Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.
Cyclo- and Polyphosphazenes Grafted with Tridentate Ligands Coordinated to Iron(II) and Ruthenium(II)

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at Massey University, Palmerston North

Ross James Davidson

2011
Acknowledgements

First, I would like to thank my supervisors, Prof. Andrew Brodie, Assoc. Prof. Eric Ainscough and Dr Mark Waterland for their continued support during the course of this project and for allowing me the freedom to pursue a project of my own design.

I would also like to thank Prof. Geoff Jameson for his extensive help with both teaching me crystallography and helping me with all the difficult structures; Prof. Keith Murray, Dr Boujemaa Moubaraki and Prof. Jean-François Létard for the magnetic moment measurements; Prof. Keith Gordon and Raphael Horvath for collecting the variable temperature solid-state resonance Raman data; Prof. Guy Jameson for collecting the Mössbauer data; Prof. Harry Allcock and Dr Mark Hindenlang for the GPC and DSC measurements; Dr Matthias Lein for the use of his supercomputer; and the MacDiarmid Institute for access to their range of instruments. Without these people, much of this project would not have been possible.

The Massey University PhD scholarship must also be acknowledged for the financial support during the course of the project.

Finally, I would like to thank my girlfriend Helen Hsu for her support through the best and worst this project had to offer.
Abstract

This thesis sought to explore the chemical and physical properties of a series of cyclotri- and polyphosphazenes with substituted tridentate ligands coordinated to iron(II) and ruthenium(II). There were two main objectives of this research i) to graft spin crossover (SCO) groups to a polymer backbone, potentially making a new malleable material, ii) to demonstrate that ruthenium(II) complexes can be used to link groups to a polyphosphazene backbone.

Seven cyclotriphosphazene (L₁–L₇) and four polyphosphazene (L₁P–L₄P) ligands¹ were synthesised with 2,6-di(pyridine-2-yl)pyridine-4(1H)-onate (OTerpy); 4-(2,6-di{pyridin-2-yl}-pyridine-4-yl)phenolate (OPhTerpy); 2,6-di(1H-benzimidazol-2-yl)pyridine-4(1H)-onate (Obbp); and 4-(2,6-di{1H-pyrazol-1-yl}pyridine-4-yl)phenolate (OPhbpp) moieties. These ligands were subsequently coordinated to either iron(II) or ruthenium(II) and the optical, vibrational, electrochemical and magnetic properties of the subsequent small molecule complexes and polymers were measured.

Sixteen iron(II) complexes were synthesised by reacting iron(II) salts with the respective ligand (L₁–L₇). Where X-ray crystal structures have been obtained, each of the small molecule iron complexes were homoleptic. Using electronic absorbance, resonance Raman (rR), magnetic and Mössbauer spectroscopy, it was shown that the polymer complex cores in the resulting cross-linked polymers were the same as those of the small molecule analogues (SMA). In addition, these techniques confirmed that the iron complexes formed with the ligands L₁, L₂, L₁P and L₂P were each determined to be low spin (LS), while those formed with L₃ displayed SCO, and the iron complex formed with L₄ remained high spin (HS) for all temperatures while its polymeric analogue remained LS for all measurable temperatures.

Fourteen ruthenium(II) small molecule complexes were synthesised by reacting ruthenium complexes of the appropriate co-ligands (2,2′:6′,2″-terpyridine (Terpy); 2,6-di(pyridin-2-yl)-4-phenylpyridine (PhTerpy); 2,6-di(1H-benzimidazol-2-yl)pyridine (bbp); and 2,6-di(1H-pyrazol-1-yl)pyridine) with the respective ligand (L₁–L₄). Using electronic absorption and rR spectroscopy it was determined that only the polymers L₁P and L₂P formed complexes ([Ru(L₁P)(Terpy)]Cl₂, [Ru(L₁P)(PhTerpy)]Cl₂.

¹ See pull out sheet for ligand structures.
Abstract

[Ru(L^{2p})(Terpy)]Cl_2 and [Ru(L^{2p})(PhTerpy)]Cl_2) analogous to that of their SMA ([Ru(L^1)(Terpy)](PF_6)_2, [Ru(L^1)(PhTerpy)](PF_6)_2, [Ru(L^2)(Terpy)](PF_6)_2 and [Ru(L^2)(PhTerpy)](PF_6)_2), and are therefore the most suitable for linking groups to polyphosphazenes.

Although the ruthenium-bbp-terpy based complexes proved to be unsuitable for attaching groups to a phosphazene due to the low loading of metal complex on the polymer (L^{3p}), the SMA ([Ru(L^1)(bbp)](PF_6)_2, [Ru(L^2)(bbp)](PF_6)_2, [Ru(L^3)(Terpy)](PF_6)_2 and [Ru(L^3)(PhTerpy)](PF_6)_2) displayed a dependence on the basicity of the solution. As it was increased, the imidazole groups were deprotonated causing a bathochromic shifting of the metal-to-ligand charge transfer, oxidation potential and selected vibrational modes.
## Table of Contents

**Chapter 1: An introduction to phosphazenes** ........................................... 1

1.1 Introduction and applications ................................................................. 5

1.2 Benefits and effects of heterosubstituted phosphazenes ......................... 11

1.3 Phosphazenes and metals ........................................................................ 15

1.4 Phosphazene polymers ........................................................................... 19

   1.4.1 Phosphazene polymer history ............................................................. 19

   1.4.2 Polymerization methods ..................................................................... 20

   1.4.3 Polyphosphazenes and their common substituents ............................... 24

   1.4.4 Polyphosphazene structure ................................................................. 26

1.5 References ............................................................................................... 27

**Chapter 2: Synthesis and characterisation of cyclotriphosphazene based ligands** ................................................................. 33

2.1 Introduction .............................................................................................. 37

   2.1.1 Synthetic approach .......................................................................... 38

   2.1.2 Phosphazene decay .......................................................................... 39

2.2 Synthesis of ligands .................................................................................. 41

2.3 Comments and observations about ligand synthesis ................................. 43

   2.3.1 2,6-bis(2-pyridyl)-4(1H)-pyridonate and 2,6-di(1H-benzimidazol-2-yl)pyridine-4(1H)-onate based ligands ........................................ 43

