

Contents

Preface	<i>vii</i>
Reference	<i>ix</i>
1	General Concepts 1
1.1	Devices and Machines at the Molecular Level 1
1.2	Miniaturization of Devices and Machines 1
1.3	Top-down (Large-downward) Approach 2
1.4	Bottom-up (Small-upward) Approach 4
1.4.1	Bottom-up Atom-by-atom 4
1.4.2	Bottom-up Molecule-by-molecule 6
1.5	Supramolecular (Multicomponent) Chemistry 7
1.5.1	Comparison of Large Molecules with Supramolecular (Multicomponent) Systems 10
1.5.2	Self-organization and Covalent Synthetic Design 11
1.5.3	Supramolecular Chemistry, Art, and Nanotechnology 11
	References 14
Part I	Devices for Processing Electrons and Electronic Energy 19
2	Fundamental Principles of Electron and Energy Transfer 21
2.1	Introduction 21
2.2	Photoinduced Electron- and Energy-transfer Processes 22
2.2.1	Electron Transfer 22
2.2.1.1	The Electronic Factor 23
2.2.1.2	The Nuclear Factor 25
2.2.2	Energy Transfer 25
2.2.2.1	Coulombic Mechanism 26
2.2.2.2	Exchange Mechanism 28
2.2.3	Role of the Bridge 28
	References 31
3	Wires and Related Systems 33
3.1	Introduction 33
3.2	Conductivity Measurements 33

3.3	Electron-transfer Processes at Electrodes	36
3.4	Photoinduced Electron Transfer	37
3.4.1	Covalently Linked Systems Containing Metal Complexes	37
3.4.2	Covalently Linked Systems Based on Organic Compounds	39
3.4.3	Covalently Linked Systems Containing Porphyrins	42
3.4.4	DNA and Related Systems	44
3.5	Heterogeneous Photoinduced Electron Transfer	47
3.6	Energy Transfer	48
3.6.1	Covalently Linked Systems Containing Metal Complexes	48
3.6.2	Covalently Linked Systems Based on Organic Compounds	53
3.6.3	Covalently Linked Systems Containing Porphyrins	55
3.6.4	DNA and Related Systems	57
	References	57
4	Switching Electron- and Energy-transfer Processes	64
4.1	Introduction	64
4.2	Switching Electron-transfer Processes	65
4.2.1	Photon Inputs	65
4.2.1.1	Long-lived Switching	66
4.2.1.2	Fast and Ultrafast Switching	70
4.2.2	Redox Inputs	75
4.2.3	Acid–Base Inputs	77
4.2.4	Other Factors	82
4.3	Switching Energy-transfer Processes	83
4.3.1	Photon Inputs	83
4.3.2	Redox Inputs	86
4.3.3	Acid–Base Inputs	88
4.3.4	Other Factors	89
	References	92
5	Light-harvesting Antennae	96
5.1	Introduction	96
5.2	Natural Antenna Systems	97
5.3	Porphyrin-based Arrays	99
5.4	Multichromophoric Cyclodextrins	103
5.5	Dendrimers	103
5.5.1	Dendrimers Containing Metal Complexes	104
5.5.1.1	Metal Complexes as Cores	104
5.5.1.2	Metal Complexes in Each Branching Center	108
5.5.2	Dendrimers Based on Organic Chromophores	110
5.5.3	Dendrimers Containing Porphyrins	111
5.5.4	Host–Guest Systems	118
5.5.5	Photoinduced Electron Transfer	122
5.6	Other Systems	123
5.6.1	Polyelectrolytes	123
5.6.2	Polymers	123

