

Contents

List of Contributors XI

| | | |
|----------|--|----------|
| 1 | Introduction: Organic Photochromic Molecules | 1 |
| | <i>Keitaro Nakatani, Jonathan Piard, Pei Yu, and Rémi Métivier</i> | |
| 1.1 | Photochromic Systems | 1 |
| 1.1.1 | General Introduction | 1 |
| 1.1.2 | Basic Principles | 4 |
| 1.1.3 | Photochromic Molecules: Some History | 5 |
| 1.2 | Organic Photochromic Molecules: Main Families | 8 |
| 1.2.1 | Proton Transfer | 9 |
| 1.2.2 | Trans–Cis Photoisomerization | 12 |
| 1.2.3 | Homolytic Cleavage | 13 |
| 1.2.4 | Cyclization Reaction | 14 |
| 1.2.4.1 | Spiropyrans, Spirooxazines, and Chromenes | 14 |
| 1.2.4.2 | Fulgides and Fulgimides | 17 |
| 1.2.4.3 | Diarylethenes | 18 |
| 1.3 | Molecular Design to Improve the Performance | 20 |
| 1.3.1 | Figures of Merit | 20 |
| 1.3.2 | Fatigue Resistance: Increasing the Number of Operating Cycles | 21 |
| 1.3.3 | Bistability: Avoiding Unwanted Thermal Back-Reaction in the Dark | 23 |
| 1.3.3.1 | Influence of Ethenic Bridge on the Thermal Stability of the B Form | 24 |
| 1.3.3.2 | Impact of the Heteroaryl Substituents on the Thermal Stability of the B Form | 24 |
| 1.3.4 | Fast Photochromic Systems: Reverting Back Spontaneously to the Colorless State in a Glance | 25 |
| 1.3.5 | Gaining Efficiency of the Photoreaction: the Example of Diarylethenes | 26 |
| 1.4 | Conclusion | 31 |
| | Irradiation at a Specific Wavelength: Isosbestic Point | 32 |

Case A: When the Thermal Back-Reaction is Negligible Compared to the Photochemical Reaction (Typically P-type) 33

Case B: When the Thermal Back-Reaction is More Efficient than the Photochemical $B \rightarrow A$ Reaction (Typically T type) 34

