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978-0-521-49623-0 - Phthalocyanine Materials: Synthesis, Structure and Function

Neil B. McKeown

Frontmatter

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Since their discovery earlier this century, phthalocyanines have been of great interest to chemists, physicists and industrial scientists. They remain among the most studied functional molecular materials and a vast literature devoted to their structure–property relationships has evolved on the basis of continuous advances in phthalocyanine synthesis. This book assimilates this information and uses recent advances in the study of phthalocyanine-based materials to evaluate critically their potential role in emerging technologies.

After a brief historical overview and a chapter devoted to chemical synthesis, the various types of molecular and polymeric phthalocyanine materials are described in detail. These include crystals, thin films (including those fabricated by molecular epitaxial deposition and the Langmuir–Blodgett technique), composites, liquid crystals and self-assembled materials. The fundamental optical and electronic properties of these materials are explained and their potential in nonlinear optics, optical data storage, electronic sensors, Xerography, solar energy conversion, nuclear chemistry, molecular magnetism, electrochromic displays and heterogeneous catalysis is evaluated. The book includes more than 600 references to the primary literature.

This book will be of value to industrial and academic chemists, physicists and materials scientists studying organic materials generally and phthalocyanines in particular.

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Contents

	<i>Preface</i>	<i>xi</i>
	<i>Symbols and abbreviations</i>	<i>xiii</i>
	<i>Summary of phthalocyanine nomenclature</i>	<i>xvii</i>
Chapter 1	An introduction to the phthalocyanines	1
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
Chapter 2	Phthalocyanine synthesis	12
2.1	The synthesis of unsubstituted Pcs	13
	2.1.1 Metal-free Pc (H ₂ Pc)	13
	2.1.2 Metal-ion-containing Pcs (MPcs)	14
	2.1.3 Pc sandwich complexes (MPc ₂)	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 (NPcs)	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
Chapter 3	The fabrication of phthalocyanine materials	32
3.1	Crystals	32
	3.1.1 The crystal structures of H ₂ 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
Chapter 4	Optical properties	88
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
Chapter 5	Electronic conductivity	101
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	Contents	
	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
Chapter 6	Optoelectronic properties of phthalocyanine materials	126
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
Chapter 7	Miscellaneous properties and uses of Pc materials	140
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
Chapter 8	Future developments	145
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
Appendix	Commercially available Pcs	151
	<i>References</i>	154
	<i>Index</i>	184
	<i>Colour plates</i>	facing p. 78

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[More information](#)

Preface

Travel is one of the great benefits of an academic career. The prospect of another dreary December in Manchester contrasts starkly with last year's magnificent trip to Hawaii. The excuse for this holiday was a one-day symposium dealing with phthalocyanines (Pcs), which formed part of the massive Pacificchem '95 conference. This was the first international symposium devoted to the subject. We were packed into an unsuitably small room in the Honolulu Hilton but the variety and high quality of the presentations allowed us to survive the desperate lack of air-conditioning. The participants noted that the equivalent fullerene symposia received better accommodation and much more attention than our own. This fashionable 'Johnny come lately' has certainly captured the imagination of scientists and the accompanying attention given to functional molecular materials is to be welcomed. Indeed, it is interesting to compare and contrast the history and properties of phthalocyanine and fullerene. Both were discovered by accident (Cronshaw, 1942; Kroto, 1992) and their beautiful symmetrical structures were both elucidated by logical deduction from carefully formulated experiments. In addition, both molecular systems can encompass metals and, with appropriate reagents, form highly conducting charge-transfer complexes. However, in many ways the Pc and fullerene systems possess complementary properties. Most obviously, fullerenes are reddish-pink in colour whereas Pcs are strongly blue or blue-green. The planarity of the Pc macrocycle encourages self-association into highly ordered molecular stacks; however, the spherical shape of fullerene results in a crystalline form in which the molecules possess rotational disorder at room temperature. Importantly for their respective electronic properties, fullerenes have a high electron affinity but Pcs donate electrons readily.