5.6.3	Rotaxanes	124
5.6.4	Zeolites	124
	References	127
6	Photoinduced Charge Separation and Solar Energy Conversion	132
6.1	Introduction	132
6.2	Natural Reaction Centers	133
6.2.1	Introduction	133
6.2.2	Bacterial Photosynthesis	133
6.2.3	Photosystem II	136
6.3	Artificial Reaction Centers	138
6.3.1	Introduction	138
6.3.2	Dyads	139
6.3.3	Triads	140
6.3.4	Tetrads and Pentads	147
6.3.5	Antenna-Reaction Center Systems	150
6.3.5.1	Porphyrin-based Arrays	150
6.3.5.2	Bilayer Membranes	153
6.3.5.3	Self-assembled Monolayers	153
6.3.5.4	Lamellar Assemblies and Zeolites	155
6.3.6	Oxygen-evolving Systems	155
6.4	Hybrid Systems	159
6.4.1	Conversion of Light to a Proton-motive Force	159
6.4.2	Light-driven Production of ATP	161
6.5	Artificial Solar Energy Conversion	162
6.5.1	Conversion of Light into Fuels	162
6.5.2	Conversion of Light into Electricity	164
	References	167
Part II	Memories, Logic Gates, and Related Systems	175
7	Bistable Systems	177
7.1	Introduction	177
7.2	Photochromic Systems	178
7.3	Modulation of Host–Guest Interactions	181
7.4	Fluorescent Switches	182
7.5	Chiroptical Switches	185
7.5.1	Overcrowded Alkenes	186
7.5.2	Diarylethenes	187
7.6	Photochemical Biomolecular Switches	188
7.7	Electrochromic Systems	191
7.8	Redox Switches	193
7.9	Other Systems	194
	References	195
8	Multistate–Multifunctional Systems	200
8.1	Introduction	200

8.2	Biphotochromic Supramolecular Systems	200
8.3	Photochemical Inputs Coupled with Other Stimuli	201
8.3.1	Three-state Systems. Write–Lock–Read–Unlock–Erase Cycles	203
8.3.2	Orthogonal Photochemical–Electrochemical Stimulation	206
8.3.3	Orthogonal Photochemical–(Acid–Base) Stimulation	208
8.3.4	Molecular Shift Register	213
8.4	Multielectron Redox Processes	218
8.4.1	Systems with Equivalent Redox Units	219
8.4.2	Systems with Nonequivalent Redox Units	223
8.5	Electrochemical Inputs Coupled with Chemical Inputs	228
8.6	Multiple Chemical Inputs	229
	References	230
9	Logic Gates	235
9.1	Introduction	235
9.2	Fundamental Concepts of Logic Gates	236
9.3	Molecular Switches as Logic Gates	237
9.4	Basic Logic Gates	239
9.4.1	YES Gate	239
9.4.2	NOT Gate	240
9.4.3	OR Gate	241
9.4.4	AND Gate	241
9.4.5	NOR Gate	243
9.4.6	NAND Gate	243
9.4.7	XOR Gate	245
9.4.8	XNOR Gate	246
9.5	Combinational Logic	247
9.5.1	INH Function	247
9.5.2	EnOR Function	248
9.5.3	Half Adder	250
9.5.4	A Three-state, Three-input, Two-output Molecular Switch	252
9.6	Neural-type Systems	253
9.6.1	An XOR Logic System Under the Control of an Intrinsic Threshold Mechanism	253
9.6.2	A Perceptron-type Scheme	255
9.7	Signal Communication Between Molecular Switches	257
9.8	Computation Based on Oligonucleotides	260
9.9	Molecule-based Electronic Circuits	261
9.10	Conclusions	262
	References	263
Part III	Molecular-scale Machines	267
10	Basic Principles of Molecular Machines	269
10.1	Introduction	269