References 34

2 Photochromic Transitional Metal Complexes for

Photosensitization 47

Chi-Chiu Ko and Vivian Wing-Wah Yam

2.1 Introduction 47

2.2 Photosensitization of Stilbene- and Azo-Containing Ligands 48

2.3 Photosensitization of Spirooxazine-Containing Ligands 51

2.4 Photosensitization of Diarylethene-Containing Ligands 54

2.5 Photosensitization of Photochromic N⁺C-Chelate Organoboranes 63

2.6 Conclusion 65

References 66

3 Multi-addressable Photochromic Materials 71

Shangjun Chen, Wenlong Li, and Weihong Zhu

3.1 Molecular Logic Gates 71

3.1.1 Two-Input Logic Gates 71

3.1.2 Combinatorial Logic Systems 74

3.1.2.1 Half-Adder and Half-Subtractor 74

3.1.2.2 Keypad Locks 77

3.1.2.3 Digital Encoder and Decoder 82

3.2 Data Storage and Molecular Memory 84

3.2.1 Fluorescence Spectroscopy 85

3.2.2 Infrared Spectroscopy 90

3.2.3 Optical Rotation 92

3.3 Gated Photochromores 95

3.3.1 Hydrogen Bonding 95

3.3.2 Coordination 98

3.3.3 Chemical Reaction 99

References 105

4 Photoswitchable Supramolecular Systems 109

Guanglei Lv, Liang Chen, Haichuang Lan, and Tao Yi

4.1 Introduction 109

4.2 Photoreversible Amphiphilic Systems 110

4.2.1 Photoreversible Diarylethene-Based Amphiphilic System 110

4.2.2 Photoreversible Azobenzene-Based Amphiphilic System 116

4.2.3 Photoreversible Spiropyran-Based Amphiphilic System 119

4.3 Photoswitchable Host–Guest Systems 122

4.3.1 Photocontrolled Supramolecular Self-Assembly 123

| | | |
|----------|---|------------|
| 4.3.2 | Photocontrolled Capture and Release of Guest Molecules | 128 |
| 4.3.3 | Fluorescent Switching Promoted by Host–Guest Interaction | 133 |
| 4.3.4 | Photoswitchable Molecular Devices | 137 |
| 4.4 | Photochromic Metal Complexes and Sensors | 141 |
| 4.4.1 | Metal Complexes with Azobenzene Groups | 141 |
| 4.4.2 | Metal Complexes with Diarylethene Groups | 144 |
| 4.4.3 | Metal Complexes with Spirocyclic Groups | 150 |
| 4.4.4 | Metal Complexes with Rhodamine | 152 |
| 4.5 | Other Light-Modulated Supramolecular Interactions | 153 |
| 4.6 | Conclusions and Outlook | 159 |
| | References | 159 |
| 5 | Light-Gated Chemical Reactions and Catalytic Processes | 167 |
| | <i>Robert Göstl, Antti Senf, and Stefan Hecht</i> | |
| 5.1 | Introduction | 167 |
| 5.2 | General Design Considerations | 169 |
| 5.3 | Photoswitchable Stoichiometric Processes | 171 |
| 5.3.1 | Starting Material Control | 172 |
| 5.3.2 | Product Control | 175 |
| 5.3.3 | Starting Material and Product Control | 177 |
| 5.3.4 | Template Control | 178 |
| 5.4 | Photoswitchable Catalytic Processes | 182 |
| 5.4.1 | Activity Control | 182 |
| 5.4.2 | Selectivity Control | 185 |
| 5.5 | Outlook | 187 |
| | References | 190 |
| 6 | Surface and Interfacial Photoswitches | 195 |
| | <i>Junji Zhang and He Tian</i> | |
| 6.1 | Photochromic SAMs | 196 |
| 6.1.1 | Photochromic Electrode SAMs | 196 |
| 6.1.2 | Photoreversible Functional Surfaces | 198 |
| 6.1.2.1 | Photoswitchable Surface Wettability | 198 |
| 6.1.2.2 | Photocontrolled Capture-and-Release System | 202 |
| 6.1.2.3 | Smart Photochromic Surface Based on Supramolecular Systems | 203 |
| 6.1.2.4 | Photochromic Surface for Molecular Data Processing | 205 |
| 6.2 | Photoregulated Nanoparticles | 206 |
| 6.2.1 | Photochromic Switches on Traditional Metal Nanoparticles | 208 |
| 6.2.1.1 | Photoswitching on the Metal Nanoparticles | 208 |
| 6.2.1.2 | Photoinduced Reversible Aggregation of Nanoparticles and Their Versatile Applications | 210 |
| 6.2.2 | Photochromic Switches on Other Novel Functional Nanoparticles | 215 |
| 6.2.2.1 | Photoswitchable Magnetic Nanoparticles | 215 |

- 6.2.2.2 Photomanipulated Quantum Dots 215
- 6.2.2.3 Photochromic with Upconversion Nanoparticles 218
- 6.2.3 Photocontrolled Mesoporous Silica Nanoparticles 220
- 6.2.3.1 Photo-nanovalves 220
- 6.2.3.2 Photo-nanoimpellers 223
- 6.2.3.3 NIR Light-Triggered MSN Drug Delivery and Therapeutic Systems 224
- 6.3 Photocontrolled Surface Conductance 226
- 6.3.1 Photochromic Conductance Switching Based on SAMs 226
- 6.3.2 Photochromic Conductance on Single-Molecule Level 228
- References 231

- 7 Hybrid Organic/Photochromic Approaches to Generate Multifunctional Materials, Interfaces, and Devices 243**
Emanuele Orgiu and Paolo Samori
- 7.1 Introduction 243
- 7.1.1 Tuning the Charge Injection in Organic-Based Devices by Means of Photochromic Molecules 245
- 7.2 Tuning the Polaronic Transport in Organic Semiconductors by Means of Photochromic Molecules 251
- 7.2.1 Photochromic Molecules and Organic Semiconductors Incorporated in Dyads, Multiads, and Polymers 251
- 7.2.2 The Multilayer Approach 254
- 7.2.3 The Blending Approach 255
- 7.3 Photoresponsive Dielectric Interfaces and Bulk 262
- 7.4 Conclusions and Future Outlooks 267
- Acknowledgments 268
- References 268

