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# **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  
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North

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## 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 objective 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 ( $L^1-L^7$ ) and four polyphosphazene ( $L^{1P}-L^{4P}$ ) ligands<sup>1</sup> were synthesised with 2,6-di(pyridine-2-yl)pyridine-4(1*H*)-onate (OTerpy); 4-(2,6-di{pyridin-2-yl}-pyridine-4-yl)phenolate (OPhTerpy); 2,6-di(1*H*-benzimidazol-2-yl)pyridine-4(1*H*)-onate (Obbp); and 4-(2,6-di{1*H*-pyrazol-1-yl}pyridine-4-yl)phenolate (OPhbbp) 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 ( $L^1-L^7$ ). 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  $L^1$ ,  $L^2$ ,  $L^{1P}$  and  $L^{2P}$  were each determined to be low spin (LS), while those formed with  $L^3$  displayed SCO, and the iron complex formed with  $L^4$  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(1*H*-benzimidazol-2-yl)pyridine (bbp); and 2,6-di(1*H*-pyrazol-1-yl)pyridine) with the respective ligand ( $L^1-L^4$ ). Using electronic absorption and rR spectroscopy it was determined that only the polymers  $L^{1P}$  and  $L^{2P}$  formed complexes ( $[Ru(L^{1P})(Terpy)]Cl_2$ ,  $[Ru(L^{1P})(PhTerpy)]Cl_2$ ,

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<sup>1</sup> See pull out sheet for ligand structures.

$[\text{Ru}(\text{L}^{2\text{P}})(\text{Terpy})]\text{Cl}_2$  and  $[\text{Ru}(\text{L}^{2\text{P}})(\text{PhTerpy})]\text{Cl}_2$  analogous to that of their SMA ( $[\text{Ru}(\text{L}^1)(\text{Terpy})](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{L}^1)(\text{PhTerpy})](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{L}^2)(\text{Terpy})](\text{PF}_6)_2$  and  $[\text{Ru}(\text{L}^2)(\text{PhTerpy})](\text{PF}_6)_2$ ), 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 ( $\text{L}^{3\text{P}}$ ), the SMA ( $[\text{Ru}(\text{L}^1)(\text{bbp})](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{L}^2)(\text{bbp})](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{L}^3)(\text{Terpy})](\text{PF}_6)_2$  and  $[\text{Ru}(\text{L}^3)(\text{PhTerpy})](\text{PF}_6)_2$ ) 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.

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