   2.3.2 4-(2,6-di{pyridin-2-yl}-pyridine-4-yl)phenolate and 4-(2,6-di{1H-pyrazol-1-yl}pyridine-4-yl)phenolate based ligands .................. 45

   2.3.4 HOQSal ............................................................................................ 46
Chapter 3: Reactions of cyclotriphosphazene ligands with selected iron(II) salts

3.1 Introduction ........................................................................................................................................ 65

3.1.1 2,2’:6’,2”-terpyridine .................................................................................................................... 67

3.1.2 2,6-di(1H-benzimidazol-2-yl)pyridine ......................................................................................... 69

3.1.3 2,6-di(1H-pyrazol-yl)pyridine .................................................................................................... 71

3.2 Synthesis of the iron(II) complexes .................................................................................................. 73

3.3 Observations from synthesis ........................................................................................................... 75

3.4 Crystallography ................................................................................................................................ 79

3.4.1 Crystal structure of [Fe(L^1)_2](PF_6)_2·CH_3CN ........................................................................ 83

3.4.2 Crystal structure of [Fe(L^1)_2](ClO_4)_2·CH_3CN ................................................................... 85

3.4.3 Crystal structure of [Fe(L^2)_2](PF_6)_2·CH_3CN .................................................................... 86

3.4.4 Crystal structure of [Fe(L^3)_2](BF_4)_2·C_3H_6O·C_5H_12O ......................................................... 88

3.5 Conclusion ....................................................................................................................................... 91
Chapter 4: Reactions of cyclotriphosphazene ligands with selected ruthenium(II) complexes ................................................................. 99

4.1 Introduction ................................................................................................................................................................................. 103
  4.1.1 2,2':6',2"-terpyridine ......................................................................................................................................................... 104
  4.1.2 2,6-di(1H-benzimidazol-2-yl)pyridine ......................................................... 105
  4.1.3 2,6-di(1H-pyrazol-1-yl)pyridine ............................................................................................................................... 107

4.2 Synthesis of the ruthenium(II) complexes ......................................................................................................................... 109

4.3 Observations from synthesis ................................................................................................................................................... 111
  4.3.1 Homoleptic ruthenium(II) complexes ......................................................................................................................... 112
  4.3.2 Heteroleptic ruthenium(II) complexes ....................................................................................................................... 113

4.4 Crystallography ......................................................................................................................................................................... 115
  4.4.1 L\textsuperscript{1} based complexes .................................................................................................................................. 116
  4.4.2 Packing of the L\textsuperscript{1} based complexes ............................................................................................................. 124
  4.4.3 L\textsuperscript{2} based complexes .................................................................................................................................. 127
  4.4.4 [Ru(L\textsuperscript{2})\textsubscript{2}(PF\textsubscript{6})\textsubscript{2}] packing .............................................................................................. 129
  4.4.5 L\textsuperscript{3} based complexes .................................................................................................................................. 130
  4.4.6 Packing of L\textsuperscript{3} based complexes .................................................................................................................. 133

4.5 Conclusion .............................................................................................................................................................................. 135

4.6 References .............................................................................................................................................................................. 137
Chapter 5: Synthesis and reactions of polyphosphazenes with iron(II) perchlorate and ruthenium complexes ................................................................. 139

5.1 Introduction .......................................................................................................................... 143
  5.1.1 Polyphosphazenes and metal ......................................................................................... 143
  5.1.2 Cross-linked polyphosphazenes .................................................................................... 144

5.2 Polymer characterisation ..................................................................................................... 148
  5.2.1 NMR spectroscopy ......................................................................................................... 148
  5.2.2 Gel permeation chromatography .................................................................................... 149
  5.2.3 Differential scanning calorimetry .................................................................................. 150
  5.2.4 Polyphosphazene standard ............................................................................................ 154

5.3 Synthesis of polymers ......................................................................................................... 155

5.4 Observations from polymer synthesis ............................................................................... 157
  5.4.1 Unreacted P-Cl units ....................................................................................................... 157
  5.4.2 2,6-bis(2-pyridyl)-4(1H)-pyridonate based polymer (L\textsuperscript{1P}) ...................... 159
  5.4.3 2,6-di(1H-benzimidazol-2-yl)pyridine-4(1H)-onate based polymer (L\textsuperscript{3P}) .......................................................... 160
  5.4.4 4-(2,6-di{pyridin-2-yl})pyridine-4-ylphenolate and 4-(2,6-di{1H-pyrazol-1-yl})pyridine-4-ylphenolate based polymers (L\textsuperscript{2P} and L\textsuperscript{4P}) .......................................................................................................................... 160

5.5 Molecular weights of the metal-free polyphosphazenes ................................................. 163

5.6 Observations from metal-coordinated polymer (metallo-polymer) synthesis .................. 165
  5.6.1 Iron(II) metallo-polymers ............................................................................................. 166

5.7 Observations from metal-coordinated polymer (metallo-polymer) synthesis ..................... 169
Chapter 6: Coordination site characterisation of the ruthenium(II) metallo polymer and the physical behaviour of both the cyclotriphosphazene and polyphosphazene ruthenium(II) metallo polymer .......................................................... 177

6.1 Introduction ........................................................................................................ 181
  6.1.1 Metallo-polymers ...................................................................................... 181
  6.1.2 Ruthenium(II) bis(2,2':6',2"-terpyridine) complexes .............................. 183
  6.1.3 Ruthenium(II) (2,6-di{1H-benzimidazol-2-yl}pyridine) (2,2':6',2"-terpyridine) complexes ................................................................. 185
  6.1.4 Ruthenium(II) (2,6-di{1H-pyrazol-1-yl}pyridine) (2,2':6',2"-terpyridine) complexes ................................................................. 186

