

# Contents

---

## Part I Redox Systems via d, $\pi$ -Conjugation

---

<b>1</b>	<b>Conjugated Complexes with Quinonediiimine Derivatives</b>	
	<i>Toshiyuki Moriuchi, Toshikazu Hirao</i> .....	3
1.1	Introduction .....	4
1.2	Architecturally Controlled Formation of Conjugated Complexes with 1,4-Benzoquinonediiimines ....	5
1.3	Redox-Switching Properties of Conjugated Complexes with 1,4-Benzoquinonediiimines .....	17
1.4	Conclusion .....	24
1.5	References .....	25
<b>2</b>	<b>Realizing the Ultimate Amplification in Conducting Polymer Sensors: Isolated Nanoscopic Pathways</b>	
	<i>Timothy M. Swager</i> .....	29
2.1	Dimensionality in Molecular-Wire Sensors .....	29
2.2	Analyte-Triggered Barrier Creation in Conducting Polymers ..	32
2.3	Isolated Nanoscopic Pathways .....	34
2.4	Langmuir–Blodgett Approaches to Nanofibrils .....	34
2.5	Molecular Scaffolds for the Isolation of Molecular Wires .....	37
2.6	Summary and Future Prospects .....	43
2.7	References .....	43
<b>3</b>	<b>Metal-Containing <math>\pi</math>-Conjugated Materials</b>	
	<i>Michael O. Wolf</i> .....	45
3.1	Introduction .....	46
3.1.1	$\pi$ -Conjugated Materials .....	46
3.1.2	Nanomaterials .....	46
3.2	Metal-Complex-Containing Conjugated Materials .....	47
3.2.1	Preparation .....	47
3.2.2	Properties .....	49
3.3	Metal-Nanoparticle-Containing Conjugated Materials .....	51
3.3.1	Preparation .....	51

3.3.2	Properties .....	51
3.4	Applications .....	52
3.5	Conclusions .....	53
3.6	References .....	53
<b>4</b>	<b>Redox Active Architectures and Carbon-Rich Ruthenium Complexes as Models for Molecular Wires</b>	
	<i>Stéphane Rigaut, Daniel Touchard, Pierre H. Dixneuf</i> .....	55
4.1	Introduction .....	56
4.2	Ruthenium Allenylidene and Acetylide Building Blocks:	
	Basic Properties .....	57
4.2.1	Synthetic Routes .....	57
4.2.2	Redox Properties .....	60
4.2.2.1	Oxidation of Ruthenium Metal Acetylides:	
	Stable Ru <sup>II</sup> /Ru <sup>III</sup> Systems and a New Route	
	to Allenylidene Metal Complexes .....	60
4.2.2.2	Reduction of Metal Allenylidenes:	
	Access to Stable “Organic” Radicals and a Route to Acetylides .	61
4.3	Bimetallic Complexes from the Ru(dppe) <sub>2</sub> System .....	63
4.3.1	A Binuclear Bis-Acetylide Ruthenium Complex .....	63
4.3.2	Bis-Allenylidene Bridges Linking Two Ruthenium Complexes .	64
4.3.3	C <sub>7</sub> Bridged Binuclear Ruthenium Complexes .....	67
4.4	Connection of Two Carbon-Rich Chains	
	with the Ruthenium System .....	71
4.5	Trimetallic and Oligomeric Metal Complexes	
	with Carbon-Rich Bridges .....	74
4.6	Star Organometallic-Containing Multiple Identical Metal Sites .	77
4.7	Conclusion .....	79
4.8	References .....	79
<b>5</b>	<b>Molecular Metal Wires Built from a Linear Metal Atom Chain Supported by Oligopyridylamido Ligands</b>	
	<i>Chen-Yu Yeh, Chih-Chieh Wang, Chun-Hsien Chen,</i>	
	<i>Shie-Ming Peng</i> .....	85
5.1	Introduction .....	86
5.2	Synthesis of Oligopyridylamine Ligands .....	87
5.3	Dimerization by Self-Complementary Hydrogen Bonding .....	90
5.4	Complexation of Oligopyridylamine Ligands .....	91
5.5	Mono- and Dinuclear Complexes .....	91
5.6	Structures of Linear Multinuclear Nickel Complexes .....	92
5.7	Structures of Linear Multinuclear Cobalt Complexes .....	98
5.8	Structures of Linear Multinuclear Chromium Complexes .....	100
5.9	Structures of Triruthenium and Trirhodium Complexes .....	103
5.10	Complexes of Modified Ligands .....	104

5.11	Electrochemical Properties of the Complexes .....	105
5.12	Scanning Tunneling Microscopy Studies .....	112
5.13	Summary .....	114
5.14	References .....	115