- 8 Photochromic Bulk Materials 281**
Masakazu Morimoto, Seiya Kobatake, Masahiro Irie, Hari Krishna Bisoyi, Quan Li, Sheng Wang, and He Tian
- 8.1 Photochromic Polymers 281
- 8.1.1 Glass Transition Temperature 281
- 8.1.2 Fluorescence 283
- 8.1.3 Conductivity 287
- 8.1.4 Living Radical Polymerization 288
- 8.1.5 Surface Relief Grating 290
- 8.1.6 Photomechanical Effect 290
- 8.2 Single-Crystalline Photoswitches 293
- 8.2.1 Crystalline-State Photochromic Materials 293
- 8.2.2 Photochromic Diarylethene Single Crystals 293
- 8.2.3 *In situ* X-ray Crystallographic Analysis of Photoisomerization Reaction 295
- 8.2.4 Photoisomerization Quantum Yields 296

| | | |
|----------|---|------------|
| 8.2.5 | Multicolor Photochromism of Multicomponent Crystals | 297 |
| 8.2.6 | Nanoperiodic Structures Fabricated by Photochromic Reactions | 299 |
| 8.2.7 | Photoinduced Shape Changes and Mechanical Performance | 301 |
| 8.3 | Photochromic Liquid Crystals | 305 |
| 8.3.1 | Introduction | 305 |
| 8.3.2 | Spiropyran- and Spirooxazine-Based Photochromic Liquid Crystals | 309 |
| 8.3.3 | Diarylethene-Based Photochromic Liquid Crystals | 314 |
| 8.3.4 | Azobenzene-Based Photochromic Liquid Crystals | 320 |
| 8.3.5 | Other Photochromic Liquid Crystals | 327 |
| 8.3.6 | Conclusions and Outlook | 328 |
| 8.4 | Photochromic Gels | 329 |
| 8.4.1 | Introduction | 329 |
| 8.4.2 | Azobenzene Gels | 330 |
| 8.4.3 | Spiropyran and Spirooxazine Gels | 335 |
| 8.4.4 | Diarylethenes Gels | 337 |
| 8.4.5 | Naphthopyran Gels | 342 |
| 8.4.6 | The Other Photochromic Gels | 343 |
| 8.4.7 | Conclusion | 346 |
| | References | 346 |
| 9 | Photochromic Materials in Biochemistry | 361 |
| | <i>Danielle Wilson and Neil R. Branda</i> | |
| 9.1 | Introduction | 361 |
| 9.2 | Reversible Photochemical Switching of Biomaterial Function | 362 |
| 9.3 | General Design Strategies and Considerations | 362 |
| 9.3.1 | Photoswitchable Tethers | 364 |
| 9.3.1.1 | The Incorporation Method | 364 |
| 9.3.1.2 | Considerations | 364 |
| 9.3.2 | Photoswitchable Small Molecules | 365 |
| 9.3.2.1 | The Incorporation Method | 365 |
| 9.3.2.2 | Considerations | 365 |
| 9.3.3 | Chromophore Selection | 367 |
| 9.4 | Selected Examples | 367 |
| 9.4.1 | Photoswitchable Enzymes | 367 |
| 9.4.1.1 | Drug-Inspired Small Molecule Inhibitors | 367 |
| 9.4.1.2 | Phosphoribosyl Isomerase Inhibitor with Two Binding Units | 370 |
| 9.4.1.3 | Direct Modification of Enzymes with Photochromic Groups | 372 |
| 9.4.2 | Photoswitchable Peptides and Proteins | 373 |
| 9.4.2.1 | Peptide Cross-Linking | 373 |
| 9.4.2.2 | Cyclic Antimicrobial Peptide | 375 |
| 9.4.2.3 | Genetically Encoded Amino Acids | 376 |
| 9.4.2.4 | Control of Motor Protein Function Using Site-Selective Mutation | 377 |

| | | |
|-----------|--|------------|
| 9.4.3 | Photoswitchable Ion Channels and Receptors | 379 |
| 9.4.3.1 | Photocontrol of Channel Activation and Desensitization with a Tethered Glutamate | 380 |
| 9.4.3.2 | Photocontrol of Insulin Release Using a Small Molecular Sulfonylurea | 380 |
| 9.4.3.3 | Photocontrol of Receptors Using Red Light | 381 |
| 9.4.4 | Photoswitchable Nucleotides | 382 |
| 9.4.4.1 | Spiropyran-Modified Oligonucleotide Backbones | 382 |
| 9.4.4.2 | Controlling RNA Duplex Hybridization with Light | 384 |
| 9.4.4.3 | Diarylethene-Modified Oligonucleotides | 385 |
| 9.5 | Summary | 386 |
| | References | 386 |
| 10 | Industrial Applications and Perspectives | 393 |
| | <i>Junji Zhang and He Tian</i> | |
| 10.1 | Industrialization and Commercialization of Organic Photochromic Materials | 393 |
| 10.1.1 | Commercialized T-type Photochromic Materials | 395 |
| 10.1.2 | Commercialized P-Type Photochromic Materials | 398 |
| 10.2 | Perspectives for Organic Photochromic Materials | 399 |
| | References | 409 |
| | Index | 417 |