Contents

List of Boxes *XVII*
Preface *XIX*
Acknowledgments *XXV*
List of Abbreviations *XXVII*

1 Introduction *1*
1.1 Photochemistry and Photophysics in Science and Technology *1*
1.2 Historical Notes *2*
1.3 A New Dimension of Chemistry and Physics *3*
1.4 The Nature of Light *5*
1.5 Absorption of Light *7*
1.6 Quantum Yield, Efficiencies, and Excited-State Reactivity *8*
References *10*

2 Elementary Molecular Orbital Theory *11*
2.1 Introduction *11*
2.2 The Hydrogen Atom *11*
2.3 Polyelectronic Atoms *13*
2.4 From Atoms to Molecules *17*
2.5 Electronic Structure of Homonuclear Diatomic Molecules *21*
2.6 Electronic Structure of Heteronuclear Diatomic Molecules *25*
2.7 Simple Polyatomic Molecules and Elements of Group Theory *26*
2.7.1 Elements of Group Theory *26*
2.7.2 Water *29*
2.7.3 Ammonia *31*
2.8 Typical Organic Molecules *33*
2.8.1 Methane *33*
2.8.2 Ethene *35*
2.8.3 Benzene *37*
2.8.4 Formaldehyde *39*
2.9 Transition Metal Complexes *41*
2.9.1 General Concepts *41*

2.9.2 Typical Metal Complexes *48*
References *52*

3 Light Absorption and Excited-State Deactivation *55*
3.1 Light Absorption *55*
3.1.1 Selection Rules *57*
3.1.2 Symmetry Selection Rules *58*
3.1.3 Spin Selection Rules *59*
3.1.4 The Franck–Condon Principle *60*
3.1.5 Visualization of Photochemical Reactions on Potential Energy Surfaces *62*
3.2 Jablonski Diagram *64*
3.3 Excited-State Deactivation *68*
3.3.1 Vibrational Relaxation *68*
3.3.2 Radiationless Deactivation *68*
3.3.3 Radiative Deactivation *71*
3.3.4 Radiative Lifetime *72*
3.4 Chemical Reactions *73*
3.5 Kinetic Aspects *74*
3.6 Solvent and Temperature Effects *75*
3.6.1 Solvatochromic Shift *75*
3.6.2 Crossing of States *77*
3.6.3 Temperature Effects on Excited-State Lifetime *79*
3.6.4 Thermally Activated Delayed Fluorescence *80*
3.7 Selected Molecules *81*
3.7.1 Oxygen *81*
3.7.2 Naphthalene *83*
3.7.3 Benzophenone *85*
3.7.4 Zinc(II) Tetraphenyl Porphyrin *87*
3.7.5 $[Cr(en)_3]^{3+}$ *90*
3.7.6 $[Co(NH_3)_6]^{3+}$ *92*
3.7.7 $[Ru(bpy)_3]^{2+}$ *94*
3.8 Semiconductors *96*
References *100*

4 Excited States: Physical and Chemical Properties *103*
4.1 Excited State as a New Molecule *103*
4.2 Lifetime *103*
4.3 Energy *104*
4.4 Geometry *105*
4.4.1 Small Molecules *106*
4.4.2 Ethene *107*
4.4.3 Ethyne *108*
4.4.4 Benzene *109*
4.4.5 Formaldehyde *109*

4.4.6 Square Planar Metal Complexes *111*
4.5 Dipole Moments *112*
4.6 Electron Transfer *114*
4.7 Proton Transfer *117*
4.8 Excimers and Exciplexes *120*
References *122*

5 From Molecules to Supramolecular Systems *125*
5.1 Supramolecular (Multicomponent) Systems and Large Molecules *125*
5.2 Electronic Interaction in Mixed-Valence Compounds *127*
5.3 Electronic Interaction in Donor–Acceptor Complexes *129*
5.4 Electronic Stimulation and Electronic Interaction in the Excited State *131*
5.5 Formation of Excimers and Exciplexes in Supramolecular Systems *134*
References *136*

