

Contents

Preface XIII

List of Contributors XVIII

Part I 3-D Carbon-rich π -Systems – Nanotubes and Segments

1	Functionalization of Carbon Nanotubes	3
	<i>Andreas Hirsch and Otto Vostrowsky</i>	
1.1	Introduction to Carbon Nanotubes – A New Carbon Allotrope	3
1.2	Functionalization of Carbon Nanotubes	4
1.3	Covalent Functionalization	5
1.3.1	Halogenation of Carbon Nanotubes	5
1.3.1.1	Fluorination of Carbon Nanotubes	5
1.3.1.2	Chlorination of Carbon Nanotubes	7
1.3.1.3	Bromination of MWCNTs	7
1.3.1.4	Chemical Derivatization of “Fluoronanotubes”	7
1.3.2	Oxidation of CNTs – Oxidative Purification	8
1.3.2.1	Carboxylation of CNTs	8
1.3.2.2	Defect Functionalization – Transformation of Carboxylic Functions	10
1.3.3	Hydrogenation of Carbon Nanotubes	19
1.3.4	Addition of Radicals	19
1.3.5	Addition of Nucleophilic Carbenes	20
1.3.6	Sidewall Functionalization Through Electrophilic Addition	21
1.3.7	Functionalization Through Cycloadditions	21
1.3.7.1	Addition of Carbenes	21
1.3.7.2	Addition of Nitrenes	22
1.3.7.3	Nucleophilic Cyclopropanation – Bingel Reaction	24
1.3.7.4	Azomethine Ylides	24
1.3.7.5	[4+2]-Cycloaddition – Diels–Alder Reaction	26
1.3.7.6	Sidewall Osmylation of Individual SWCNTs	27
1.3.8	Aryl Diazonium Chemistry – Electrochemical Modification of Nanotubes	27

1.3.9	Reductive Alkylation and Arylation of Carbon Nanotubes	29
1.3.10	Addition of Carbanions – Reactions with Alkylolithium	30
1.3.11	Covalent Functionalization by Polymerization – “Grafting To” and “Grafting From”	31
1.4	Noncovalent Exohedral Functionalization – Functionalization with Biomolecules	32
1.5	Endohedral Functionalization	42
1.6	Conclusions	44
1.7	Experimental	44
	References	49
2	Cyclophenacene Cut Out of Fullerene	59
	<i>Yutaka Matsuo and Eiichi Nakamura</i>	
2.1	Introduction	59
2.2	Synthesis of [10]Cyclophenacene π -Conjugated Systems from [60]Fullerene	63
2.2.1	Synthetic Strategy	63
2.2.2	Synthesis and Characterization of [10]Cyclophenacenes	64
2.2.3	Structural Studies and Aromaticity of [10]Cyclophenacene	67
2.2.4	Synthesis of Dibenzo-fused Corannulenes	69
2.2.5	Absorption and Emission of [10]Cyclophenacenes and Dibenzo Fused Corannulenes	70
2.3	Conclusion	72
2.4	Experimental	72
	References	78
 Part II Strategic Advances in Chromophore and Materials Synthesis		
3	Cruciform π-Conjugated Oligomers	83
	<i>Frank Galbrecht, Torsten W. Bünnagel, Askin Bilge, Ullrich Scherf and Tony Farrell</i>	
3.1	Introduction	83
3.2	Oligomers with a Tetrahedral Core Unit	85
3.3	Oligomers with a Tetrasubstituted Benzene Core	91
3.4	Oligomers with a Tetrasubstituted Biaryl Core	95
3.5	Conclusion	113
3.6	Experimental	113
	Acknowledgments	115
	References	116