6.2 Current research .............................................................................................. 187

6.3 Electronic absorbance spectroscopy .............................................................. 191
  6.3.1 Ruthenium(II) bis(2,2':6',2"-terpyridine) complexes .............................. 191
  6.3.2 Ruthenium(II) (2,6-di{1H-benzimidazol-2-yl}pyridine) (2,2':6',2"-terpyridine) complexes ................................................................. 195
  6.3.3 Ruthenium(II) (2,6-di{1H-pyrazol-1-yl}pyridine) (2,2':6',2"-terpyridine) complexes ................................................................. 198

6.4 Vibrational spectroscopy .............................................................................. 201
  6.4.1 Ruthenium(II) bis(2,2':6',2"-terpyridine) complexes .............................. 201
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.4 Vibrational spectroscopy</td>
<td>240</td>
</tr>
<tr>
<td>7.3 Current research</td>
<td>243</td>
</tr>
<tr>
<td>7.4 Electrochemistry</td>
<td>247</td>
</tr>
<tr>
<td>7.5 Electronic absorbance spectroscopy</td>
<td>249</td>
</tr>
<tr>
<td>7.5.1 Iron(II) bis(2,2':6',2&quot;-terpyridine) based complexes</td>
<td>249</td>
</tr>
<tr>
<td>7.5.2 Iron(II) bis(2,6-di{1H-benzimidazol-2-yl)pyridine) based complexes</td>
<td>252</td>
</tr>
<tr>
<td>7.5.3 Iron(II) bis(2,6-di{1H-pyrazol-1-yl)pyridine) based complexes</td>
<td>254</td>
</tr>
<tr>
<td>7.6 Vibrational</td>
<td>255</td>
</tr>
<tr>
<td>7.6.1 Iron(II) bis(2,2':6',2&quot;-terpyridine) based complexes</td>
<td>255</td>
</tr>
<tr>
<td>7.6.2 Iron(II) bis(2,6-di{1H-benzimidazol-2-yl)pyridine) based complexes</td>
<td>258</td>
</tr>
<tr>
<td>7.6.3 Iron(II) bis(2,6-di{1H-pyrazol-1-yl)pyridine) based complexes</td>
<td>260</td>
</tr>
<tr>
<td>7.7 Magnetic moments</td>
<td>261</td>
</tr>
<tr>
<td>7.7.1 Iron(II) bis(2,2':6',2&quot;-terpyridine) based complexes</td>
<td>261</td>
</tr>
<tr>
<td>7.7.2 Iron(II) bis(2,6-di{1H-benzimidazol-2-yl)pyridine) based complexes</td>
<td>263</td>
</tr>
<tr>
<td>7.7.3 Iron(II) bis(2,6-di{1H-pyrazol-1-yl)pyridine) based complexes</td>
<td>264</td>
</tr>
<tr>
<td>7.8 Mössbauer spectroscopy</td>
<td>265</td>
</tr>
<tr>
<td>7.8.1 Iron(II) bis(2,2':6',2&quot;-terpyridine) based complexes</td>
<td>265</td>
</tr>
<tr>
<td>7.8.2 Iron(II) bis(2,6-di{1H-benzimidazol-2-yl)pyridine) based complexes</td>
<td>268</td>
</tr>
</tbody>
</table>
7.8.3 Iron(II) bis(2,6-di{1H-pyrazol-1-yl}pyridine) based complexes ............................................................. 269

7.9 Conclusion ................................................................................................................................. 271

7.10 References ............................................................................................................................ 273

Conclusion and final remarks ........................................................................................................ 277

Appendix A: Chapter 2 Supplementary ....................................................................................... 283
A.1 Ligand Synthesis .................................................................................................................... 283
A.2 Selected bond lengths ............................................................................................................. 289
A.3 References .............................................................................................................................. 289

Appendix B: Chapter 3 Supplementary ....................................................................................... 291
B.1 Iron(II) Complex Synthesis ................................................................................................... 291
B.2 Selected Bond Lengths ......................................................................................................... 300
B.3 References ............................................................................................................................ 301

Appendix C: Chapter 4 Supplementary ....................................................................................... 303
C.1 Ruthenium(II) Complex Synthesis ....................................................................................... 303
C.2 Selected Bond Lengths ......................................................................................................... 312
C.3 References ............................................................................................................................ 315

Appendix D: Chapter 5 Supplementary ....................................................................................... 317
D.1 Metal-free polyphosphazene synthesis .................................................................................. 317
D.2 Synthesis of iron(II) polyphosphazene complexes .............................................................. 320
D.3 Synthesis of ruthenium(II) polyphosphazene complexes ................................................... 322
D.4 References ............................................................................................................................ 325

Appendix E: Chapter 6 Supplementary (Digital copy only) ....................................................... 327
Contents

E.1 Instrumentation ..................................................................................... 327
E.2 Computational ....................................................................................... 328
E.3 Electronic spectra assignment ................................................................. 331
E.4 Assignment of vibrational modes ............................................................. 386
E.5 References .............................................................................................. 419

Appendix F: Chapter 7 Supplementary (Digital copy only) ......................... 421
F.1 Instrumentation ..................................................................................... 421
F.2 Computational ....................................................................................... 423
F.3 Electronic spectra assignment ................................................................. 426
F.4 Iron titration of L³ ................................................................................. 438
F.5 Assignment of vibrational modes ............................................................. 439
F.6 References .............................................................................................. 445

Copyright Permissions (Digital copy only) ................................................. 447
List of Figures

