1.341(7)	C(30)-C(31)	1.391(8)	O(5)-N(4)-O(6)	124.9(7)
N(6)-C(32)	1.354(7)	C(31)-C(32)	1.463(7)	O(5)-N(4)-C(12)	118.9(7)
O(3)-C(7)	1.275(6)	C(32)-C(33)	1.386(7)	O(6)-N(4)-C(12)	116.2(7)
O(4)-C(8)	1.285(6)	C(33)-C(34)	1.360(9)	C(25)-N(5)-C(21)	120.8(5)
C(1)-C(2)	1.354(9)	C(34)-C(35)	1.377(8)	C(25)-N(5)-Pt(1)	122.5(4)
C(1)-C(6)	1.391(8)	C(35)-C(36)	1.371(8)	C(21)-N(5)-Pt(1)	116.6(4)
C(2)-C(3)	1.400(8)	C(37)-Cl(5)	1.666(13)	C(36)-N(6)-C(32)	119.7(5)
C(3)-C(4)	1.396(7)	C(37)-Cl(3)	1.685(13)	C(36)-N(6)-Pt(2)	122.7(4)
C(4)-C(5)	1.382(7)	C(37)-Cl(2)	1.722(14)	C(32)-N(6)-Pt(2)	117.5(3)
C(4)-C(7)	1.496(7)	C(37)-Cl(1)	1.733(11)	C(7)-O(3)-Pt(1)	111.4(3)
C(5)-C(6)	1.362(8)	Cl(3)-Cl(5)	0.783(10)	C(8)-O(4)-Pt(2)	109.2(3)
C(8)-C(9)	1.483(7)	Cl(3)-Cl(4)	1.630(16)	C(2)-C(1)-C(6)	121.6(6)
C(9)-C(14)	1.393(8)	Cl(4)-Cl(5)	0.916(13)	C(2)-C(1)-N(1)	119.0(6)
C(9)-C(10)	1.401(7)	C(15)-Pt(1)-N(5)	80.3(2)	C(6)-C(1)-N(1)	119.4(5)
C(10)-C(11)	1.395(8)	C(15)-Pt(1)-N(3)	105.8(2)	C(1)-C(2)-C(3)	119.4(6)