4	Design of π-Conjugated Systems Using Organophosphorus Building Blocks	119
	<i>Philip W. Dyer and Régis Réau</i>	
4.1	Introduction	119
4.2	Phosphole-containing π -Conjugated Systems	121
4.2.1	α,α' -Oligo(phosphole)s	123
4.2.2	Derivatives Based on 1,1'-Biphosphole Units	126
4.2.3	Mixed Oligomers Based on Phospholes with Other (Hetero)aromatics	129
4.2.4	Mixed Oligomers Based on Biphospholes with other (Hetero)aromatics	137
4.2.5	Mixed Oligomers Based on Phospholes with Ethenyl or Ethynyl Units	138
4.2.6	Polymers Incorporating Phospholes	140
4.2.7	Mixed Oligomers and Polymers Based on Dibenzophosphole or Dithienophosphole	143
4.3	Phosphine-containing π -Conjugated Systems	147
4.3.1	Polymers Based on <i>p</i> -Phenylenephosphine Units	147
4.3.2	Oligomers Based on Phosphine–Ethynyl Units	151
4.3.3	Mixed Derivatives Based on Arylphosphino Units	155
4.4	Phosphaalkene- and Diphosphene-containing π -Conjugated Systems	161
4.5	Conclusion	168
4.6	Selected Experimental Procedures	169
	References	172
5	Diversity-oriented Synthesis of Chromophores by Combinatorial Strategies and Multi-component Reactions	179
	<i>Thomas J. J. Müller</i>	
5.1	Introduction	179
5.2	Combinatorial Syntheses of Chromophores	180
5.2.1	Combinatorial Azo Coupling	181
5.2.2	Combinatorial Condensation Reactions	182
5.2.3	Combinatorial Cross-coupling Reactions	187
5.2.4	Combinatorial Coordination Chemistry	197
5.3	Novel Multi-component Syntheses of Chromophores	199
5.3.1	Multi-component Condensation Reactions	199
5.3.2	Multi-component Cross-coupling Reactions	204
5.4	Conclusion and Outlook	215
5.5	Experimental Procedures	215
	References	218

6	High-yield Synthesis of Shape-persistent Phenylene–Ethynylene Macrocycles	225
	<i>Sigurd Höger</i>	
6.1	Introduction	225
6.2	Synthesis	227
6.2.1	General	227
6.2.2	The Kinetic Approach	227
6.2.2.1	Statistical Reactions	227
6.2.2.2	Template-controlled Cyclizations	238
6.2.3	The Thermodynamic Approach	251
6.3	Conclusion	254
6.4	Experimental Procedures	255
	References	258
7	Functional Materials via Multiple Noncovalent Interactions	261
	<i>Joseph R. Carlisle and Marcus Weck</i>	
7.1	Introduction	261
7.2	Biologically Inspired Materials via Multi-step Self-assembly	262
7.3	Small Molecule-based Multi-step Self-assembly	265
7.4	Polymer-based Self-assembly	275
7.4.1	Main-chain Self-assembly	276
7.4.2	Side-chain Self-assembly	279
7.4.3	Macroscopic Self-assembly	287
7.5	Conclusion and Outlook	288
	References	289
Part III Molecular Muscles, Switches and Electronics		
8	Molecular Motors and Muscles	295
	<i>Sourav Saha and J. Fraser Stoddart</i>	
8.1	Introduction	295
8.2	Mechanically Interlocked Molecules as Artificial Molecular Machines	297
8.3	Chemically Induced Switching of the Bistable Rotaxanes	299
8.3.1	A Bistable [2]Rotaxane Driven by Acid–Base Chemistry	300
8.3.2	A pH-driven Molecular Elevator	301
8.3.3	A Molecular Muscle Powered by Metal Ion Exchange	303
8.3.4	Redox and Chemically Controlled Molecular Switches and Muscles	304
8.3.4.1	Solution-phase Switching	305
8.3.4.2	Condensed-phase Switching	306
8.3.4.3	A Solid-state Nanomechanical Device	308
8.4	Electrochemically Controllable Bistable Rotaxanes	309
8.4.1	A Benzidine/Biphenol-based Molecular Switch	310

