

Contents

Chapter 1	Production, Isolation and Purification of Fullerenes	1
	<i>Roger Taylor, Glenn A. Burley</i>	
1.1	Introduction	1
1.2	Production	3
1.2.1	The Hufmann–Krätschmer Method	3
1.2.2	The Combustion Process	4
1.2.3	Condensation of Polycyclic Aromatic Hydrocarbons through Pyrolytic Dehydrogenation or Dehydrohalogenation	4
1.3	Isolation and Purification of Fullerenes	4
1.4	Formation and Stability	5
1.5	Fullerenes with Incarcerated Atoms: <i>incar</i> Fullerenes (Endohedrals)	6
1.5.1	Nitrogen	6
1.5.2	Noble Gases	6
1.5.3	Hydrogen	7
1.5.4	Other Atoms	7
1.5.5	The <i>incar</i> trimetalnitridofullerenes, <i>i</i> -NR ₃ C _{<i>n</i>}	9
1.6	Concluding Remarks	9
	References	9
Chapter 2	Basic Principles of the Chemical Reactivity of Fullerenes	15
	<i>Fernando Langa, Pilar de la Cruz</i>	
2.1	[60]Fullerene Reactivity	15
2.1.1	Introduction	15
2.1.2	[4 + 2] Cycloadditions: Diels–Alder Reaction	21
2.1.3	[3 + 2] Cycloaddition Reactions	26
2.2	Multiaddition Reactions	35
2.3	Reactivity of Higher Fullerenes (C ₇₀ , C ₇₆ , C ₈₄)	40
	References	43

Chapter 3	Three Electrodes and a Cage: An Account of Electrochemical Research on C₆₀, C₇₀ and their Derivatives	51
	<i>Maurizio Carano, Massimo Marcaccio, Francesco Paolucci</i>	
3.1	Introduction	51
3.2	The Electrochemical Properties of Fullerenes	53
3.2.1	Increasing the Electronegativity of Fullerenes	53
3.2.2	Fulleropyrrolidines: Mono and Bis-Adducts	54
3.2.3	Polyphenylated Derivatives	55
3.2.4	C ₆₀ Ph ₅ Cl, a Very Special Polyphenylated Fullerene Derivative	57
3.3	Electrochemically Induced Reactivity in Fullerene Derivatives	58
3.3.1	The Electrochemically Induced Retro-cyclopropanation Reaction	60
3.3.2	The Role of Digital Simulation of the CV Experiments in Mechanistic Studies	61
3.4	Fullerenes as Active Components of Molecular Devices	63
3.4.1	Photoactive Dyads	63
3.4.2	Fullerene-Based Photoactive Liquid Crystals	65
3.4.3	Fullerene-[Ru(bpy) ₃] ²⁺ Systems	66
3.4.4	Fullerenes Containing Crown Ethers	69
3.4.5	Trannulenes	69
3.4.6	Electropolymerizable C ₆₀ Derivatives	71
3.4.7	C ₆₀ as a Mediator in Bio Electrochemical Sensors	71
3.5	Back to the Basics: The Oxidative Electrochemistry of C ₆₀	72
3.6	Final Remarks	74
	References	75
Chapter 4	Light-Induced Processes in Fullerene Multicomponent Systems	79
	<i>Nicola Armaroli, Gianluca Accorsi</i>	
4.1	Introduction	79
4.2	Photophysical Properties of C ₆₀ and its Derivatives	80
4.3	Dyads with Oligophenylenevinylenes	81
4.4	Fullerodendrimers	88
4.4.1	Fullerene Inside	89
4.4.2	Fullerene Outside	99
4.5	C ₆₀ : Metal Complex Arrays	105
4.6	C ₆₀ -Porphyrin Assemblies	109

<i>Contents</i>	ix
4.7 Conclusions	113
Acknowledgements	115
References	115
Chapter 5 Encapsulation of [60]Fullerene into Dendritic Materials to Facilitate their Nanoscopic Organization	127
<i>Jean-François Nierengarten, Nathalie Solladie, Robert Deschenaux</i>	
5.1 Introduction	127
5.2 Langmuir-Blodgett Films with Fullerene-Containing Dendrimers	128
5.3 Fullerene-Containing Thermotropic Liquid Crystals	140
5.3.1 Non-Covalent Fullerene-Containing Liquid Crystals	140
5.3.2 Covalent Fullerene-Containing Thermotropic Liquid Crystals	142
5.4 Conclusions	149
References	149
Chapter 6 Hydrogen Bonding Donor–Acceptor Carbon Nanostructures	152
<i>M. Ángeles Herranz, Francesco Giacalone, Luis Sánchez, Nazario Martín</i>	
6.1 Introduction	152
6.2 Hydrogen Bonded C ₆₀ •Donor (C ₆₀ •D) Ensembles	154
6.2.1 H-bonding interfaced metallomacrocycles•C ₆₀ dyads	154
6.2.2 H-Bonding Tethered π-Conjugated Oligomer•C ₆₀ Dyads	158
6.3 Other Electron Donor Moieties H-Bonding Interfaced with [60]fullerene	163
6.4 H-Bonded Supramolecular C ₆₀ -Based Polymers	166
6.5 Non-Covalent Functionalization of Carbon Nanotubes (CNTs)	172
6.5.1 Polymer Wrapping	174
6.5.2 Electrostatic Interactions	178
6.5.3 van der Waals and Complementary Electrostatic Interactions	179
6.6 Conclusions and Outlook	181
Acknowledgments	182
References	182
Chapter 7 Fullerenes for Material Science	191
<i>Stéphane Campidelli, Aurelio Mateo-Alonso, Maurizio Prato</i>	
7.1 Introduction	191
7.2 Donor–Acceptor Systems	191

