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Silica Immobilised Metal Ion Activated Molecular Receptors

A Thesis Presented for the Degree of

Doctor of Philosophy

by

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ABSTRACT

Immobilisation of functional entities, such as, enzymes, onto solid supports, as a means of facilitating their removal from the surrounding environment and subsequent regeneration has been in practice for many decades. This work focuses on the immobilisation and analysis of three-walled (pendant armed), cyclen based receptor complexes immobilised onto a silica surface for the purpose of sequestering aromatic anions from aqueous solution: Si-GPS-[Cd(Trac)]$(ClO_4)_2$, Si-GPS-[Cd(DiPTrac)]$(ClO_4)_2$, and Si-GPS-[Cd(TriPTrac)]$(ClO_4)_2$ were the immobilised receptors used.

Initially, synthesis of a three-walled model receptor, [Cd(TracHP12)]$(ClO_4)_2$, that is not bound to silica yet mimics the properties of the silica anchored receptor complexes with a hydroxypropyl pendant arm was effected. Aromatic anion binding constant measurements were made on the model receptor using ^{1}H NMR monitored titrations in DMSO-d_6 which showed that, in comparison to the first generation four-walled receptors, the removal of one of the pendant arms did not affect the binding capability of the receptor's cavity significantly. It was shown that the binding strength correlated well with the pK_a of the particular anion with, for example, *p*-hydroxybenzoate > *m*-hydroxybenzoate > *o*-hydroxybenzoate. The precursor to this receptor was then immobilised onto a silica surface and subjected to metal ion uptake studies to gauge its coordination properties with a number of divalent metal(II) ions: Cd(II), Pb(II), Zn(II), Cu(II) and Ca(II). The three Cd(II) coordinated receptor complexes mentioned above were then subjected to inclusion studies with a number of aromatic anions in aqueous conditions whereupon a reversal of the previously mentioned trend, *i.e.* *o*-hydroxybenzoate > *m*-hydroxybenzoate > *p*-hydroxybenzoate was observed. This indicated that the presence of water in the system changes the

hydrogen bonding mode of the host-guest complexes, and was a major discovery arising from this work.

DECLARATION

I certify that this thesis does not incorporate, without acknowledgement, any material previously submitted for any degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

signed.....

Jozef Andrew Zbigniew Hodyl

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ABBREVIATIONS

Å	Ångstrom (10^{-10} m)
APT	attached proton test
b	broad
c	g ml^{-1}
cbz	carboxybenzyl
CD	cyclodextrin
CP	cross polarisation
CTAB	cetyltrimethylammonium bromide
cyclam	1,4,8,11-tetraazacyclotetradecane
cyclen	1,4,7,10-tetraazacyclododecane
δ	chemical shift
DiPTrac	1,4,7-*tris*(*S*)-2-hydroxy-3-[4-((2-(2-hydroxyethoxy)ethoxy)phenoxypropyl]-1,4,7,10-tetraazacyclododecane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DNA	deoxyribonucleic acid
DOTA	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid
DOTAM	1,4,7,10-tetrakis(acetamido)cyclen
DOTEP	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrakis(methyleneethylphosphinate)
DRIFT	Diffuse Reflectance Infrared Fourier Transform spectroscopy
EC	endcapped

EtOH	ethanol
GPDMS	glycidoxypropyldimethylsilane
GPDMES	3-(glycidoxypropyl)dimethylethoxysilane
GPS	glycidoxypropylsilane
GPTS	3-(glycidoxypropyl)trimethoxysilane
$\{^1H\}$	proton decoupled
HTPE	hydroxy terminated polyether
J	coupling constant
K	apparent stability constant
K	Kelvin
kHz	kilohertz (10^3 s^{-1})
kJ	kilo Joule
m	multiplet
M^{2+}	unspecified divalent metal ion
MAS	magic angle spinning
MCM-41	Mobil catalytic or crystalline material - batch 41
MeCN	acetonitrile
MeOH	methanol
MHz	megahertz (10^6 s^{-1})
NMR	nuclear magnetic resonance
OTs	tosylate
PEG	polyethylene glycol
pK_a	$-\log_{10}K_a$
pm	picometre
ppm	parts per million
r	radius
s	singlet

SBP	sulfate binding protein
t	triplet
tert	tertiary
tlc	thin layer chromatography
TMCS	trimethylchlorosilane
TOSS	TOtal Suppression of Spinning Side-bands
Trac	1,4,7-*tris*-((*S*)-2-hydroxy-3-phenoxypropyl)-1,4,7,10-tetraazacyclododecane
TracHP12	1-(2-hydroxypropyl)-4,7,10-*tris*-((*S*)-2-hydroxy-3-phenoxypropyl)-1,4,7,10-tetraazacyclododecane
TriPTrac	1,4,7-*tris*(*S*)-2-hydroxy-3-[4-(2-(2-(2-hydroxyethoxy)ethoxy)-ethoxy)phenoxypropyl]-1,4,7,10-tetraazacyclododecane
UV-vis	ultraviolet-visible spectroscopy
VOC	volatile organic compound