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by

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Declaration

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Abstract

This thesis will be in three parts describing three projects which investigated different areas of new materials science in the context of nanotechnological chemistry. The parts include: the synthesis and characterisation of novel metalloporphyrin complexes with the geometry of 'molecular cogs'; physical analysis of simple, new cyclodextrin-based inclusion compounds, and attempts to generate rotaxanes there-from; and analysis of the behaviour of aromatic hydrophobically-modified water-soluble polymers as components in supramolecular complexing complementary polymer systems.

A synthetic approach through a vinyl sulfone–modified Barton and Zard pyrrole was successfully utilised. It was envisaged that this functionality could be extended further into a cyclic spiro substituent: where the spiro functionality incorporated aromaticity, it would constitute a planar, non-rotating substituent arranged orthogonally to the macrocyclic plane. Symmetrical, tetraspiro annulated porphyrin systems including indanyl and fluorenyl derivatives were synthesised and spectroscopically characterised. The fluorenyl-derived zinc metalloporphyrin gave suitable crystals for X-ray crystallographic analysis.

The design and synthesis of a series of cyclodextrin inclusion compounds incorporating relatively simple amino-substituted biaryl axle was carried out. The pseudorotaxanes were asymmetric in character, incorporating functionalised homo- and heteroaromatic rings at either end, joined by an unsaturated linker. The heterocycle was an azine ring (pyridine or pyrimidine), and therefore bore one or more nitrogen protonation sites; pK_as in water-methanol solutions were determined. Distinct inclusion in α-cyclodextrin was observed and quantified in dilute basic aqueous solution by UV-visible spectroscopy. Corresponding inclusion in concentrated acidic conditions was studied through 2D NMR techniques, revealing a clear temperature dependence for the α-cyclodextrin/pyridine-based axle, and site-exchange analysis was performed to determine the rate of inclusion compound formation. Generation of corresponding rotaxanes was not achieved, most

likely due to the reactivity of azine ring-bound amine groups in the necessary reaction conditions.

The range of hydrophobically modified polymers was expanded by appending amide-bonded aromatic side chains to poly(acrylic acid), to give phenyl-, diphenyl-, naphthyl- and anthryl-type modification. This procedure allowed control over the molecular weights of the polymer products, and a degree of direction of the amount of each new polymer's modification observed primarily through 2D NMR techniques, and absorbance/fluorescence where applicable. It was generally found that aromatic substituents lacked the tendency to aggregate in solution that is observed for long polymer-bound alkyl groups. This is likely due to the relative length and rigidity of aromatic species. For naphthyl and anthryl groups excimer emission would be a likely consequence of aggregation but its absence suggests that π-CH hydrophobic association between aromatic groups and the alkane backbone is more favoured. For the anthryl-bearing polymer in particular this means that the likely form of substitution consistent with the fluorescence data is not suitable for studying anthracene fluorescence behaviour in an aqueous-polymer environment. The interactions of these modified polymers with native α- and β-cyclodextrin and the corresponding cyclodextrin-modified PAAs in aqueous solution were assessed with 2D NOESY NMR spectroscopy.

Abbreviations

AIBN	2,2′-Azobis(2-methylpropionitrile)
aq.	aqueous
cat.	catalyst
CD	cyclodextrin
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	Dicyclohexylcarbodiimide
DMF	*N*,*N*-dimethylformamide
EIMS	electron impact mass spectrometry
Et	ethyl
hr(s)	hour(s)
IR	infra red
lit.	literature
MHz	megahertz
min(s)	minute(s)
m.p.	melting point
NMP	1-methylpyrrolidin-2-one
NMR	nuclear magnetic resonance
ppm	parts per million
PTSA	*p*-toluenesulfinic acid
R_f	retention factor
sat.	saturated
TFA	trifluoroacetic acid
THF	tetrahydrofuran
tlc	thin layer chromatography
TMS	tetramethylsilane
Tol	*p*-toluene
UV-Vis	ultraviolet–visible
w%	weight percent

Contents