6 Quenching and Sensitization Processes in Molecular and Supramolecular Species *139*
6.1 Introduction *139*
6.2 Bimolecular Quenching *140*
6.2.1 Stern–Volmer Equation *140*
6.2.2 Kinetic Details *143*
6.2.3 Static versus Dynamic Quenching *144*
6.2.4 Sensitized Processes *145*
6.2.5 Spin Considerations *146*
6.3 Quenching and Sensitization Processes in Supramolecular Systems *146*
6.4 Electron-Transfer Kinetics *150*
6.4.1 Marcus Theory *150*
6.4.2 Quantum Mechanical Theory *153*
6.4.2.1 The Electronic Factor *154*
6.4.2.2 The Nuclear Factor *156*
6.4.2.3 Optical Electron Transfer *156*
6.5 Energy Transfer *157*
6.5.1 Coulombic Mechanism *159*
6.5.2 Exchange Mechanism *161*
6.6 Role of the Bridge *163*
6.7 Catalyzed Deactivation *164*
References *166*

7 Molecular Organic Photochemistry *169*
7.1 Introduction *169*
7.2 Alkenes and Related Compounds *169*

7.2.1 Basic Concepts *169*
7.2.2 Photoisomerization of Double Bonds *170*
7.2.3 Electrocyclic Processes *172*
7.2.4 Sigmatropic Rearrangements *173*
7.2.5 Di-π-Methane Reaction *174*
7.2.6 Photocycloaddition Reactions *174*
7.2.7 Photoinduced Nucleophile, Proton, and Electron Addition *175*
7.3 Aromatic Compounds *176*
7.3.1 Introduction *176*
7.3.2 Photosubstitution *179*
7.3.3 Photorearrangement *180*
7.3.4 Phototransposition *181*
7.3.5 Photocycloadditions *181*
7.4 Carbonyl Compounds *182*
7.4.1 Introduction *182*
7.4.2 Photochemical Primary Processes *183*
7.5 Photochemistry of Other Organic Compounds *185*
7.5.1 Nitrogen Compounds *185*
7.5.1.1 Overview *185*
7.5.1.2 Photoisomerization of Azocompounds *186*
7.5.2 Saturated Oxygen and Sulfur Compounds *186*
7.5.3 Halogen Compounds *187*
References *189*

8 Photochemistry and Photophysics of Metal Complexes *191*
8.1 Metal Complexes *191*
8.2 Photophysical Properties *191*
8.3 Photochemical Reactivity *192*
8.4 Relationships between Electrochemistry and Photochemistry *194*
8.4.1 Cobalt (III) Complexes *195*
8.4.2 Copper (I) Complexes *196*
8.4.3 Ru(II) Polypyridine Complexes *196*
8.4.4 Excited-State Redox Potentials *199*
8.5 Luminescent Metal Complexes *201*
8.5.1 Polypyridine Metal Complexes *201*
8.5.2 Cyclometallated Complexes *203*
8.5.2.1 Ruthenium Complexes *204*
8.5.2.2 Rhodium Complexes *204*
8.5.2.3 Iridium Complexes *205*
8.5.2.4 Platinum Complexes *207*
8.5.2.5 Orbital Nature of the Emitting Excited State *212*
8.5.3 Porphyrin Complexes *213*
8.5.4 Chromium (III) Complexes *216*
8.5.5 Lanthanoid Complexes *219*
8.6 Photochemical Processes *223*

8.6.1 Types of Photoreactions *223*
8.6.1.1 Photodissociation and Related Reactions *223*
8.6.1.2 Photooxidation–Reduction Reactions *224*
8.6.1.3 Intramolecular Rearrangements *225*
References *226*

9 Interconversion of Light and Chemical Energy by Bimolecular Redox Processes *231*
9.1 Light as a Reactant *231*
9.2 Light as a Product *232*
9.3 Conversion of Light into Chemical Energy *233*
9.4 Chemiluminescence *235*
9.5 Electrochemiluminescence *235*
9.6 Light Absorption Sensitizers *237*
9.7 Light Emission Sensitizers *240*
References *242*

10 Light-Powered Molecular Devices and Machines *245*
10.1 Molecules, Self-Organization, and Covalent Synthetic Design *245*
10.2 Light Inputs and Outputs: Reading, Writing, and Erasing *246*
10.3 Molecular Devices for Information Processing *247*
10.3.1 Photochromic Systems as Molecular Memories *247*
10.3.2 Molecular Logics *249*
10.3.2.1 Luminescent Sensors as Simple Logic Gates *250*
10.3.2.2 AND Logic Gate *251*
10.3.2.3 XOR Logic Gate with an Intrinsic Threshold Mechanism *251*
10.3.2.4 Encoding and Decoding *253*
10.4 Molecular Devices Based on Energy Transfer *255*
10.4.1 Wires *255*
10.4.2 Switches *257*
10.4.3 Plug/Socket Systems *258*
10.4.4 Light-Harvesting Antennas *259*
10.5 Molecular Devices Based on Electron Transfer *260*
10.5.1 Wires *260*
10.5.2 Switches *263*
10.5.3 Extension Cables *265*
10.6 Light-Powered Molecular Machines *268*
10.6.1 Basic Remarks *268*
10.6.2 The Role of Light *268*
10.6.3 Rotary Motors Based on cis–trans Photoisomerization *269*
10.6.4 Linear Motions: Molecular Shuttles and Related Systems *271*
10.6.5 Photocontrolled Valves, Boxes, and Related Systems *275*
References *276*