Chapter 1

Figure 1.1.1 The PN backbone of a phosphazene 5
Figure 1.1.2 Example of a phosphazene substitution reaction with phenol 5
Figure 1.1.3 Examples of cyclic phosphazenes (R can be any substituent) 6
Figure 1.1.4 A schematic view of how a phosphazene-lithium ion membrane works 7
Figure 1.1.5 An example of an OLED dendrimer unit based on a phosphazene trimer 8
Figure 1.1.6 A phosphazene polymer substituted with a liquid crystalline-type substituent for NLO properties 9
Figure 1.2.1 (a) One biphenol used to control coordination. (b) Two biphenols used to control coordination. (c) a phenol controlling coordinating behaviour. (d) the absence of a phenol controlling the coordination behaviour. 11
Figure 1.2.2 Semi-hard donor (pyridine) and soft donor (phosphine) groups attached to a phosphazene 12
Figure 1.2.3 Examples of the variation of substituent linkers 13
Figure 1.3.1 Example of an ionic phosphazene salt 15
Figure 1.3.2 Examples of metal ions coordinating to ring nitrogens 16
Figure 1.3.3 Examples of exocyclic substituents coordinating to metal ions 16
Figure 1.3.4 Example of a metal coordinating to the phosphazene phosphorus 16
Figure 1.3.5 An example of an anionic phosphazene interacting with a metal, Li$_6$[P$_3$N$_3${N(C$_6$H$_{10}$)}$_2$] 17
Figure 1.4.2.1.1 Trimer initially being sublimed 20
Figure 1.4.2.1.2 Left: Trimer under vacuum in tube. Right: Trimer in sealed tube  

Figure 1.4.2.1.3 Left: Trimer rocked in oven. Right: Molten polymer  

Figure 1.4.2.1.4 Polymer remaining at the bottom of the sublimator  

Figure 1.4.2.1.5 Accepted mechanism for ROP, X = Cl, Br or F  

Figure 1.4.3.1 A TFE-substituted polymer (R can be any substituent)  

Figure 1.4.3.2 Biphen-substituted polymer (R can be substituent)  

Figure 1.4.3.3 A pyridine-substituted polymer stabilized with biphen  

Figure 1.4.4.1 A schematic diagram showing the difference in steric hindrance between a trans-trans and cis-trans polymer  

Figure 1.4.4.2 Proposed structure of the phosphazene backbone  

Chapter 2  

Figure 2.1.1.1 Nucleophilic substitution of hexachlorocyclotriphosphazene  

Figure 2.1.1.2 Mechanism for the aryloxy substitution of a chlorine for a phosphazene  

Figure 2.1.1.3 Potential substitution patterns for a cyclotriphosphazene  

Figure 2.1.2.1 Schematic view of hydrolytic decay  

Figure 2.1.2.2 Schematic view of decay via a substituent interaction  

Figure 2.2.1 Ligands investigated using the trimeric phosphazene. Black: compounds that have already been reported. Green: proposed compounds  

Figure 2.2.2 Substitution patterns of the proposed compounds  

Figure 2.3.1 Synthesised ligands  

Figure 2.3.1.1 The enone structures of HOTerpy (left) and HObbp (right)
**Figure 2.3.1.2** Reaction scheme for $L^5$ showing the formation of the $N_3P_3$(Biphen)$_2$(OTerpy)Cl intermediate species 45

**Figure 2.3.2.1** Phenyl ring twisting 46

**Figure 2.3.4.1** [OQSal]$^{2-}$ resonance structure 47

**Figure 2.3.5.1** Proposed deprotection of MeObpp 48

**Figure 2.3.5.2** Reaction scheme for the formation of HOPhbbp 48

**Figure 2.4.1.1** Unit cell for $L^3\cdot3H_2O\cdotC_3H_6O$ (hydrogen atoms removed for clarity) 51

**Figure 2.4.1.2** Packing behaviour of $L^3\cdot3H_2O\cdotC_3H_6O$ (hydrogens were removed for clarity), lines indicating hydrogen bonding 52

**Figure 2.4.2.1** Unit cell of $L^5\cdot2CH_2Cl_2$ (hydrogen atoms and dichloromethane molecules removed for clarity) 53

**Figure 2.4.2.2** Packing of $L^5\cdot2CH_2Cl_2$, dotted lines indicate bonding interactions (hydrogen atoms removed for clarity) 54

**Figure 2.4.3.1** Unit cell for $L^7\cdotC_3H_6O\cdotH_2O$ (hydrogen atoms removed for clarity) 55

**Figure 2.4.3.2** Crystal structure of a single molecule of $L^7\cdotC_3H_6O\cdotH_2O$ (hydrogen atoms and solvents removed for clarity), dotted lines indicate bonding interactions 56

**Chapter 3** 61

**Figure 3.1.1.1** A Grätzel dye based on a terpy for use in a solar cell 67

**Figure 3.1.1.2** Left: A crystal structure of a terpy complex substituted at the ortho and para positions reducing the SCO temperature (hydrogens, anions and
solvent removed for clarity). Right: The visible spectrum of this compound as a function of temperature (300 – 323 K)

**Figure 3.1.1.3** Substitution of terpy at the para position, where R can be any substituent

**Figure 3.1.2.1** From left: Parent bbp, deprotonated bbp, N-substituted bbp (where R can be a range of substituents)

**Figure 3.1.2.2** Left: A Monte-Carlo simulation of a substituted iron-bbp complex. Right: The magnetic behaviour of the complex

**Figure 3.1.2.3** Differences in the calculated heats of formation between the HS and LS forms ($\Delta E_{\text{tot}}$ since calculations are for single molecules) in [Fe(Xbbp)$_2$]$^{2+}$ vs. $\Delta \delta$ ($^1$H NMR increment for para-substituents X in benzene)

**Figure 3.1.2.1** A schematic view of iron(II) coordinating to a bpp ligand, forming a SCO complex

**Figure 3.1.3.2** Left: [Fe(Pybpp)$_2$]$^{3+}$. Right: thermal magnetic behaviour of [Fe(Pybpp)$_2$]$^{3+}$

**Figure 3.1.3.3** Left: [Fe(bppMe)$_2$]$^{2+}$. Right: thermal and LIESST magnetic behaviour of [Fe(bppMe)$_2$]$^{2+}$

**Figure 3.2.1** Ligands to be coordinated with iron(II)

**Figure 3.3.1** Iron(II) complexes synthesised in this chapter, X = ClO$_4^-$, PF$_6^-$ or BF$_4^-$

**Figure 3.3.2** The schematic reaction for the tridentate ligands

**Figure 3.4.1.1** Unit cell of [Fe(L$_1$)$_2$](PF$_6$)$_2$·CH$_3$CN (hydrogen atoms, solvents and anions were removed for clarity). Right: Green lines indicate $\pi$-H interactions