## **6 Multielectron Redox Catalysts**

### **in Metal-Assembled Macromolecular Systems**

	<i>Takane Imaoka, Kimihisa Yamamoto</i> .....	119
6.1	Introduction .....	119
6.2	Multielectron Redox Systems .....	120
6.3	Multinuclear Complexes as Redox Catalysts .....	122
6.4	Macromolecule-Metal Complexes .....	123
6.5	Metal Ion Assembly on Dendritic Macromolecules .....	124
6.6	Conclusion .....	129
6.7	References .....	129

---

## **Part II Redox Systems via Coordination Control**

---

## **7 Triruthenium Cluster Oligomers**

### **that Show Multistep/Multielectron Redox Behavior**

	<i>Tomohiko Hamaguchi, Tadashi Yamaguchi, Tasuku Ito</i> .....	133
7.1	Introduction .....	133
7.2	Syntheses of Oligomers 1 and 2 .....	135
7.3	Redox Behavior of 1 and 2 .....	136
7.4	Conclusion .....	139
7.5	References .....	139

## **8 Molecular Architecture**

### **of Redox-Active Multilayered Metal Complexes**

#### **Based on Surface Coordination Chemistry**

	<i>Masa-aki Haga</i> .....	141
8.1	Introduction .....	141
8.2	Fabrication of Multilayer Nanoarchitectures by Surface Coordination Chemistry .....	142
8.2.1	Layer-by-Layer Assembly on Solid Surfaces .....	142
8.2.2	Molecular Design of Anchoring Groups for Control of Molecular Orientation on Surfaces .....	143
8.2.3	Molecular Design of Redox-Active Metal Complex Units for the Control of Energy Levels on Surfaces .....	146
8.3	Chemical Functions of Redox-Active Multilayered Complexes on Surface .....	148
8.3.1	Electron Transfer Events in Multilayer Nanostructures .....	148

8.3.2	Combinatorial Approach to Electrochemical Molecular Devices in a Multilayer Nanostructure on Surfaces . . . . .	149
8.3.3	Surface DNA Trapping by Immobilized Metal Complexes with Intercalator Moiety Toward Nanowiring . . . . .	151
8.4	Conclusion . . . . .	153
8.5	References . . . . .	153
<b>9</b>	<b>Programmed Metal Arrays by Means of Designable Biological Macromolecules</b> <i>Kentaro Tanaka, Tomoko Okada, Mitsuhiro Shionoya</i> . . . . .	155
9.1	Introduction . . . . .	155
9.2	DNA-Directed Metal Arrays . . . . .	156
9.2.1	Metal-Mediated Base Pairing in DNA . . . . .	156
9.2.2	Single-Site Incorporation of a Metal-Mediated Base Pair into DNA . . . . .	157
9.2.3	Discrete Self-Assembled Metal Arrays in DNA . . . . .	159
9.3	Peptide-Directed Metal Arrays . . . . .	161
9.3.1	Design Concept . . . . .	161
9.3.2	Heterogeneous Metal Arrays Using Cyclic Peptides . . . . .	162
9.3.3	Metal Ion Selectivity in Supramolecular Complexation . . . . .	163
9.4	Conclusion . . . . .	164
9.5	References . . . . .	164
<b>10</b>	<b>Metal-Incorporated Hosts for Cooperative and Responsive Recognition to External Stimulus</b> <i>Tatsuya Nabeshima, Shigehisa Akine</i> . . . . .	167
10.1	Introduction . . . . .	167
10.2	Pseudomacrocycles for Cooperative Molecular Functional Systems . . . . .	168
10.3	Oligo( $\text{N}_2\text{O}_2$ -Chelate) Macrocycles . . . . .	172
10.3.1	Design of Macrocyclic Oligo( $\text{N}_2\text{O}_2$ -Chelate) Ligands and Metallohosts . . . . .	172
10.3.2	Synthesis and Structure of Tris( $\text{N}_2\text{O}_2$ -Chelate) Macrocycles . . . . .	173
10.4	Acyclic Oligo( $\text{N}_2\text{O}_2$ -Chelate) Ligands . . . . .	174
10.4.1	Design of Acyclic Oligo( $\text{N}_2\text{O}_2$ -Chelate) Ligands . . . . .	174
10.4.2	Complexes of a New $\text{N}_2\text{O}_2$ -Chelate Ligand, Salamo . . . . .	175
10.4.3	Synthesis, Structure, and Properties of Acyclic Oligo( $\text{N}_2\text{O}_2$ -Chelate) Ligands . . . . .	176
10.5	Conclusion . . . . .	177
10.6	References . . . . .	177

<b>11</b>	<b>Synthesis of Poly(binaphthol) via Controlled Oxidative Coupling</b> <i>Shigeki Habaue, Bunpei Hatano</i> . . . . .	179
11.1	Introduction . . . . .	179
11.2	Asymmetric Oxidative Coupling with Dinuclear Metal Complexes . . . . .	181
11.3	Oxidative Coupling Polymerization of Phenols . . . . .	183
11.4	Oxidative Coupling Polymerization of 2,3-Dihydroxynaphthalene . . . . .	184
11.5	Conclusion . . . . .	188
11.6	References . . . . .	188