C(4)-C(3)-C(2)	119.5(5)	C(16)-C(15)-Pt(1)	128.8(4)	C(30)-C(31)-C(26)	120.1(5)
C(5)-C(4)-C(3)	119.4(5)	C(20)-C(15)-Pt(1)	113.8(4)	C(30)-C(31)-C(32)	124.4(5)
C(5)-C(4)-C(7)	123.0(5)	C(15)-C(16)-C(17)	122.2(6)	C(26)-C(31)-C(32)	115.5(5)
C(3)-C(4)-C(7)	117.3(5)	C(18)-C(17)-C(16)	120.0(7)	N(6)-C(32)-C(33)	120.2(5)
C(6)-C(5)-C(4)	121.0(5)	C(17)-C(18)-C(19)	119.5(6)	N(6)-C(32)-C(31)	112.5(4)
C(5)-C(6)-C(1)	119.1(5)	C(18)-C(19)-C(20)	119.5(6)	C(33)-C(32)-C(31)	127.2(5)
O(3)-C(7)-N(2)	122.6(5)	C(15)-C(20)-C(19)	121.2(6)	C(34)-C(33)-C(32)	119.6(6)
O(3)-C(7)-C(4)	115.6(4)	C(15)-C(20)-C(21)	116.1(5)	C(33)-C(34)-C(35)	120.0(5)
N(2)-C(7)-C(4)	121.5(4)	C(19)-C(20)-C(21)	122.6(5)	C(36)-C(35)-C(34)	118.7(6)
O(4)-C(8)-N(3)	122.9(5)	N(5)-C(21)-C(22)	118.8(6)	N(6)-C(36)-C(35)	121.8(6)
O(4)-C(8)-C(9)	116.5(5)	N(5)-C(21)-C(20)	112.7(5)	Cl(5)-C(37)-Cl(3)	27.0(4)
N(3)-C(8)-C(9)	120.6(5)	C(22)-C(21)-C(20)	128.4(6)	Cl(5)-C(37)-Cl(2)	98.4(7)
C(14)-C(9)-C(10)	119.6(5)	C(23)-C(22)-C(21)	120.4(6)	Cl(3)-C(37)-Cl(2)	107.7(7)
C(14)-C(9)-C(8)	119.0(5)	C(24)-C(23)-C(22)	119.2(6)	Cl(5)-C(37)-Cl(1)	113.2(7)
C(10)-C(9)-C(8)	121.2(5)	C(23)-C(24)-C(25)	119.4(6)	Cl(3)-C(37)-Cl(1)	120.0(7)
C(11)-C(10)-C(9)	119.6(5)	N(5)-C(25)-C(24)	121.4(6)	Cl(2)-C(37)-Cl(1)	14.8(3)
C(12)-C(11)-C(10)	118.3(6)	C(27)-C(26)-C(31)	116.5(5)	Cl(5)-Cl(3)-Cl(4)	17.8(10)
C(13)-C(12)-C(11)	122.4(6)	C(27)-C(26)-Pt(2)	130.1(4)	Cl(5)-Cl(3)-C(37)	75.1(11)
C(13)-C(12)-N(4)	119.9(6)	C(31)-C(26)-Pt(2)	113.4(4)	Cl(4)-Cl(3)-C(37)	86.5(7)
C(11)-C(12)-N(4)	117.7(6)	C(28)-C(27)-C(26)	122.0(5)	Cl(5)-Cl(4)-Cl(3)	15.2(8)
C(12)-C(13)-C(14)	119.8(6)	C(27)-C(28)-C(29)	121.6(6)	Cl(3)-Cl(5)-Cl(4)	147.0(18)
C(13)-C(14)-C(9)	120.1(6)	C(30)-C(29)-C(28)	117.3(6)	Cl(3)-Cl(5)-C(37)	77.8(11)
C(16)-C(15)-C(20)	117.3(5)	C(29)-C(30)-C(31)	122.4(6)	Cl(4)-Cl(5)-C(37)	120.5(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **46**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	34(1)	30(1)	39(1)	11(1)	-1(1)	3(1)
Pt(2)	38(1)	30(1)	33(1)	12(1)	-1(1)	3(1)
N(1)	81(4)	61(4)	63(4)	37(3)	-3(3)	12(3)
N(2)	44(3)	26(2)	38(2)	13(2)	0(2)	4(2)
N(3)	43(2)	30(2)	34(2)	14(2)	-4(2)	4(2)
N(4)	117(6)	65(4)	92(5)	50(4)	10(4)	-3(4)
N(5)	39(2)	32(2)	41(2)	8(2)	-2(2)	0(2)
N(6)	42(3)	34(2)	37(2)	14(2)	-3(2)	3(2)
O(1)	132(5)	89(4)	71(4)	48(3)	-7(3)	32(4)
O(2)	165(7)	92(4)	94(4)	53(4)	27(4)	77(5)
O(3)	47(2)	38(2)	35(2)	12(2)	-3(2)	4(2)
O(4)	54(2)	37(2)	37(2)	14(2)	3(2)	0(2)
O(5)	208(8)	56(4)	120(5)	49(4)	-26(5)	-37(4)
O(6)	248(10)	93(5)	108(5)	79(4)	3(6)	-26(5)
C(1)	53(3)	42(3)	56(3)	26(3)	-4(3)	8(3)
C(2)	89(5)	52(4)	43(3)	24(3)	1(3)	8(3)
C(3)	59(4)	40(3)	37(3)	12(2)	5(2)	14(3)
C(4)	37(3)	39(3)	39(3)	19(2)	1(2)	3(2)
C(5)	39(3)	48(3)	40(3)	16(2)	1(2)	11(2)
C(6)	49(3)	49(3)	52(3)	22(3)	5(3)	13(3)
C(7)	35(3)	35(3)	36(3)	10(2)	1(2)	3(2)
C(8)	33(3)	37(3)	41(3)	16(2)	-8(2)	0(2)
C(9)	53(3)	32(3)	42(3)	18(2)	1(2)	3(2)
C(10)	47(3)	43(3)	45(3)	17(3)	-4(2)	-6(3)
C(11)	52(4)	41(3)	65(4)	23(3)	-2(3)	-5(3)
C(12)	71(4)	50(4)	70(4)	34(3)	4(3)	-1(3)
C(13)	85(5)	63(4)	47(3)	30(3)	0(3)	3(4)
C(14)	72(4)	41(3)	47(3)	17(3)	-4(3)	0(3)
C(15)	36(3)	34(3)	50(3)	13(2)	-3(2)	0(2)
C(16)	44(3)	46(3)	61(4)	24(3)	-6(3)	8(3)
C(17)	54(4)	63(4)	70(4)	25(3)	-12(3)	16(3)

