

Abstract

Name: Joseph Peter Byrne

Title: Novel **btp** [2,6-bis(1,2,3-triazol-4-yl)pyridine] systems: a versatile motif for the formation of supramolecular self-assembly structures

This thesis, entitled “Novel **btp** [2,6-bis(1,2,3-triazol-4-yl)pyridine] systems: a versatile motif for the formation of supramolecular self-assembly structures” describes the synthesis and characterisation of a range of new ligands containing the **btp** binding motif and their various supramolecular self-assembly formations, particularly with metal ions.

Chapter 1 introduces the **btp** motif, comparing it to other terdentate binding motifs and describing synthetic routes for its formation *via* the Cu(I)-catalysed azide–alkyne ‘click’ reaction, as well as some key features of these systems. All of the literature concerning **btp** is summarised, with particular interest paid to *d*- and *f*-metal coordination chemistry and anion binding. Some specific applications and the formation of polymeric and supramolecular systems are presented as well. Prior studies of Ln(III)-directed self-assembly studies in the Gunnlaugsson laboratory are also summarised.

Chapter 2 describes the design and synthesis of two new **btp** ligands, by means of a one pot ‘click’ reaction, and their coordination chemistry with *d*-metal ions Ru(II), Ni(II), Ir(III) and Pt(II). X-ray crystal structures of a number of these compounds were obtained. All complexes display non-classical triazolyl C–H...Cl[−] hydrogen bonding. Photophysical studies of the Ru(II), Ir(III) and Pt(II) complexes at room temperature are described, where all but one complex showed only ligand-centred fluorescence; measurements at 77K gave more interesting emission properties. Electrochemical properties of the Ru(II) systems are reported and the formation of a metallo-supramolecular gel is described, which was imaged by SEM and HIM.

Chapter 3 principally focusses on *f*-metal ions and the formation of Ln(III)-directed self-assemblies of ligands, including an allyl amide **btp** derivative and a range of amino acid derivatives. These complexes are luminescent, with modest to very high quantum yields ($\Phi_{Eu} = 0.4\text{--}3.0\%$, $\Phi_{Tb} = 6.3\text{--}70\%$). Self-assembly was monitored by various spectroscopic titration techniques and global stability constants for the assemblies determined by fitting the data to models ($\log\beta_{1:3} = 18.9\text{--}23.0$). This chapter also describes the formation of a self-templated [2]catenane through olefin ring-closing metathesis and supramolecular pre-organisation, confirmed by single crystal X-ray diffraction. This elegant structure shows promise for selective anion binding.

Chapter 4 details the design and synthesis of a number of chiral **btp** ligands from either carbohydrate azide, or chiral amine starting materials, the latter through a one-pot diazo-transfer–deprotection–‘click’ protocol. Three of the ligand were characterised by X-ray crystallography. These ligands all form luminescent Eu(III)-directed self-assemblies ($\Phi_{Eu} = 0.5\text{--}1.9\%$) and one enantiomeric pair forms very emissive Tb(III)-directed self-assemblies ($\Phi_{Tb} = 56\text{--}67\%$). These complexes possess chiroptical properties (namely circular dichroism and circularly polarised luminescence). Self-assembly in solution was monitored by means of various spectroscopic titrations as in the previous chapter, and also, by virtue of the chiroptical properties of these assemblies, by CD titration. Determination of stability constants from CD titrations is not commonly reported; here such values are comparable to those determined by fitting absorbance and emission titration data ($\log\beta_{1:3} = 19.0\text{--}23.2$).

Finally, Chapter 5 gives experimental details and procedures for the work carried out in the other chapters. Supplementary spectra and data are provided in the Appendices.