---

### Part III Redox Systems via Molecular Chain Control

---

<b>12</b>	<b>Nano Meccano</b> <i>Yi Liu, Amar H. Flood, J. Fraser Stoddart</i> . . . . .	193
12.1	Introduction . . . . .	194
12.2	Redox-Controllable Molecular Switches in Solution . . . . .	196
12.2.1	Bistable [2]Catenanes . . . . .	196
12.2.2	Bistable [2]Rotaxanes . . . . .	197
12.2.3	Self-Complexing Molecular Switches . . . . .	198
12.3	Application of Redox-Controllable Molecular Machines in Electronic Devices . . . . .	201
12.4	Application of Redox-Controllable Molecular Machines in Mechanical Devices . . . . .	204
12.4.1	Switching in Langmuir–Blodgett Film . . . . .	205
12.4.2	Molecular Machines Functioning as Nanovalves . . . . .	207
12.4.3	Artificial Molecular Muscles . . . . .	208
12.5	Conclusions . . . . .	211
12.6	References . . . . .	212
<b>13</b>	<b>Through-Space Control of Redox Reactions Using Interlocked Structure of Rotaxanes</b> <i>Nobuhiro Kihara, Toshikazu Takata</i> . . . . .	215
13.1	Introduction . . . . .	215
13.2	Redox Behavior and Conformation of Ferrocene-End-Capped Rotaxane . . . . .	217
13.3	Reduction of Ketone by Rotaxane Bearing a Dihydronicotinamide Group . . . . .	225
13.4	Conclusion . . . . .	230
13.5	References . . . . .	231

<b>14</b>	<b>Metal-Containing Star and Hyperbranched Polymers</b>	
	<i>Masami Kamigaito</i> . . . . .	233
14.1	Introduction . . . . .	233
14.2	Metal-Containing Star Polymers . . . . .	235
14.2.1	Metal-Containing Star Polymers with a Small and Well-Defined Number of Arms . . . . .	236
14.2.2	Metal-Containing Star Polymers with a Large and Statistically Distributed Number of Arms . . . .	240
14.3	Metal-Containing Hyperbranched Polymers . . . . .	243
14.4	Concluding Remarks . . . . .	245
14.5	References . . . . .	246
<b>15</b>	<b>Electronic Properties of Helical Peptide Derivatives at a Single Molecular Level</b>	
	<i>Shunsaku Kimura, Kazuya Kitagawa, Kazuyuki Yanagisawa, Tomoyuki Morita</i> . . . . .	249
15.1	Molecular Electronics . . . . .	249
15.2	Electron Transfer Through Molecules . . . . .	250
15.3	Electronic Properties of Helical Peptides . . . . .	251
15.4	Electron Transfer Mechanism over a Long Distance . . . . .	254
15.5	Effect of Linkers on Electron Transfer . . . . .	254
15.6	Helical-Peptide Scaffold for Electron Hopping . . . . .	256
15.7	Photocurrent Generation with Helical Peptides Carrying Naphthyl Groups . . . . .	259
15.8	Conclusion . . . . .	261
15.9	References . . . . .	261
<b>16</b>	<b>Construction of Redox-Induced Systems Using Antigen-Combining Sites of Antibodies and Functionalization of Antibody Supramolecules</b>	
	<i>Hiroyasu Yamaguchi, Akira Harada</i> . . . . .	263
16.1	Introduction . . . . .	264
16.2	Photoinduced Electron Transfer from Porphyrins to Electron Acceptor Molecules . . . . .	266
16.2.1	Monoclonal Antibodies for <i>meso</i> -Tetrakis(4-carboxyphenyl)porphyrin (TCPP) . . . . .	267
16.2.2	Photoinduced Electron Transfer from a Porphyrin to an Electron Acceptor in an Antibody-Combining Site . . . . .	273
16.3	Peroxidase Activity of Fe-Porphyrin-Antibody Complexes . . . .	275
16.3.1	Preparation of Monoclonal Antibodies Against Cationic Porphyrins . . . . .	276
16.3.2	Peroxidase Activity of Antibody-Fe-TMPyP Complex . . . . .	280
16.4	Dendritic Antibody Supramolecules . . . . .	282

16.5	Linear Antibody Supramolecules: Application for Novel Biosensing Method .....	285
16.5.1	Antiviologen Antibodies .....	286
16.5.2	Applications for Highly Sensitive Detection Method of Methyl Viologen by Supramolecular Complex Formation Between Antibodies and Divalent Antigens.....	287
16.6	Conclusions .....	289
16.7	References .....	290
<b>Subject Index .....</b>		<b>293</b>

Redox Systems Under Nano-Space Control

Hirao, T. (Ed.)

2006, XVIII, 292 p. 233 illus., Hardcover

ISBN: 978-3-540-29579-2