**Figure 3.4.1.2** Packing of [Fe(L$_1$)$_2$](PF$_6$)$_2$·CH$_3$CN, dotted lines indicate bonding interactions
Figure 3.4.2.1 Unit cell for \([\text{Fe}(L^1)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}\) (hydrogen atoms, solvents and anions were removed for clarity). Left: Green lines indicate \(\pi\)-H interactions

Figure 3.4.3.1 Unit cell for \([\text{Fe}(L^2)_2](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}\) (hydrogen atoms, solvents and anions were removed for clarity)

Figure 3.4.3.2 Packing of \([\text{Fe}(L^2)_2](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}\), dotted lines indicate hydrogen bonding (hydrogen atoms removed for clarity)

Figure 3.4.4.1 Unit cell contents for \([\text{Fe}(L^3)_2](\text{BF}_4)_2 \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{C}_5\text{H}_{12}\text{O}\) (hydrogen atoms, solvents and anions were removed for clarity)

Figure 3.4.4.2 Packing structure of \([\text{Fe}(L^3)_2](\text{BF}_4)_2 \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{C}_5\text{H}_{12}\text{O}\), dotted lines indicate hydrogen bonding (hydrogen atoms removed for clarity)

Chapter 4

Figure 4.1.1 Schematic view of the metal complex used as a linker between a polymer and the R group

Figure 4.1.1.1 Examples of ruthenium(II)-terpy solar cell dyes

Figure 4.1.2.1 Solar cell dye based on bpp

Figure 4.1.2.2 Various states of protonation for \([\text{Ru}(\text{bpp})(\text{Terpy})]^{2+}\). From left: \([\text{Ru}(\text{bpp})(\text{Terpy})]^{2+}\), \([\text{Ru}(\text{bpp})(\text{Terpy})]^+\) and \([\text{Ru}(\text{bpp})(\text{Terpy})]\)

Figure 4.1.2.3 pH dependence of \([\text{Ru}(\text{bpp})(\text{Terpy})]^{n+}\) (\(n = 0–2\)) electronic spectra

Figure 4.1.3.1 Solar cell dye based on bpp

Figure 4.1.3.2 Left: monomer and dimer ruthenium complexes of bpp. Right: Absorbance (dashed line monomer, solid line dimer) and emission (dotted line monomer, dash-dotted line dimer) spectra of the monomer and dimer ruthenium complexes
Figure 4.2.1 Ligands to be coordinated with ruthenium(II), green indicates co-ligands

Figure 4.3.1 Ruthenium complexes synthesised in this chapter, hexafluorophosphate was used as the counter ion for each complex

Figure 4.3.1.1 Homoleptic reaction schemes for L₁, L₂, L₃ and L₄

Figure 4.3.2.1 Controlled synthesis of both the protonated and deprotonated bbp complexes

Figure 4.3.2.2 Synthetic scheme for the synthesis of L₃ complexes

Figure 4.4.1.1 Unit cell of [Ru(L₁)₂](PF₆)₂·CH₃CN (hydrogen atoms, solvents and anions removed for clarity). Left: Red lines indicate π-H interactions

Figure 4.4.1.2 Unit cell of [Ru(L¹)(Terpy)](PF₆)₂·CH₃CN (hydrogen atoms removed for clarity). Left: Red lines indicate π-H interactions

Figure 4.4.1.3 Unit cell of [Ru(L¹)(PhTerpy)](PF₆)₂ (hydrogen atoms and anions removed for clarity)

Figure 4.4.1.4 Unit cell of [Ru(L¹)(bpp)](PF₆)₂·CH₃CN (hydrogen atoms, solvents and anions removed for clarity). Left: Red lines indicate π-H interactions.

Figure 4.4.1.5 Unit cell of [Ru(L¹)(bpp)](PF₆)₂·C₃H₅O (hydrogen atoms, solvents and anions removed for clarity).

Figure 4.4.2.1 Packing of [Ru(L₁)₂](PF₆)₂·CH₃CN, dotted lines indicate bonding interactions

Figure 4.4.2.2 Packing of [Ru(L¹)(Terpy)](PF₆)₂·CH₃CN and [Ru(L¹)(bpp)](PF₆)₂·CH₃CN, dotted lines indicate bonding interactions

Figure 4.4.2.3 Packing of [Ru(L¹)(PhTerpy)](PF₆)₂, dotted lines indicate bonding interactions

Figure 4.4.2.4 Packing of [Ru(L¹)(bpp)](PF₆)₂·C₃H₅O, dotted lines indicate bonding interactions
**Figure 4.4.3.1** Unit cell of [Ru(L$_2^2$)](PF$_6$)$_2$ (hydrogen atoms and anions removed for clarity) 128

**Figure 4.4.4.1** Packing of [Ru(L$_2^2$)](PF$_6$)$_2$, dotted lines indicate bonding interactions 129

**Figure 4.4.5.1** Unit cell of [Ru(L$_3^3$)(Terpy)](PF$_6$)$_2$·CH$_3$CN (hydrogen atoms, solvents and anions removed for clarity). Right: Red lines indicate $\pi$-H interactions 131

**Figure 4.4.5.2** Unit cell of [Ru(L$_3^3$)(PhTerpy)](PF$_6$)$_2$·CH$_3$CN (hydrogen atoms, solvents and anions removed for clarity). Right: Red lines indicate $\pi$-H interactions 132

**Figure 4.4.6.1** Packing of [Ru(L$_3^3$)(Terpy)](PF$_6$)$_2$·CH$_3$CN, dotted lines indicate bonding interactions 133

**Chapter 5** 139

**Figure 5.1.1.1** Examples of phosphazene polymers with metal coordinating substituents 143

**Figure 5.1.1.2** Examples of multidentate ligands attached to polyphosphazene backbones forming luminescent polymers 144

**Figure 5.1.2.1** Left: Example of polyphosphazene beads for the use of bone growth. Right: Cell growth between polyphosphazene beads 145

**Figure 5.1.2.2** Example of a hydrogel (MEEP), dried and solvent absorbed 145

**Figure 5.1.2.3** Left: Suggested mechanism for cross-linking via radical formation. Right: Cross-linking via hydrogen bonding 146

**Figure 5.1.2.4** A proposed structure for the cross-linking of polyphosphazene chains via a metal ion 147

**Figure 5.1.2.5** Carriedo’s MOF based on polyphosphazenes cross-linked via gold 147
Figure 5.2.1.1 Left: Example $^{31}$P NMR of a blocky distributed substitution polyphosphazene ($[\text{NP(O-2-Py-6-Me)}_2]_n$). Right: Example $^{31}$P NMR of a randomly distributed substitution polyphosphazene $([\text{NP(OPh}^{\text{tBu}}_2]_{0.75}\{\text{NP(OPh}^{\text{tBu}})(\text{OPh-4-Bipy -2-Ph})\}_{0.25}]_n)$.

