The Design, Synthesis and Geometric Analysis of Large Centrally Functionalised Porphyrin-Spacer-Porphyrins

By

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The work described in this thesis was carried out at the Department of Chemistry at the University of New England under the supervision of Associate Professor Maxwell J. Gunter.

I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

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SUMMARY

This thesis describes the design, synthesis and geometric analysis of centrally functionalised Porphyrin-Spacer-Porphyrins (PSPs) that have potential as 'molecular switches' and/or 'artificial enzymes'. The synthetic approach adopted made use of specifically designed functionalised building blocks that could be 'glued' together using a number of well established protocols based on various stereospecific [2+2] and [4+2] cycloaddition reactions.

Chapter 2 describes the screening of potential binane and polynorbornane spacer groups using simple computationally generated molecular mechanics models. Details of the subsequent development of general synthetic methods toward fused-oxabridged norbornenes that were judged to have suitable geometric and functional characteristics follow. A general method for the synthesis of variously substituted aryl imides allowed for an efficient introduction of central functionalities into the spacer building blocks. The extension of these systems based on tandem [2+2] cycloaddition reactions (Mitsudo reaction) followed by epoxidation (Sharpless) gave the dual functionalised spacer building blocks. A new porphyrin building block (PBlock) was developed in conjunction with the spacer building blocks and its synthesis and reactivity were compared with a known PBlock analogue, also synthesised as part of this work using published methods. Results from the synthesis of two new PSP systems allowed for a comparison between the two PBlocks and their ability to undergo the final coupling (ACE reaction) step with the *bis*-epoxide spacer units.

The third chapter focuses on the various experimental methods (UV-Vis and NMR spectroscopy) used to explore both the static and dynamic geometric characteristics of the arch-shaped *bis*-porphryrins. A series of flexible *bis*-pyridines were collectively used as a 'molecular ruler' to measure the interporphyrin distance of a dizinc PSP host. The experimentally determined porphyrin-porphyrin distance was compared with the same distance determined from semi-empirical molecular modelling calculations (AM1). The use of more rigid *bis*-pyridines gave information about the flexibility of the PSP host system. Large conformational changes in the PSP host system were measured upon formation of a 1:1 complex with a 'small' *bis*-pyridine porphyrin guest confirming results from molecular modelling and comparative UV-Vis binding study results.

All the experimental details are given in Chapter 4.

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