

Contents

Chapter 1

Porphyris and Metalloporphyrins: A General Outlook

1.1	Introduction.....	1
1.2	The Ubiquitous Porphyrin System	2
1.3	Porphyris in Life Processes.....	7
1.3.1	Enzymes.....	8
1.3.2	Hemoglobin and Myoglobin.....	11
1.3.3	The Cytochromes	13
1.3.4	Chlorophyll.....	14
1.4	Metalloporphyrins as Catalysts	15
1.4.1	Catalysis of oxidation reactions by metalloporphyrins.....	17
1.4.2	Catalysis of electrochemical processes by metalloporphyrins	18
1.4.3	Catalysis of isomerisation and polymerisation reactions by metalloporphyrins.....	20
1.4.4	Catalysis of photochemical reactions by metalloporphyrins	21
1.5	References.....	23

Chapter 2

Polymer Supported Metalloporphyrins

2.1	Introduction.....	27
2.2	Metalloporphyrins Covalently Bonded to Polymer Supports	28
2.3	Metalloporphyrins Bonded to Higher Exchange Resins.....	33
2.4	Metalloporphyrins Bonded to Inorganic Supports.....	36
2.5	Metalloporphyrins Intercalated into Layered Matrices	37
2.6	Immobilisation of Metalloporphyrins in Electropolymerised Films-Modified Electrodes.....	39
2.6.1	Polypyrrole films doped with anionic porphyrins	39
2.6.2	Electropolymerisation of pyrrole-substituted metalloporphyrins	39
2.6.3	Electropolymerisation of amino-, hydroxy-, methoxy- and vinyl- substituted porphyrins	41
2.6.4	Immobilisation of charged metalloporphyrins into pre-electropolymerised polypyrrole films bearing functional groups.....	41
2.6.5	Catalytic applications of electropolymerised metalloporphyrins films.....	42
2.6.6	Electropolymerised metalloporphyrins- analytical and biological applications	44
2.7	Outline of the Present Work.....	45
2.8	References.....	48

Chapter 3

Electronic Modulation of Metalloporphyrins Grafted/Dispersed in Polymer Matrices

3.1	Introduction.....	51
3.2	Experimental	52
	3.2.1 Preparative details	52
	3.2.2 Physical measurements.....	60
3.3	Results and Discussion	61
	3.3.1 Characterisation of porphyrins and polymer supports.....	61
	3.3.2 Polymer immobilised/dispersed porphyrins systems.....	66
	3.3.3 Electronic spectra	71
	3.3.4 Origin of electronic modulation.....	77
	3.3.5 Cyclic voltammograms.....	83
	3.3.6 EPR spectra.....	88
3.4	References.....	96

Chapter 4

Catalase-like Activities of Selected PS-MTPPS Systems

4.1	Introduction.....	97
4.2	Experimental	98
	4.2.1 Preparative details	98
	4.2.2 Catalytic reaction monitoring.....	98
4.3	Results and Discussion	99
	4.3.1 The catalase system- A brief outlook	99
	4.3.2 Catalase-like activity of PS-MTPPS systems developed.....	100
4.4	References.....	109

Chapter 5

Peroxidase-like and Photocatalytic Activities of Selected PS-MTPPS Systems

5.1	Introduction.....	110
5.2	Experimental	111
	5.2.1 Preparative details	111
	5.2.2 Preparation of polymer beads bonded to Rose-bengal	111
	5.2.3 Monitoring of peroxidase-like activity	112
	5.2.4 Detection of singlet oxygen	112
5.3	Results and Discussion	112
	5.3.1 A brief outlook on peroxidases	112
	5.3.2 Peroxidase-like activity of selected PS-MTPPS systems	114
	5.3.3 Photogeneration of singlet oxygen	120
5.4	References.....	124

Chapter 6

Binary Porphyrin Systems Grafted on Polymer Supports

6.1	Introduction.....	125
6.2	Experimental	127
	6.2.1 Preparative details	127
	6.2.2 Generation of polymer supported H_2TpyP^+ / $MTpyP^+$	127
	6.2.3 Generation of polymer grafted H_2TMPyP^{4+} / $MTMPyP^{4+}$	127
	6.2.4 Generation of binary porphyrins on polymer supports.....	128

6.2.5	Physical measurements.....	128
6.3	Results and Discussion	129
6.3.1	Synthesis of polymer grafted $H_2TpyP^+/MTPyP^+$ systems	129
6.3.2	Incorporation of additional anionic porphyrins on PS- $TpyP^+$ systems(possible porphyrin “dimer” formation)	138
6.3.3	Generation of polymer grafted tetracationic porphyrin systems	142
6.3.4	Ionically held binary metalloporphyrins grafted on polystyrene surface	146
6.4	References.....	156

Chapter 7

Summary and Conclusion