Despite the recent excitement surrounding the fullerenes (Hirsch, 1994), the proven chemical and thermal stability of the Pcs together with their wide acceptance as industrial colorants and photoconductors suggest that, if any molecular electronic materials are to be of significant technological importance, Pcs are still a good bet.

This monograph contains the same multidisciplinary spirit as the Hawaiian symposium. Its strength is that Pc synthesis, materials fabrication and properties appear in the same volume. This allows for easy cross-referencing. It is to be hoped that the integration of the many different fields of Pc materials research has resulted in an accessible survey as well as a useful reference source. The book was written with a newcomer to Pc science in mind (e.g. a graduate student) but does assume a working knowledge of chemistry. I hope that scientists from other disciplines find this book interesting too, despite my oversimplification of many aspects of molecular physics.

I would like to thank the following publishers for their kind permission to reproduce previously published figures: The Royal Society of Chemistry (Figs. 1.2(a), 1.2(c), 3.6(a), 3.6(b), Plates 7 and 8), The American Chemical Society (Figs. 1.2(d), 3.26(a) and 3.26(b)), The American Institute of Physics (Fig. 1.26), R. Oldenbourg Verlag (Figs. 3.3(a) and 3.3(b)), The International Union of Crystallography (Figs. 3.2(a) and 3.2(b)) and Elsevier Science, Amsterdam (Fig. 5.2).

Finally, I would like to acknowledge the people who have helped me write this book. First and most importantly my wife, Andrea Weninger, who used her considerable organisational skills (I have none) to collect and collate many hundreds of references. Professor Richard Tredgold and Dr Neil Thompson read and corrected the manuscript – the book is much better thanks to their eye for detail and strong opinions. In addition, I would like to thank Professor Mike Cook (University of East Anglia) and Professor Cliff Leznoff (York University, Toronto) for initiating my interest in Pcs.

If you, the reader, have any comments or questions, please feel free to contact me.

Neil B. McKeown

Neil.Mckeown@man.ac.uk
Department of Chemistry
University of Manchester
Manchester, M13 9PL, UK.

