

## Contents

	<i>Preface</i>	<i>xi</i>
	<i>Symbols and abbreviations</i>	<i>xiii</i>
	<i>Summary of phthalocyanine nomenclature</i>	<i>xvii</i>
<b>Chapter 1</b>	<b>An introduction to the phthalocyanines</b>	<b>1</b>
1.1	Discovery and structural determination	1
1.2	The use of Pcs as industrial colorants	3
1.3	Metal phthalocyanines (MPcs)	3
1.4	A gift to molecular physics	7
1.5	A brief note on Pc nomenclature	9
1.6	The Pc literature	10
<b>Chapter 2</b>	<b>Phthalocyanine synthesis</b>	<b>12</b>
2.1	The synthesis of unsubstituted Pcs	13
	2.1.1 Metal-free Pc (H <sub>2</sub> Pc)	13
	2.1.2 Metal-ion-containing Pcs (MPcs)	14
	2.1.3 Pc sandwich complexes (MPc <sub>2</sub> )	15
2.2	Axially substituted Pcs	16
	2.2.1 <i>oxo</i> -Titanium(IV) Pc and related compounds	16
	2.2.2 Axially substituted SiPc, GePc and SnPc	16
2.3	Benzo-substituted Pcs	17

	2.3.1	Tetra-substituted Pcs	18
	2.3.2	Peripheral octa( <i>op</i> )-substituted Pcs	20
	2.3.3	Non-peripheral octa( <i>onp</i> )-substituted Pcs	22
2.4		Naphthalocyanines (NPs)	24
2.5		Asymmetrically substituted Pcs	25
2.6		Phthalocyanine polymers	26
	2.6.1	Network polymers	27
	2.6.2	Cofacial (bridged) polymers	28
	2.6.3	Side-chain polymers	30
<b>Chapter 3</b>		<b>The fabrication of phthalocyanine materials</b>	<b>32</b>
3.1		Crystals	32
	3.1.1	The crystal structures of H <sub>2</sub> Pc and the planar MPcs	33
	3.1.2	The crystal forms of non-planar MPcs	36
	3.1.3	Crystal structures of substituted Pcs	39
3.2		Thin films	41
	3.2.1	Vacuum sublimation	43
	3.2.2	Molecular epitaxial deposition	45
3.3		Langmuir–Blodgett films	47
	3.3.1	Film fabrication	47
	3.3.2	LB film characterisation	50
	3.3.3	LB films from Pcs: a word of caution	50
	3.3.4	LB films from unsubstituted Pc derivatives	51
	3.3.5	Tetra-substituted Pc derivatives	52
	3.3.6	Octa-substituted derivatives	56
	3.3.7	Polymeric LB-film-forming Pcs	57
	3.3.8	General observations on the structure of Pc-derived LB films	57
3.4		Spin-coated Pc films	58
3.5		Electrochemical deposition techniques	60
3.6		Mesomorphic phthalocyanine materials	60
	3.6.1	Mesophase characterisation	62
	3.6.2	Pc mesophases	64
	3.6.3	The number and type of flexible side-chains	65
	3.6.4	The influence of side-chain length	65
	3.6.5	The effects of the linking group and site of substitution	74
	3.6.6	The influence of the central metal ion	77
	3.6.7	The influence of side-chain branching	78
	3.6.8	Non-uniformly substituted Pc mesogens	78

	3.6.9 Mesogenic oligomers and polymers	80
	3.6.10 Phthalocyanine glasses	81
	3.6.11 Phthalocyanine lyotropic mesogens	82
3.7	Other self-ordering Pc materials	84
3.8	Polymer composites	86
3.9	Inorganic composites	87
<b>Chapter 4</b>	<b>Optical properties</b>	<b>88</b>
4.1	Solution characteristics	88
4.2	Exciton coupling	91
4.3	Structural information from visible absorption spectra of Pc materials	93
4.4	Nonlinear optics	94
	4.4.1 An introduction to nonlinear optics	95
	4.4.2 Pcs as nonlinear optical materials	96
	4.4.3 The outlook for Pcs as NLO materials	99
4.5	Optical data storage	99
4.6	Spectral hole burning	100
<b>Chapter 5</b>	<b>Electronic conductivity</b>	<b>101</b>
5.1	A brief description of electronic conductivity in organic materials	102
5.2	Intrinsic electronic conductivity in Pc materials	104
5.3	Conduction in evaporated Pc films	107
5.4	Intrinsic conduction within LB Pc films	109
5.5	The conductivity of undoped polymeric Pcs	110
	5.5.1 The conductivity of polyphthalocyanine (PMPc)	111
	5.5.2 The conductivity of axially bridged polymers	111
5.6	The conductivity of Pc charge-transfer complexes	112
5.7	Partially oxidised polymeric systems	116
	5.7.1 Cofacial Pc polymers	116
	5.7.2 Charge-transfer-complex-polymer composites	117
5.8	Conductivity in columnar Pc liquid crystals	117
5.9	Electronic sensors	119
	5.9.1 Single-crystal studies	120
	5.9.2 Sensors based on sublimed films	120
	5.9.3 Sensors based on polymeric Pc materials	122
	5.9.4 Sensors derived from LB and spin-coated Pc films	122

x	<b>Contents</b>	
	5.9.5 Pc sensors based on effects other than changes in conductivity	124
	5.9.6 Pc-based biosensors	124
	5.9.7 Pc-based sensors: conclusions	124
5.10	Additional electronic devices based on Pc materials	125
<b>Chapter 6</b>	<b>Optoelectronic properties of phthalocyanine materials</b>	<b>126</b>
6.1	Photoconductivity	126
	6.1.1 An introduction to xerography	126
	6.1.2 Pc photoconductivity	128
6.2	Photovoltaic properties: solar energy conversion	131
	6.2.1 Schottky junction devices	132
	6.2.2 Pc-containing p–n junction devices	135
6.3	Electrochromism	137
	6.3.1 Electrochromism of LB films	138
	6.3.2 Liquid-crystalline electrochromic Pcs	139
	6.3.3 The outlook for Pcs in electrochromic displays	139
<b>Chapter 7</b>	<b>Miscellaneous properties and uses of Pc materials</b>	<b>140</b>
7.1	Heterogeneous catalysis	140
	7.1.1 The reduction of oxygen and water	140
	7.1.2 Other Pc catalytic processes	142
	7.1.3 The prospects for Pc heterogeneous catalysis	142
7.2	Adsorption properties	143
7.3	Magnetic properties	143
7.4	Applications in nuclear chemistry	144
7.5	Other uses for Pc materials	144
<b>Chapter 8</b>	<b>Future developments</b>	<b>145</b>
8.1	Pc synthesis	145
8.2	Materials fabrication	146
8.3	Applications – towards molecular-scale devices	147
8.4	Pc materials: the need for a multidisciplinary approach	149
<b>Appendix</b>	<b>Commercially available Pcs</b>	<b>151</b>
	<i>References</i>	154
	<i>Index</i>	184
	<i>Colour plates</i>	facing p. 78