### Contents

#### Part I  Redox Systems via d,π-Conjugation

1  Conjugated Complexes with Quinonediimine Derivatives  
*Toshiyuki Moriuchi, Toshikazu Hirao*  
1.1 Introduction  
1.2 Architecturally Controlled Formation  
of Conjugated Complexes with 1,4-Benzquinonediimines  
1.3 Redox-Switching Properties of Conjugated Complexes  
with 1,4-Benzquinonediimines  
1.4 Conclusion  
1.5 References  

2  Realizing the Ultimate Amplification  
in Conducting Polymer Sensors:  
Isolated Nanoscopic Pathways  
*Timothy M. Swager*  
2.1 Dimensionality in Molecular-Wire Sensors  
2.2 Analyte-Triggered Barrier Creation in Conducting Polymers  
2.3 Isolated Nanoscopic Pathways  
2.4 Langmuir–Blodgett Approaches to Nanofibrils  
2.5 Molecular Scaffolds for the Isolation of Molecular Wires  
2.6 Summary and Future Prospects  
2.7 References  

3  Metal-Containing π-Conjugated Materials  
*Michael O. Wolf*  
3.1 Introduction  
3.1.1 π-Conjugated Materials  
3.1.2 Nanomaterials  
3.2 Metal-Complex-Containing Conjugated Materials  
3.2.1 Preparation  
3.2.2 Properties  
3.3 Metal-Nanoparticle-Containing Conjugated Materials  
3.3.1 Preparation
4  Redox Active Architectures and Carbon-Rich Ruthenium Complexes as Models for Molecular Wires
Stéphane Rigaut, Daniel Touchard, Pierre H. Dixneuf ........ 55

3.3.2 Properties .............................................. 51
3.4 Applications ............................................ 52
3.5 Conclusions ............................................. 53
3.6 References .............................................. 53

4  Redox Active Architectures and Carbon-Rich Ruthenium Complexes as Models for Molecular Wires
Stéphane Rigaut, Daniel Touchard, Pierre H. Dixneuf ....... 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 RuII/RuIII 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)2 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 C7 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

5  Molecular Metal Wires Built from a Linear Metal Atom Chain
Supported by Oligopyridylamido Ligands
Chen-Yu Yeh, Chih-Chieh Wang, Chun-Hsien Chen,
Shie-Ming Peng ............................................. 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 Dinuculear 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
Takane Imaoka, Kimihisa Yamamoto .............................. 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
Tomohiko Hamaguchi, Tadashi Yamaguchi, Tasuku Ito ........ 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
Masa-aki Haga .......................................................... 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
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3.2</td>
<td>Combinatorial Approach to Electrochemical Molecular Devices in a Multilayer Nanostructure on Surfaces</td>
<td>149</td>
</tr>
<tr>
<td>8.3.3</td>
<td>Surface DNA Trapping by Immobilized Metal Complexes with Intercalator Moiety Toward Nanowiring</td>
<td>151</td>
</tr>
<tr>
<td>8.4</td>
<td>Conclusion</td>
<td>153</td>
</tr>
<tr>
<td>8.5</td>
<td>References</td>
<td>153</td>
</tr>
</tbody>
</table>
| 9       | **Programmed Metal Arrays by Means of Designable Biological Macromolecules**<br>
|         | *Kentaro Tanaka, Tomoko Okada, Mitsuhiko Shionoya*                   | 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  |
| 10      | **Metal-Incorporated Hosts for Cooperative and Responsive Recognition to External Stimulus**<br>
|         | *Tatsuya Nabeshima, Shigehisa Akine*                                 | 167  |
| 10.1    | Introduction                                                         | 167  |
| 10.2    | Pseudomacrocycles for Cooperative Molecular Functional Systems        | 168  |
| 10.3    | Oligo(N$_2$O$_2$-Chelate) Macrocycles                               | 172  |
| 10.3.1  | Design of Macroyclic Oligo(N$_2$O$_2$-Chelate) Ligands and Metallohosts | 172  |
| 10.3.2  | Synthesis and Structure of Tris(N$_2$O$_2$-Chelate) Macrocycles       | 173  |
| 10.4    | Acyclic Oligo(N$_2$O$_2$-Chelate) Ligands                            | 174  |
| 10.4.1  | Design of Acyclic Oligo(N$_2$O$_2$-Chelate) Ligands                  | 174  |
| 10.4.2  | Complexes of a New N$_2$O$_2$-Chelate Ligand, Salamo                 | 175  |
| 10.4.3  | Synthesis, Structure, and Properties of Acyclic Oligo(N$_2$O$_2$-Chelate) Ligands | 176  |
| 10.5    | Conclusion                                                           | 177  |
| 10.6    | References                                                           | 177  |
11 Synthesis of Poly(binaphthol) via Controlled Oxidative Coupling
Shigeki Habaue, Bunpei Hatano ........................................... 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

12 Nano Meccano
Yi Liu, Amar H. Flood, J. Fraser Stoddart ....................... 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

13 Through-Space Control of Redox Reactions
Using Interlocked Structure of Rotaxanes
Nobuhiro Kihara, Toshikazu Takata ......................... 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
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

Subject Index .................................................................... 293
Redox Systems Under Nano-Space Control
Hirao, T. (Ed.)
2006, XVIII, 292 p. 233 illus., Hardcover
ISBN: 978-3-540-29579-2