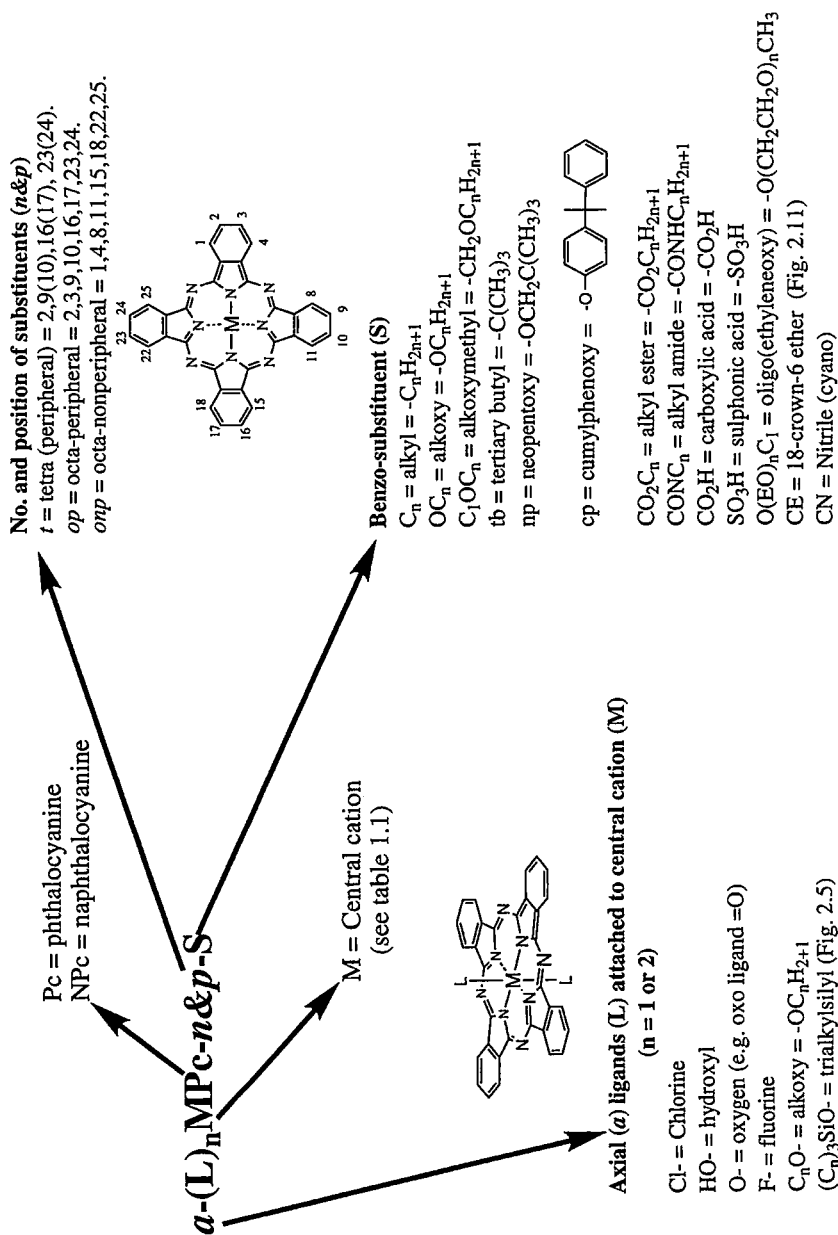
Symbols and abbreviations

A	Surface area (m^{-2})
a	Axial substitution
$[a\text{-OSiPc}]_n$	Phthalocyanine polysiloxane (Section 2.6.1; Fig. 2.19)
Å	Ångström unit (10^{-10} m)
Ac	Anthracocyanine (Fig. 4.2)
AFM	Atomic force microscopy
A_0	Area per molecule (Å^2)
AsF_6^-	Arsenic hexafluoride anion
β	Second-order molecular hyperpolarisability
BF_4^-	Boron tetrafluoride anion
Br_2	Molecular bromine
χ	Material polarisability
$\chi^{(2)}$	Second-order hyperpolarisability
$\chi^{(3)}$	Third-order hyperpolarisability
C_{60}	Fullerene
CD	Compact disc
CGL	Charge-generation layer
C_H	Columnar hexagonal lyotropic mesophase (Fig. 3.25a)
Cl_2	Molecular chlorine
ClO_4^-	Perchlorate anion
CTL	Charge-transport layer
d spacing	Bragg diffraction repeat distance
D_6 -benzene	Deuterated benzene (NMR solvent)
dabco	Diazabicyclooctane