8.4.2	Electrochemically Controlled Switching of TTF/DNP-based [2]Rotaxanes	311
8.4.2.1	Solution-phase Switching	311
8.4.2.2	Metastability of a Redox-driven [2]Rotaxane SAM on Gold Surfaces	311
8.4.2.3	A TTF/DNP [2]Rotaxane-based Electrochromic Device	313
8.4.2.4	A Redox-driven [2]Rotaxane-based Molecular Switch Tunnel Junctions (MSTJs) Device	314
8.4.3	A Redox and Chemically Controllable Bistable Neutral [2]Rotaxane	315
8.4.3.1	Electrochemical Switching	315
8.4.3.2	Chemical Switching Induced by Lithium Ion (Li ⁺)	316
8.5	Photochemically Powered Molecular Switches	316
8.5.1	Molecular Switching Caused by Photoisomerization	317
8.5.2	PET-induced Switching of an H-bonded Molecular Motor	318
8.5.3	MLCT-induced Switching of a Metal Ion-based Molecular Motor	319
8.5.4	A Photo-driven Molecular Abacus	320
8.6	Conclusions	322
	Acknowledgments	322
	References	323
9	Diarylethene as a Photoswitching Unit of Intramolecular Magnetic Interaction	329
	<i>Kenji Matsuda and Masahiro Irie</i>	
9.1	Introduction	329
9.2	Photochromic Spin Coupler	331
9.3	Synthesis of Diarylethene Biradicals	333
9.4	Photoswitching Using Bis(3-thienyl)ethene	335
9.5	Reversed Photoswitching Using Bis(2-thienyl)ethene	340
9.6	Photoswitching Using an Array of Photochromic Molecules	341
9.7	Development of a New Switching Unit	344
9.8	Conclusions	348
9.9	Experimental Procedures	348
	Acknowledgments	349
	References	350
10	Thiol End-capped Molecules for Molecular Electronics: Synthetic Methods, Molecular Junctions and Structure–Property Relationships	353
	<i>Kasper Nørgaard, Mogens Brøndsted Nielsen and Thomas Bjørnholm</i>	
10.1	Introduction	353
10.2	Synthetic Procedures	354
10.2.1	Protecting Groups for Arylthiols	354
10.2.1.1	Synthesis of Arylthiol “Alligator Clips”	354
10.2.2	One-terminal Wires	358
10.2.3	Two-terminal Wires	359
10.2.4	Three-terminal Wires	364

10.2.5	Four-terminal Wires	365
10.2.6	Caltrops	367
10.3	Electron Transport in Two- and Three-terminal Molecular Devices	368
10.3.1	Molecular Junctions	375
10.3.1.1	Scanning Tunneling-based Molecular Junctions	375
10.3.1.2	Conducting-probe Atomic Force Microscopy	379
10.3.1.3	Solution-phase Molecular STM Junctions	380
10.3.1.4	Break Junctions	381
10.3.1.5	Crossed Wires	382
10.3.1.6	Nanopore Junctions	382
10.3.1.7	Square-tip Junctions	383
10.3.1.8	Mercury Drop Junctions	384
10.3.1.9	Particle Junctions	384
10.3.1.10	Nanowire Junctions	385
10.3.1.11	Three-terminal Single-molecule Transistors	386
10.4	Summary and Outlook	387
10.5	Experimental	388
	References	389
11	Nonlinear Optical Properties of Organic Materials	393
	<i>Stephen Barlow and Seth R. Marder</i>	
11.1	Introduction to Nonlinear Optics	393
11.1.1	Introduction	393
11.1.2	Linear and Nonlinear Polarization	394
11.1.3	Second-order Nonlinear Optical Effects	396
11.1.4	Measurement Techniques for Second-order Properties, β and $\chi^{(2)}$	397
11.1.5	Third-order Nonlinear Optical Effects	399
11.1.6	Measurement Techniques for 2PA Cross-section, δ	401
11.2	Second-order Chromophores for Electrooptic Applications	404
11.2.1	Design of Second-order Chromophores: the Two-level Model	404
11.2.2	Other Chromophore Designs	409
11.2.3	Other Considerations	411
11.2.4	High-performance Electrooptic Poled-polymer Systems	413
11.3	Design and Application of Two-photon Absorbing Chromophores	418
11.3.1	Essential-state Models for Two-photon Cross-section	418
11.3.2	Chromophore Designs	420
11.3.3	Applications of Two-photon Absorption	427
11.4	Appendix: Units in NLO	430
	Acknowledgments	431
	References	431

