Porphyrin Containing Rotaxanes and Catenanes in Solution and on Solid Supports

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DECLARATION

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

SIGNED: [redacted] **DATE:** 16/7/07

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ABSTRACT

This thesis describes some approaches towards the synthesis of catenanes and rotaxanes incorporating porphyrin moieties, and a study of aspects of their physical and chemical behaviour. Two main objectives were firstly the creation of multi-functionalised rotaxanes and catenanes capable of 'controlled switching' between two or more co-conformations in solution, and secondly an extension of these and other studies towards rotaxane and catenane systems that are attached to polystyrene-based solid supports.

Firstly, the viability of utilising specific metal-ligand coordination properties between a suitably functionalised pyridine ligand and a strapped metalloporphyrin host to template the assembly of porphyrinic catenanes and rotaxanes was explored. Ruthenium(II) carbonyl and rhodium(III) iodide strapped porphyrin derivatives were selected for this purpose due to their high affinity for nitrogen-based ligands. Attempts to determine the site specificity of various pyridine-based ligands revealed interesting and hitherto unreported ligand migration and exchange properties that were explored further in some detail.

Having thus established the site-specificity and binding properties of these particular ruthenium and rhodium porphyrins, attempts to synthesise rotaxanes and catenanes incorporating both a neutral diimide 'station' and a functionalised pyridine moiety, which could function not only as a template but also as a second binding motif, were undertaken. New synthetic pathways were investigated including the "click" reaction between azides and alkynes under relatively mild conditions, producing triazole linkers in the thread component of rotaxanes, or in one of the macrocyclic links of a catenane. The potential of these triazoles produced in the synthetic pathways to act as additional recognition sites within these interlocked systems was also explored.

Modification of a previously studied solution phase three-component self-assembling rotaxane system to allow attachment of analogous individual rotaxane components to solid gel-phase polystyrene bead supports was undertaken. Studies into not only the tethering reaction of each of these components to the gel-phase resins, but also into the subsequent self-assembly of rotaxanes on solid supports were performed. HR MAS NMR techniques were utilised to study the dynamic behaviour of the systems as they assembled on the gel-phase polymer support from the surrounding solution-phase components. The dynamic behaviour of the biphasic systems were compared directly to solution-phase analogues to establish a correspondence between the two methods.

Finally having established successful tethering conditions, and a deeper understanding of the complex self-assembly dynamics of solid phase systems involving individual components, the synthesis of solid-tethered beads incorporating combinations of two or three of the components on a single bead was investigated. HR MAS NMR was again used to investigate the various intra-bead interactions between different components on a single bead, and these results were correlated with the simpler mono-substituted systems.

ABBREVIATIONS

COSY	Correlation spectroscopy
CPMG	Carr-Purcell-Meiboom-Gill
DCC	*N,N'*-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DEAD	Diethyl azodicarboxylate
DIPEA	*N,N'*-diisopropylethylamine
DMF	*N*, *N* -Dimethylformamide
EDC	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
EI-MS	Electron impact mass spectrometry
ES-MS	Electrospray mass spectrometry
HOBT	1-Hydroxybenzotriazole hydrate
HR MAS	High-resolution magic angle spinning
LUMO	Lowest unoccupied molecular orbital
MAS	Magic angle spinning
MeOD	Methanol-d_4
NOESY	Nuclear Overhauser effect spectroscopy
ROESY	Rotating frame nuclear Overhauser effect spectroscopy
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
VT	Variable temperature

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