11 Natural and Artificial Photosynthesis *281*
11.1 Energy for Spaceship Earth *281*
11.2 Natural Photosynthesis *284*
11.2.1 Light Harvesting: Absorption and Energy Transfer *285*
11.2.2 Photoinduced Electron Transfer Leading to Charge Separation *285*
11.2.2.1 Bacterial Photosynthesis *285*
11.2.2.2 Green Plants Photosynthesis: Photosystem II *287*
11.2.3 Efficiency of Photosynthesis *288*
11.3 Artificial Photosynthesis *290*
11.3.1 Artificial Antenna *293*
11.3.2 Artificial Reaction Centers *296*
11.3.3 Coupling Artificial Antenna and Reaction Center *299*
11.3.4 Coupling One-Photon Charge Separation with Multielectron Water Splitting *301*
11.4 Water Splitting by Semiconductor Photocatalysis *302*
References *304*

12 Experimental Techniques *309*
12.1 Apparatus *309*
12.1.1 Light Sources *309*
12.1.2 Monochromators, Filters, and Solvents *317*
12.1.3 Cells and Irradiation Equipment *319*
12.1.4 Detectors *321*
12.2 Steady-State Absorption and Emission Spectroscopy *323*
12.2.1 Absorption Spectroscopy *323*
12.2.1.1 Instrumentation *324*
12.2.1.2 Qualitative and Quantitative Applications *325*
12.2.1.3 Sample Measurement *325*
12.2.2 Emission Spectroscopy *326*
12.2.2.1 Instrumentation *326*
12.2.2.2 Emission Spectra *328*
12.2.2.3 Excitation Spectra *329*
12.2.2.4 Presence of Spurious Bands *330*
12.2.2.5 Quantitative Relationship between Luminescence Intensity and Concentration *331*
12.2.2.6 Stern–Volmer Luminescence Quenching *332*
12.2.2.7 Emission Quantum Yields *333*
12.3 Time-Resolved Absorption and Emission Spectroscopy *335*
12.3.1 Transient Absorption Spectroscopy *335*
12.3.1.1 Transient Absorption with Nanosecond Resolution *335*
12.3.1.2 Transient Absorption with Femtosecond Resolution *337*
12.3.2 Emission Lifetime Measurements *338*
12.3.2.1 Single Flash *338*
12.3.2.2 Gated Sampling *339*
12.3.2.3 Upconversion Techniques *339*

12.3.2.4 Single-Photon Counting *341*
12.3.2.5 Data Analysis *342*
12.3.2.6 Phase Shift *343*
12.3.2.7 Luminescence Lifetime Standards *345*
12.4 Absorption and Emission Measurements with Polarized Light *346*
12.4.1 Linear Dichroism *346*
12.4.2 Luminescence Anisotropy *347*
12.5 Reaction Quantum Yields and Actinometry *349*
12.5.1 Reaction Quantum Yields *349*
12.5.2 Actinometry *350*
12.5.2.1 Potassium Ferrioxalate *351*
12.5.2.2 Potassium Reineckate *352*
12.5.2.3 Azobenzene *353*
12.6 Other Techniques *353*
12.6.1 Photothermal Methods *353*
12.6.1.1 Photoacoustic Spectroscopy *354*
12.6.1.2 Photorefractive Spectroscopy *355*
12.6.2 Single-Molecule Spectroscopy *357*
12.6.3 Fluorescence Correlation Spectroscopy *358*
12.6.4 X-ray Techniques *360*
References *361*