Part IV Electronic Interaction and Structure

12	Photoinduced Electron Transfer Processes in Synthetically Modified DNA	441
	<i>Hans-Achim Wagenknecht</i>	
12.1	DNA as a Bioorganic Material for Electron Transport	441
12.2	Mechanism of Hole Transfer and Hole Hopping in DNA	444
12.3	Reductive Electron Transfer and Excess Electron Transport in DNA	446
12.3.1	Strategies for the Synthesis of DNA Donor–Acceptor Systems	446
12.3.2	Chromophore Functionalization of DNA Bases via Synthesis of DNA Building Blocks	448
12.3.3	DNA Base Modifications via a Solid-phase Synthetic Strategy	452
12.3.4	Chromophores as Artificial DNA Base Substitutes	454
12.4	Results from the Electron Transfer Studies	456
12.5	Outlook: Towards Synthetic Nanostructures Based on DNA-like Architecture	460
	References	463
13	Electron Transfer of π-Functional Systems and Applications	465
	<i>Shunichi Fukuzumi</i>	
13.1	Introduction	465
13.2	Efficient Electron-transfer Properties of Zinc Porphyrins	467
13.3	Efficient Electron-transfer Properties of Fullerenes	474
13.4	Photoinduced Electron Transfer in Electron Donor–Acceptor Linked Molecules Mimicking the Photosynthetic Reaction Center	477
13.5	An Orthogonal π -Donor–Acceptor Dyad Affording an Infinite CS Lifetime	485
13.6	A Long-lived ET State Acting as an Efficient ET Photocatalyst	490
13.7	Organic Solar Cells Using Simple Donor–Acceptor Dyads	494
13.8	Organic Solar Cells Composed of Multi-porphyrin/C ₆₀ Supramolecular Assemblies	499
13.9	Conclusion	506
	Acknowledgments	506
	References	507
14	Induced π-Stacking in Acenes	511
	<i>John E. Anthony</i>	
14.1	Introduction	511
14.2	Anthracene	512
14.2.1	Monosubstituted Anthracene	514
14.2.2	Disubstituted Anthracene	517
14.2.3	Edge-substituted Anthracenes (Anthracene Functionalized at the 1,8- or 1,8,9-Positions)	522

14.2.4	Liquid Crystalline Anthracenes	525
14.2.5	Anthracene Self-assembly: Hydrogen Bonding	526
14.3	Tetracene (Naphthacene)	528
14.3.1	Ethynyltetracenes	530
14.3.2	Tetrasubstituted Tetracenes	532
14.4	Pentacene	534
14.5	Higher Acenes	540
14.6	Conclusion	541
	Acknowledgments	542
	References	542
15	Synthesis and Characterization of Novel Chiral Conjugated Materials	547
	<i>Andrzej Rajca and Makoto Miyasaka</i>	
15.1	Introduction	547
15.2	Synthetic Approaches to Highly Annelated Chiral π -Conjugated Systems	548
15.2.1	Helicenes	548
15.2.1.1	Photochemical Syntheses	549
15.2.1.2	Non-photochemical Syntheses	551
15.2.2	Double Helicenes and Chiral Polycyclic Aromatic Hydrocarbons	560
15.2.3	Tetraphenylenes and π -Conjugated Double Helices	563
15.3	Barriers for Racemization of Chiral π -Conjugated Systems	567
15.4	Strong Chiroptical Properties in Absorption, Emission and Refraction	570
15.4.1	Absorption and Emission	570
15.4.2	Refraction	572
15.5	Conclusion	574
	Acknowledgments	574
	References	574
	Index	583