Figure 5.2.2.1 Left: A schematic view of the size exclusion gel. Right: A schematic view of a size exclusion column in action.

Figure 5.2.3.1 An example of a DSC curve.

Figure 5.2.3.2 Carriedo’s gold cross-linked polyphosphazenes.

Figure 5.2.4.1 $[\text{NP(TFE)}_2]_n$, used as a phosphazene polymer standard.

Figure 5.3.1 Ligands attached to the polyphosphazene backbone.

Figure 5.4.1 Metal-free polymers synthesised.

Figure 5.4.1.1 Left: Schematic diagram displaying the unreacted P-Cl units found on the polyphosphazene backbone (hydrogens removed for clarity). Right: Space-filling model displaying the unreacted chlorines found on the polyphosphazene backbone (hydrogens removed for clarity).

Figure 5.4.2.1 $^{31}$P NMR spectra of $L^{1P}$ during the course of its synthesis, showing the decay.

Figure 5.4.2.2 Left: 2-Pyridoxy interactions with the polyphosphazene backbone. Right: Proposed decay mechanism of the OTerpy based polymers.

Figure 5.4.4.1 $^{31}$P NMR spectra of the reaction progress of $L^{2P}$.

Figure 5.5.1 Example of a typical peak recorded on a GPC.

Figure 5.6.1 Iron(II) metallo-polymers synthesised.

Figure 5.6.1.1 Schematic view of the iron(II) metallo-polymers synthesis.

Figure 5.6.1.2 Left: Schematic diagram for the suggested intra-chain linkage. Right: An extended view of the looped polymer chain.
Figure 5.6.1.3 Example of the stretched cross-linked metallo-polymer
([Fe(L^1P_2)](ClO_4))

Figure 5.6.1.4 Left: schematic diagram of the suggested cross-linked polymer. Right: An extended view of the cross-linked polymer

Figure 5.7.1 Ruthenium(II) metallo-polymers synthesised

Figure 5.7.1.1 Schematic view of ruthenium(II) metallo-polymer synthesis

Chapter 6

Figure 6.1.1.1 Two examples of coordination polymers. Left: an electronically active thiophene linker. Right: an electronically mute polyether linker.

Figure 6.1.1.2 Two examples of grafted polymers. Left: an electronically active poly(phenylenevinylene) polymer with electronically mute ether linker. Right: an electronically mute alkyl polymer with an electronically mute ester linker.

Figure 6.1.2.1 Molecular orbital diagrams of an MLCT transition. Left: [Ru(Terpy)_2]^2+. Right: [Ru(Bipy)_3]^2+.

Figure 6.1.2.2 Rotation of the phenyl ring attached to the [Ru(Terpy)_2]^2+ complex.

Figure 6.1.3.1 Left: Two [Ru(bbp)(Terpy)]^2+ complexes linked by a biphenyl spacer. Right: The absorbance spectra of the complex as the pH was gradually increased.

Figure 6.1.4.1 Left: [Ru(bbp)_2]^2+ based complex; No. methyl groups = 0 (R_1, R_2, R_3, R_4 = H), 2 (R_1 = Me, R_2, R_3, R_4 = H), 4 (R_1, R_2 = Me, R_3, R_4 = H), 6 (R_1, R_2, R_3 = Me, R_4 = H) and 8 (R_1, R_2, R_3, R_4 = Me). Right: Ru^{II}/Ru^{III} oxidation potential vs. methyl substitution number.

Figure 6.2.1 Ruthenium complexes investigated in this chapter.

Figure 6.2.2 Comparison of the IR spectra for [Ru(L^1)_2](PF_6)_2 to the calculated IR spectra of [Ru(L^1)_2]^2+. 
Figure 6.3.1.1 Electronic absorbance spectra of the compounds. OPhTerpy based complexes [Ru(L²)(PF₆)₂], [Ru(L²)(Terpy)](PF₆)₂, [Ru(L²)(PhTerpy)](PF₆)₂, [Ru(L²P)(Terpy)]Cl₂ and [Ru(L²P)(PhTerpy)]Cl₂. 191

Figure 6.3.1.2 Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of [Ru(L²)₂]²⁺ 192

Figure 6.3.1.3 Electronic absorbance spectra of the compounds. OTerpy based complexes [Ru(L¹)(PF₆)₂], [Ru(L¹)(Terpy)](PF₆)₂, [Ru(L¹)(PhTerpy)](PF₆)₂, [Ru(L¹P)(Terpy)]Cl₂ and [Ru(L¹P)(PhTerpy)]Cl₂. 194

Figure 6.3.2.1 Electronic absorbance spectra of the compounds; bbp based complexes [Ru(L³)(PF₆)₂], [Ru(L³)(Terpy)](PF₆)₂, [Ru(L³)(PhTerpy)](PF₆)₂, [Ru(L³)(bbp)](PF₆)₂ and [Ru(L³)(bbp)](PF₆)₂. 195

Figure 6.3.2.2 HOMO and LUMO orbitals of [Ru(L³)(Terpy)]²⁺ and [Ru(L³)(bbp)]²⁺ 196

Figure 6.3.2.2 Electronic spectra of [Ru(L³)(Terpy)](PF₆)₂ as NEt₃ was sequentially added to the solution 197