13 Light Control of Biologically Relevant Processes *365*
13.1 Introduction *365*
13.2 Vision *365*
13.2.1 Basic Principle *365*
13.2.2 Primary Photochemical Events *367*
13.3 Light, Skin, and Sunscreens *367*
13.4 Photochemical Damage in Living Systems *369*
13.4.1 Photochemical Damage to DNA *369*
13.4.2 Photochemical Damage to Proteins *369*
13.5 Therapeutic Strategies Using Light *370*
13.5.1 Phototherapy *370*
13.5.2 Photochemotherapy of Psoriasis *370*
13.5.3 Photodynamic Therapy *371*
13.5.4 Photocontrolled Delivery *373*
13.6 Photocatalysis in Environmental Protection *375*
13.6.1 Principles *375*
13.6.2 Solar Disinfection (SODIS) *375*
13.6.3 Photoassisted Fenton Reaction *376*
13.6.4 Heterogeneous Photocatalysis *376*
13.7 DNA Photocleavage and Charge Transport *377*
13.7.1 Photocleaving Agents of Nucleic Acid *377*
13.7.2 Photoinduced Electron-Transfer Processes in DNA *378*
13.8 Fluorescence *379*

13.9 Bioluminescence *379*
References *380*

14 Technological Applications of Photochemistry and Photophysics *385*
14.1 Introduction *385*
14.2 Photochromism *385*
14.3 Luminescent Sensors *388*
14.3.1 Principles *388*
14.3.2 Amplifying Signal *389*
14.3.3 Wind Tunnel Research *389*
14.3.4 Thermometers *391*
14.3.5 Measuring Blood Analytes *393*
14.3.6 Detecting Warfare Chemical Agents *395*
14.3.7 Detecting Explosives *397*
14.4 Optical Brightening Agents *399*
14.5 Atmospheric Photochemistry *400*
14.5.1 Natural Processes Involving Oxygen *400*
14.5.2 Ozone Hole *401*
14.6 Solar Cells *402*
14.6.1 Inorganic Photovoltaic (PV) Cells *402*
14.6.2 Organic Solar Cells (OSCs) *403*
14.6.3 Dye-Sensitized Solar Cells (DSSCs) *405*
14.7 Electroluminescent Materials *407*
14.7.1 Light-Emitting Diodes (LEDs) *407*
14.7.2 Organic Light-Emitting Diodes (OLEDs) *407*
14.7.3 Light-Emitting Electrochemical Cells (LECs) *409*
14.8 Polymers and Light *411*
14.8.1 Photopolymerization *411*
14.8.2 Photodegradation *411*
14.8.3 Stabilization of Commercial Polymers *412*
14.8.4 Photochemical Curing *413*
14.8.5 Other Light-Induced Processes *413*
14.8.6 Photolithography *414*
14.8.7 Stereolithography *415*
14.8.8 Holography *416*
14.9 Light for Chemical Synthesis *417*
14.9.1 Photochlorination of Polymers *418*
14.9.2 Synthesis of Caprolactam *418*
14.9.3 Synthesis of Vitamins *418*
14.9.4 Perfumes *419*
References *420*

15 Green (Photo)Chemistry *425*
15.1 Definition, Origins, and Motivations *425*
15.2 Photochemistry for Green Chemical Synthesis *426*

15.3 Photocatalysis *428*
15.3.1 Heterogeneous Photocatalysis *428*
15.3.2 Homogeneous Photocatalysis *429*
15.4 Photocatalysis in Synthesis *429*
15.4.1 Alkanes *430*
15.4.2 Alkenes *430*
15.4.3 Alkynes *432*
15.4.4 Sulfides *432*
15.5 Photocatalytic Pollution Remediation *433*
15.6 Use of Solar Energy in Green Synthesis *434*
References *436*

16 Research Frontiers *439*
16.1 Introduction *439*
16.2 Aggregation-Induced Emission *439*
16.3 Phosphorescence from Purely Organic Materials by Crystal Design *441*
16.4 Synthesis of a 2D Polymer *443*
16.5 Photocontrolled Relative Unidirectional Transit of a Nonsymmetric Molecular Wire through a Molecular Ring *444*
16.6 Molecular Rotary Motors Powered by Visible Light via Energy Transfer *445*
16.7 Cooperation and Interference in Multifunction Compounds *447*
16.8 Singlet Fission *449*
16.9 One-Color Photochromic System *452*
16.10 Photonic Modulation of Electron Transfer with Switchable Phase Inversion *454*
16.11 Dye-Sensitized Photoelectrosynthesis Cells (DSPECs) *457*
References *459*

Index *463*