C(18)	64(4)	55(4)	98(6)	37(4)	-11(4)	17(3)
C(19)	56(4)	36(3)	75(4)	17(3)	6(3)	9(3)
C(20)	34(3)	40(3)	66(4)	21(3)	2(2)	2(2)
C(21)	29(3)	38(3)	57(3)	8(3)	2(2)	0(2)
C(22)	43(3)	45(4)	66(4)	-1(3)	7(3)	5(3)
C(23)	52(4)	57(4)	56(4)	-1(3)	8(3)	-6(3)
C(24)	50(4)	65(4)	49(3)	15(3)	3(3)	-6(3)
C(25)	44(3)	54(4)	49(3)	16(3)	3(3)	2(3)
C(26)	33(3)	36(3)	43(3)	14(2)	2(2)	8(2)
C(27)	45(3)	47(3)	41(3)	15(2)	4(2)	4(3)
C(28)	59(4)	59(4)	61(4)	33(3)	5(3)	-2(3)
C(29)	86(5)	48(4)	63(4)	26(3)	-3(4)	-13(4)
C(30)	79(5)	39(3)	58(4)	17(3)	-5(3)	-11(3)
C(31)	49(3)	35(3)	46(3)	18(2)	0(2)	1(2)
C(32)	43(3)	38(3)	40(3)	14(2)	0(2)	5(2)
C(33)	56(4)	43(3)	44(3)	4(3)	-2(3)	-5(3)
C(34)	58(4)	56(4)	39(3)	7(3)	-6(3)	-4(3)
C(35)	62(4)	58(4)	39(3)	22(3)	3(3)	8(3)
C(36)	49(3)	45(3)	44(3)	20(3)	-2(2)	2(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 46.

	x	y	z	U(eq)
H(2A)	5567	-8310	5662	72
H(3A)	4152	-7175	5232	55
H(5A)	5691	-8655	2849	51
H(6A)	7092	-9756	3280	59
H(10A)	5381	-4467	3247	54
H(11A)	5874	-3048	3001	62
H(13A)	4143	-4407	592	75
H(14A)	3748	-5826	803	64
H(16A)	1122	-4847	2347	59
H(17A)	-191	-3574	2104	75
H(18A)	-881	-2159	3240	84
H(19A)	-439	-2079	4623	68
H(22A)	-100	-2187	5931	69
H(23A)	494	-2433	7172	74
H(24A)	1928	-3832	7103	68
H(25A)	2766	-4946	5805	60
H(27A)	2018	-8924	3185	54
H(28A)	728	-10325	3146	67
H(29A)	328	-11664	1868	77
H(30A)	1046	-11493	627	71
H(33A)	1586	-11192	-581	62
H(34A)	2294	-10711	-1661	65
H(35A)	3701	-9227	-1350	62
H(36A)	4147	-8203	47	54

Appendix 6 – Reflective VOA attenuation measurement apparatus

Harrick Scientific™ Variable angle specular reflectance module (Cuvette holder in place)

Plexiglass cuvette holder construct with film and electrodes in place