Figure 6.3.3.1 Electronic absorbance spectra of the compounds: [Ru(L⁴)(PF₆)₂], [Ru(L⁴)(Terpy)](PF₆)₂, [Ru(L⁴)(PhTerpy)](PF₆)₂, [Ru(L⁴P)(Terpy)](PF₆)₂ and [Ru(L⁴P)(PhTerpy)](PF₆)₂ 198

Figure 6.3.3.2 Electronic absorbance spectra of the compounds [Ru(L⁴P)(Terpy)]Cl₂ and [Ru(L⁴P)(PhTerpy)]Cl₂ 199

Figure 6.3.3.3 Proposed complex formed on the polymer 200

Figure 6.4.1.2 Example of additional vibrational modes due to the asymmetry of a heteroleptic complex (red arrows indicate displacement vectors). a) [Ru(L¹)₂]²⁺, b) and c) [Ru(L¹)(Terpy)]²⁺. 202

Figure 6.4.1.1 rR spectra recorded using a 488 nm excitation. Left: OTerpy based complexes [Ru(L¹)(PF₆)₂], [Ru(L¹)(Terpy)](PF₆)₂, [Ru(L¹)(PhTerpy)](PF₆)₂, [Ru(L¹P)(Terpy)]Cl₂ and [Ru(L¹P)(PhTerpy)]Cl₂. Right: OPhTerpy based complexes [Ru(L²)(PF₆)₂], [Ru(L²)(Terpy)](PF₆)₂, [Ru(L²)(PhTerpy)](PF₆)₂, [Ru(L²P)(Terpy)](PF₆)₂, [Ru(L²P)(PhTerpy)](PF₆)₂ and [Ru(L²P)(PhTerpy)]Cl₂. 203
Figure 6.4.2.1 rR spectra of [Ru(L^3)(Terpy)](PF_6)_2, [Ru(L^3)(PhTerpy)](PF_6)_2, [Ru(L^1)(bbp)](PF_6)_2 and [Ru(L^2)(bbp)](PF_6)_2. Left: \( \lambda_{ex} \) 488 nm, right: \( \lambda_{ex} \) 514 nm.

Figure 6.4.2.2 1533 cm\(^{-1} \) vibrational mode of [Ru(L^2)(bbp)]\(^{2+} \) (red arrows indicate displacement vectors)

Figure 6.4.2.3 rR spectra of [Ru(L^3)(Terpy)](PF_6)_2 as triethylamine was sequentially added to the solution.

Figure 6.4.2.4 Equilibria formed by [Ru(L^3)(Terpy)](PF_6)_2

Figure 6.4.3.1 rR \( \lambda_{ex} \) 514 nm. [Ru(L^4)(Terpy)](PF_6)_2, [Ru(L^4)(PhTerpy)](PF_6)_2, [Ru(L^1)(bbp)](PF_6)_2 and [Ru(L^2)(bbp)](PF_6)_2.

Figure 6.4.3.2 \( \lambda_{ex} \) 514 nm. [Ru(L^4P)(Terpy)]Cl_2 and [Ru(L^4P)(PhTerpy)]Cl_2

Figure 6.5.1.1 Components of the [Ru(L^2)_2]\(^{2+} \) complex

Figure 6.5.2.1 \( E_{1/2} \) of the Ru\(^{II} \)/Ru\(^{III} \) oxidation vs. NEt_3 addition for: [Ru(L^3)(Terpy)](PF_6)_2 (black squares), [Ru(L^3)(PhTerpy)](PF_6)_2 (red circles), [Ru(L^1)(bbp)](PF_6)_2 (blue triangles) and [Ru(L^2)(bbp)](PF_6)_2 (green diamonds).

Chapter 7

Figure 7.1 Schematic view of SCO for an octahedral Fe(II) complex

Figure 7.1.1.1 The electron arrangement of strong field and weak field complexes

Figure 7.1.2.1 Potential wells of the HS and LS states

Figure 7.1.3.1 A schematic mechanism for optical excitation

Figure 7.1.3.2 UV/Vis spectra for the before bleaching (b b) and after bleaching (a b) Left: [Fe(Ptz)_3](BF_4)_2. Right: [Fe(Pic)_3]Cl_2·EtOH

Figure 7.1.3.3 Magnetic moment vs. temperature, and magnetic moment before bleaching and after-bleaching for [Fe(Ptz)_3](BF_4)_2
Figure 7.1.5.1 Example of an iron triazole complex hydrogen-bonded to a polymer backbone 233

Figure 7.1.5.2 Left: Terthiophene OQSals based metallo-complex. Right: Thiophene OQSals based metallo-complex 234

Figure 7.2.1.1 An SCO curve for iron(II) complex of a dipyridyltriazole ligand 235

Figure 7.2.2.1 Nuclei energy splitting responsible for quadrupole splitting 237

Figure 7.2.2.2 Example Mössbauer spectra of an SCO complex, [Fe(3-Br-phen)$_2$(NCS)$_2$]-0.5MeOH (black = LS, grey = HS) 237

Figure 7.2.3.1 [Fe(2-mephen)$_3$]$^{2+}$ Left: variable temperature UV/Vis. Right: irradiated sample 239

Figure 7.2.4.1 Example IR spectra of SCO compounds. I [Fe{HC(pz)$_3$}$_2$]SiF$_6$, II [Fe{HC(pz)$_3$}$_2$(TCAS). HC(pz)$_3$ (tris(pyrazol-1-yl)methane) and TCAS (p-sulfonatothiacylic[4]arene). Blue line (room temperature), green lines (373 K) and red lines (433 K) 240

Figure 7.2.4.2 Example of a change in Raman spectra as a result of SCO for a Fe(Pyrazine)Pt(CN)$_4$ complex 241

Figure 7.3.1 Small molecule and polymeric complexes studied in this chapter. OPh (Phe noxy), OPh$_{tBu}$ (tert-buty lphenoxy) 243

Figure 7.3.2 Comparison of IR spectrum for [Fe(L$_3^1$)$_2$(ClO$_4$)$_2$ with the B3LYP and OLYP predicted spectra for [Fe(L$_3^1$)$_2$]$^{2+}$. 246