7.2.1	Covalently Linked Donor–Acceptor Systems	192
7.2.2	Donor–Acceptor Systems Assembled by Supramolecular Interactions	193
7.2.3	Polyads	198
7.3	Fullerenes for Nonlinear Optical Applications	200
7.3.1	Functionalized Fullerenes for Nonlinear Optics	201
7.3.2	Donor–Acceptor Derivatives	202
7.4	Amphiphilic Fullerenes	205
7.4.1	Langmuir Films	205
7.4.2	Fullerene in Smectite Clays	208
7.4.3	Self Organization	208
7.5	Conclusion	211
	References	211
Chapter 8	Plastic Solar Cells Using Fullerene Derivatives in the Photoactive Layer	221
	<i>Piétrick Hudhomme, Jack Cousseau</i>	
8.1	Introduction	221
8.2	From Inorganic to Fullerene-Based Organic Solar Cells	222
8.3	Principle of Fullerene-Based Organic Solar Cells	224
8.4	Polymer – C ₆₀ Derivatives Heterojunctions	226
8.4.1	p/n Heterojunction Devices	226
8.4.2	“bulk-heterojunction” Devices	230
8.4.3	“Double-cable” Polymer-C ₆₀ Derivatives	242
8.5	Molecular Scale C ₆₀ -Based Heterojunctions	244
8.5.1	Low-Molecular-Weight Materials	244
8.5.2	Molecular π -Donor – C ₆₀ Derivatives Solar Cells	245
8.6	Supramolecular Nanostructured C ₆₀ -Based Devices	249
8.6.1	Self-Assembled Monolayers	249
8.6.2	Langmuir and Layer by Layer (LBL) Films	252
8.6.3	Hydrogen-Bonding Supramolecular Devices	254
8.7	Conclusion and Outlook	254
	References	259
Chapter 9	Fullerene Modified Electrodes and Solar Cells	266
	<i>Hiroshi Imahori, Tomokazu Umeyama</i>	
9.1	Introduction	266
9.2	Langmuir–Blodgett Films	267
9.3	Self-Assembled Monolayers	269

9.3.1	Self-Assembled Monolayers of Fullerene-Containing Systems on Gold Electrodes	269
9.3.2	Self-Assembled Monolayers of Fullerene-Containing Systems on ITO Electrodes	275
9.4	Layer-by-Layer Deposition	280
9.5	Vacuum Deposition	281
9.6	Electrochemical Deposition	283
9.6.1	Fullerenes and Their Derivatives	283
9.6.2	Donor–Acceptor Linked Systems Involving Fullerene	284
9.6.3	Donor and Fullerene Composite Systems	285
9.6.4	Pre-Organized Multi-Donor Systems	287
9.7	Chemical Adsorption and Spin Coating Deposition	292
9.8	Summary	295
	References	295
Chapter 10	Biological Applications of Fullerenes	301
	<i>Alberto Bianco, Tatiana Da Ros</i>	
10.1	Methodologies for Fullerene Solubilisation	301
10.2	Health and Environment Impact of Fullerenes	304
10.3	Fullerenes for Drug Delivery	307
10.4	Neuroprotection and Antioxidant Activity	310
10.5	DNA Photocleavage and Photodynamic Approach Using Fullerenes	312
10.6	Antibacterial, Antiviral Activity and Enzymatic Inhibition	317
10.7	Immunological Properties of Fullerenes	319
10.8	Biological Applications of Radio Labelled Fullerenes	322
10.9	General Conclusions	324
	References	324
Chapter 11	Covalent and Non-Covalent Approaches Toward Multifunctional Carbon Nanotube Materials	329
	<i>Vito Sgobba, G.M. Aminur Rahman, Christian Ehli, Dirk M. Guldi</i>	
11.1	Introduction	329
11.2	End Tips and Defect Functionalization	331
11.2.1	Oxidation	332

11.2.2	Derivatization of the Carboxylic Functionalities	333
11.2.3	Solvent-Free Amination and Thiolation	338
11.3	Sidewall Chemistry	338
11.3.1	Fluorination	338
11.3.2	Derivatization of Fluorinated Carbon Nanotubes	339
11.3.3	1,3 Dipolar Cycloadditions – Ozonolysis, Cycloaddition of Azomethine Ylide, and Cycloaddition of Nitrile Ymine	340
11.3.4	Diels–Alder Cycloaddition	344
11.3.5	Osmylation	344
11.3.6	[2 + 1] Cycloadditions – Carbenes or Nitrenes	344
11.3.7	[2 + 2] Cycloaddition of Singlet O ₂ and Sidewall Oxidation	346
11.3.8	Reductive Hydrogenation/Alkylation/ Arylation of CNT Sidewall	346
11.3.9	Addition of Radicals	348
11.3.10	Replacements of Carbon Atoms – Chemical Doping	349
11.3.11	Mechanochemical Functionalization	350
11.4	Non-Covalent Functionalization of Carbon Nanotubes	350
11.4.1	π - π Interactions with π -Electron Rich Polymeric Blocks – Polymer Wrapping	351
11.4.2	π - π Interactions with π -Electron Rich Molecular Building Blocks	357
11.5	Separation of Metallic and Semiconducting CNT	361
	References	363
	Subject Index	380