10.2	The Concept of a Molecular Machine	270
10.3	Energy Supply	272
10.3.1	Chemical Energy	272
10.3.2	Light Energy	273
10.3.3	Electrochemical Energy	274
10.4	Other Requirements	274
10.4.1	Types of Motion	274
10.4.2	Control and Monitoring	275
10.4.3	Reset	275
10.4.4	Time Scale	275
10.4.5	Functions	275
	References	276
11	Spontaneous Mechanical-like Motions	278
11.1	Introduction	278
11.2	Rotors	278
11.3	Cogwheels	278
11.4	Gears	279
11.5	Paddle Wheels	281
11.6	Turnstiles	281
11.7	Brakes	282
11.8	Ratchets	283
11.9	Gyroscopes and Gyroscopes	284
	References	286
12	Movements Related to Opening, Closing, and Translocation Functions	288
12.1	Introduction	288
12.2	Allosteric Movements	288
12.2.1	Allosteric Enzymes	288
12.2.2	Artificial Allosteric Systems	290
12.3	Tweezers and Harpoons	293
12.3.1	Tweezers	293
12.3.2	Harpoons and Related Systems	296
12.4	Controlled Assembly and Disassembly of Host–Guest Systems	297
12.4.1	Introduction	297
12.4.2	Photoinduced Processes	299
12.4.2.1	Inclusion Complexes	299
12.4.2.2	Metal-ion Ejection	301
12.4.3	Redox-induced Processes	302
12.5	Conformational Changes in Proteins and DNA	306
12.5.1	Protein Folding-Unfolding Processes	306
12.5.2	Molecular Machines Based on DNA	307
12.6	Molecular Locks	309
12.7	Translocation of Metal Ions	311
12.7.1	Redox-Driven Processes	311

12.7.2	(Acid–Base)-Driven Processes	312
12.8	Ion Channels	314
12.8.1	Metal-ion Channels in Nature	314
12.8.2	A Natural Proton Pump	316
12.8.3	Artificial Ion Channels	316
12.8.3.1	Introduction	316
12.8.3.2	Modification of Natural Channel-formers	318
12.8.3.3	Ion Channels Based on Biopolymers	318
12.8.3.4	Synthetic Ion-channel Models	320
	References	321
13	Rotary Movements	329
13.1	Introduction	329
13.2	Natural Rotary Motors	329
13.3	Hybrid Rotary Motors	331
13.4	Rotary Movements in Artificial Systems	333
13.4.1	Chemically Driven Processes	333
13.4.2	Photochemically Driven Processes	339
13.4.3	Electrochemically Driven Processes	342
13.4.4	Other Effects	345
	References	345
14	Threading–Dethreading Movements	348
14.1	Introduction	348
14.2	Chemically Driven Movements	351
14.2.1	Systems Based on Metal–Ligand Bonds	351
14.2.2	Systems Based on Hydrogen Bonds and Electrostatic Interactions	351
14.2.3	Systems Based on Donor–Acceptor Interactions	356
14.3	Electrochemically Driven Movements	364
14.4	Photochemically Driven Movements	370
14.5	Heterogeneous Systems	376
	References	380
15	Linear Movements	387
15.1	Introduction	387
15.2	Natural Linear Motors	387
15.3	Linear Movements in Rotaxanes	391
15.3.1	Introduction	391
15.3.2	Chemically Driven Systems	393
15.3.2.1	Rotaxanes Based on Metal Complexes	393
15.3.2.2	Rotaxanes Based on Hydrogen Bonds and Donor–Acceptor Interactions	397
15.3.2.3	Rotaxanes Based on Cucurbituril	399
15.3.2.4	Rotaxanes Based on Cyclodextrins	401
15.3.3	Electrochemically Driven Systems	403

15.3.4	Photochemically Driven Systems	409
15.3.5	Perspectives	416
15.3.5.1	Three-station Rotaxanes	416
15.3.5.2	Rotaxanes as Carriers	416
15.4	Interfacing Rotaxanes with Surfaces and Solid Supports	418
15.4.1	A Surface-bound Photoswitchable Rotaxane	418
15.4.2	Rotaxane-based Electronic Devices	420
	References	421
16	Motions in Catenanes	426
16.1	Introduction	426
16.1.1	Synthesis	426
16.1.2	Circumrotational Processes	429
16.1.3	Functional Catenanes	431
16.2	Chemically Driven Motions	435
16.3	Electrochemically Driven Motions	439
16.4	Photochemically Driven Motions	445
16.5	Perspectives	447
16.5.1	Unidirectional Ring Rotation in Catenanes	447
16.5.2	Rotacatenane Molecular Gears	448
16.6	Interfacing Catenanes with Surfaces and Solid Supports	449
16.6.1	Aligning Catenanes in Two Dimensions	449
16.6.2	A Catenane-based Solid-state Device	450
	References	454
	Appendix	459
	Glossary	459
	List of Abbreviations	474
	Subject Index	479