Figure 7.5.1.1 Electronic absorption spectra. Left: [Fe(L$_1^1$)$_2$(ClO$_4$)$_2$, [Fe(L$_1^1$)$_2$(PF$_6$)$_2$, [Fe(L$_2^1$)$_2$(ClO$_4$)$_2$ and [Fe(L$_2^1$)$_2$(PF$_6$)$_2$. Right: [Fe(L$_1^{1P}$)$_2$(ClO$_4$)$_2$ and [Fe(L$_2^{1P}$)$_2$(ClO$_4$)$_2$ 249

Figure 7.5.1.2 Molecular orbitals associated with the 549 nm transition 250

Figure 7.5.2.1 MLCT band absorbance as a function of temperature for [Fe(L$_3^1$)$_2$(ClO$_4$)$_2$ (recorded in benzonitrile) 252
**Figure 7.5.2.2** Extinction coefficient vs. temperature for [Fe(L\textsuperscript{3})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} and [Fe(L\textsuperscript{3})\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} (recorded in benzonitrile) 253

**Figure 7.5.3.1** Left: Absorbance spectra of [Fe(L\textsuperscript{4P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} collected at a range of temperatures. Right: the extinction coefficient of [Fe(L\textsuperscript{4P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} at 524 nm as a function of temperature. 254

**Figure 7.6.1.1** Solid-state rR spectra recorded using 568 nm excitation. Left: [Fe(L\textsuperscript{1})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} and [Fe(L\textsuperscript{1P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}. Right: [Fe(L\textsuperscript{2})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} and [Fe(L\textsuperscript{2P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}. 256

**Figure 7.6.1.2** Two different vibrational modes of [Fe(L\textsuperscript{1})\textsubscript{2}]\textsuperscript{2+}. Red arrows indicate displacement vectors 256

**Figure 7.6.2.1** Solid-state rR collected for [Fe(L\textsuperscript{3})\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}. \(\lambda_{\text{ex}}\) 568 nm. 258

**Figure 7.6.2.2** Vibrational mode assigned to 1556 cm\textsuperscript{-1} for HS-[Fe(L\textsuperscript{3})\textsubscript{2}]\textsuperscript{2+}, red arrows indicate displacement vectors (exaggerated for clarity) 259

**Figure 7.7.1.1** Variable temperature magnetic moments. Left: [Fe(L\textsuperscript{1})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} and [Fe(L\textsuperscript{1P})\textsubscript{2}](PF\textsubscript{6})\textsubscript{2}. Right: [Fe(L\textsuperscript{2})\textsubscript{2}](PF\textsubscript{6})\textsubscript{2}. 262

**Figure 7.7.2.1** Magnetic moment vs. temperature. Left: [Fe(L\textsuperscript{3})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}. Right: [Fe(L\textsuperscript{3})\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}. 263

**Figure 7.7.3.1** Magnetic moment of [Fe(L\textsuperscript{4})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}. 264

**Figure 7.8.1.1** Mössbauer spectra of [Fe(L\textsuperscript{1})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} and [Fe(L\textsuperscript{1P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} collected at 4 K. [Fe(L\textsuperscript{1P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} enriched with iron-57 266

**Figure 7.8.1.2** Mössbauer spectra of [Fe(L\textsuperscript{3})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} and [Fe(L\textsuperscript{2P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} collected at 4 K ([Fe(L\textsuperscript{2P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} enriched with iron-57) 267

**Figure 7.8.2.1** Mössbauer spectra of [Fe(L\textsuperscript{3})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} recorded at 4.2 K, 200 K and 294 K 268

**Figure 7.8.3.1** Mössbauer spectra of [Fe(L\textsuperscript{4})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} and [Fe(L\textsuperscript{4P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} collected at 5.6 K and 4.6 K respectively ([Fe(L\textsuperscript{4P})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} enriched with iron-57) 269
List of Tables

Chapter 2

Table 2.4.1 Crystal and refinement data for the ligands

Chapter 3

Table 3.4.1 Crystallographic and refinement data for complexes
[Fe(L^1)_2](PF_6)_2 and [Fe(L^1)_2](ClO_4)_2

Table 3.4.2 Crystallographic and refinement data for complexes
[Fe(L^2)_2](PF_6)_2, [Fe(L^3)_2](BF_4)_2

Chapter 4

Table 4.4.1.1 Crystallographic and refinement data for complexes

Table 4.4.3.1 Crystallographic and refinement data for the complexes

Table 4.4.5.1 Crystallographic and refinement data for complexes

Chapter 5

Table 5.2.3.1 Examples of T_g temperature for different substituents

Table 5.2.3.2 T_g values for Carriedo’s gold cross-linked polyphosphazenes

Table 5.5.1 Molecular weights and PDIs of the metal-free polyphosphazenes

Table 5.8.1 T_g values for metal-free, iron(II) and ruthenium(II) complexes of the polyphosphazenes
Chapter 6

Table 6.3.1.1 Extinction coefficients of MLCT bands for the OPhTerpy based complexes 192

Table 6.3.1.2 Extinction coefficients of MLCT bands for the OTerp y based complexes 194

Table 6.3.2.1 Peak MLCT absorption wavelengths and extinction coefficient of the bbp based complexes as NEt₃ was sequentially added 197

Table 6.3.3.1 Extinction coefficients of MLCT bands for the bpp based complexes recorded in acetonitrile 199

Table 6.5.1.1. Electrochemical data for the small molecule complexes, parentheses indicate ΔEₚ (mV) 209

Table 6.3.2.1 Electrochemical data for the [Ru(bbp)(Terpy)]²⁺ based complexes, parentheses indicate ΔEₚ (mV) 211

Table 6.5.3.1 Electrochemical data for the small molecule complexes, parentheses indicate ΔEₚ (mV) 215

Chapter 7

Table 7.4.1 Electrochemical data in CH₃CN at 293 K 248

Table 7.5.1.1 Peak MLCT absorption wavelengths and extinction coefficient 251