DBN	1,8-diazabicyclo[4.3.0]non-5-ene (a hindered base)
DDQ	2,3-dichloro-5,6-dicyano- <i>p</i> -benzoquinone
ΔE_a	Activation energy for charge-carrier formation
DFWM	Degenerate four-wave mixing
D_{hd}	Discotic hexagonal disordered mesophase (Fig. 3.19c)
D_{ho}	Discotic hexagonal ordered mesophase (Fig. 3.19b)
ΔH_t	Change in enthalpy of transition
DMF	Dimethylformamide
D_{ob}	Discotic oblique mesophase (Fig. 3.19g)
D_{rd}	Discotic rectangular disordered mesophase (Fig. 3.19d;e;f)
DSC	Differential scanning calorimetry
e	Electronic charge (1.602×10^{-19} C)
$E_{1/2^{ox}}$	Half-wave oxidation potential
$E_{1/2^{red}}$	Half-wave reduction potential
EDTA	Ethylenediaminetetraacetic acid
E_g	Band gap
EO	Ethyleneoxy ($\text{CH}_2\text{CH}_2\text{O}$)
ϵ_0	Permittivity of free space
EPR	Electron spin resonance (spectroscopy)
FAB	Fast atom bombardment (mass spectrometry)
FET	Field effect transistor
FF	Fill factor
γ	Third-order molecular hyperpolarisability
η	Power efficiency
H_2	Molecular hydrogen
H_2Pc	Metal-free phthalocyanine
HOMO	Highest occupied molecular orbital
HOPG	Highly oriented pyrolytic graphite
HREM	High-resolution electron microscopy
I	Intensity of light
I_2	Molecular iodine
ICI	Imperial Chemical Industries
IR	Infra-red
ITO	Indium–tin oxide
IUPAC	International Union of Pure and Applied Chemistry
J	Current
J_{\max}	Maximum current
J_{sc}	Short-circuit current
K	Kelvin
k	Boltzmann's constant (1.380×10^{-23} J K ⁻¹)
KBr	Potassium bromide
KCl	Potassium chloride

L	Bridging ligand (Fig. 2.20)
λ	Light wavelength
LB	Langmuir–Blodgett
LCD	Liquid-crystal display
LEED	Low-energy electron diffraction
λ_{\max}	Wavelength of the band of maximum absorption (nm)
LUMO	Lowest unoccupied molecular orbital
μ	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
MALDI	Matrix-assisted laser desorption ionisation (mass spectrometry)
MHz	Megahertz
MLCT	Metal-to-ligand charge transfer
mg	Milligramme
ml	Millilitre
μm	Micrometer (10^{-6}m)
mm	Millimetre (10^{-3}m)
MoS_2	Molybdenum disulphide (a semiconductor)
MPc	Metal-ion-containing phthalocyanine (Table 1.1)
MPc_2	Metal-ion sandwich complexes (Table 1.1; Fig. 2.4)
MPcI	Iodine charge-transfer complex (Section 5.6; Fig. 5.4)
NaCl	Sodium chloride
N_c	Columnar nematic lyotropic mesophase (Fig. 3.25b)
N_D	Discotic nematic mesophase (Fig. 3.19a)
NH_3	Ammonia
NLO	Nonlinear optics
nm	Nanometre (10^{-9}m)
NMR	Nuclear magnetic resonance
n_0	Refractive index
n_{eff}	Effective refractive index
NO_2	Nitrogen dioxide
NPc	Naphthalocyanine (Fig. 2.15)
O_2	Molecular oxygen
<i>onp</i>	Octa-non-peripheral substitution
<i>op</i>	Octa-peripheral substitution
<i>P</i>	Oscillating polarisation
π	Surface pressure (mN m^{-1})
Pc	Phthalocyanine
Pe	Perylene (Fig. 6.4)
PMMA	Poly(methylmethacrylate)
PMPc	Polymetallophthalocyanine (Section 2.6.1; Fig. 2.17)
ppb	Parts per billion (10^9)
ppm	Parts per million
ps	Picoseconds

PTFE	Poly(tetrafluoroethylene)
pyr	Pyrazine
rpm	Revolutions per minute
S	Siemens ($=\Omega^{-1}$)
σ	Conductivity (S cm^{-1})
σ_{max}	Maximum conductivity
σ_{rt}	Room-temperature conductivity
SCLC	Space-charge-limited current
SnS_2	Tin disulphide (a semiconductor)
STM	Scanning tunnelling microscopy
T	Temperature
t	Tetra-substitution
TEM	Transmission electron microscopy
THG	Third-harmonic generation
tz	Tetrazine
UPS	Ultra-violet photoelectron spectroscopy
UV	Ultra-violet
V	Voltage
V_{bi}	Built-in voltage
V_{max}	Maximum current
V_{oc}	Open-circuit voltage
WORM	Write-once, read-many-times compact disc



Summary of phthalocyanine nomenclature