

Part I

Introduction

COPYRIGHTED MATERIAL

1

Philosophy of Bioinorganic Photochemistry

*The most important thing in science is not so much to obtain new facts
as to discover new ways of thinking about them.*

Sir William Bragg

Bioinorganic photochemistry is a rapidly growing and evolving new interdisciplinary research area integrating inorganic photochemistry with biological, medical, and environmental sciences (Figure 1.1) [1]. The role of light and inorganic species in natural systems and the possibility of their application in artificial systems of medical or environmental importance are in the limelight of bioinorganic photochemistry. From the earliest times humans have been aware of the influence that solar radiation exerts on matter and life; however, it is mainly during the last century that a systematic understanding of this phenomena has been developed [2–9]. Photochemistry of the inorganic species had its contribution in the creation of the world and has played a fundamental role in the evolution of life. Photosynthesis and many photoreactions proceeding in the atmosphere, hydrosphere and soil, involving inorganic species, ensure life on Earth. Bioinorganic solar photochemistry deals with the interaction of sunlight with inorganic matter, which has a huge impact on all forms of life on the Earth from its origin until now.

Sunlight supplies energy to the whole terrestrial environment: atmosphere, hydrosphere, lithosphere and biosphere. The spectral range of sunlight reaching our planet has varied with time. Atmospheric oxygen appeared owing to photosynthesis around 2.7 billion years ago. Atomic oxygen produced by short-wavelength ultraviolet (UV) irradiation ($<240\text{nm}$) reacted then with molecular dioxygen to form an ozone layer shielding the Earth's surface from the most harmful UV. Four hundred million years ago the concentration of ozone reached 10% of the present level and allowed living systems to evolve from aquatic to terrestrial life. Today this ozone layer, with a maximum concentration in the stratosphere at 25km above sea level, absorbs solar UV at wavelengths shorter than 290nm. The radiation energy effective

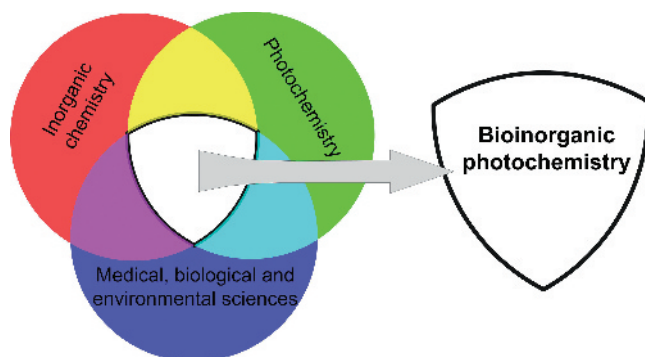


Figure 1.1 *Bioinorganic photochemistry connects inorganic photochemistry with biological, medical, and environmental sciences.*

for photobiology lies between 300 and 900 nm. Practically all photobiological behaviour of plants and animals, photosynthesis, phototropism, phototaxis, photoperiodism, and visions utilize this range of radiation [2–4, 10].

Natural photobiochemical processes, as a result of evolution, follow essentially the biologically desirable pathways [11]. In contrast, adventitious photobiochemical processes are likely to follow a multiplicity of pathways and usually find a variety of targets [11]. The mechanisms that underline both types of photoprocesses are highly complex, and their elucidation requires knowledge of the physics of light, the chemistry and structure of a photoacceptor molecule and its microenvironment, as well as physical and chemical processes leading to the final effect. Light is composed of energy packets called photons, which at the same time are energy quanta and bits of information. All the phenomena related to the interaction between light and matter, and the great number of photochemical and photophysical applications in science and technology, can ultimately be traced back to these two aspects of light [12]. Sun is the main light source, but nowadays light can also be provided by various artificial light sources. Introduction of lasers has caused an enormous increase of research on the interaction of light with biomatter [13–15].

The results obtained from the interaction of light with matter depend on the degree of organization of the receiving matter. To be useful for solar energy harvesting, organic synthesis, degradation of pollutants, therapeutic or diagnostic processes, etc the systems activated by light must fulfil various requirements [4, 12, 16–19]. In this context, inorganic photochemistry has recently attracted much attention because it offers feasible solutions [2, 12, 18–36]. Metal ions and other inorganic species can be involved in both natural and adventitious processes. There are numerous systems containing various metal ions and other inorganic species that are flexible enough to drive their photochemistry or photophysics towards desired actions [1, 13, 37, 38].

There is better understanding of the natural systems and phenomena that speeds the design of various molecular devices of medical, biochemical, or environmental importance. Metal complexes exhibit a high level of organization, so they

are quite useful as components of molecular level photochemical devices. Moreover, a variety of transition metal-based supramolecular systems, or heterogeneous nanoassemblies supplemented with transition metal compounds, can be carefully designed to perform desired functions such as energy conversion, molecular sensing, labelling, switching, catalysis, etc [16, 17, 20, 29, 39–44]. Photochemical or photophysical processes induced by sunlight or artificial light sources are often damaging to biological systems, especially when suitable photoprotective mechanisms are absent or insufficient – typical examples are photocarcinogenesis and the photoinduced generation of pollutants. In many cases it is possible to take advantage of the damaging action of light to obtain beneficial effects. Achieving this goal requires a detailed knowledge of the mechanisms involved in a given photoprocess, so that their progress can be strictly controlled and intermediates and ultimate actions directed towards defined targets.

Photochemistry is the chemistry of excited electronic states. The change in electron distribution caused by photon absorption can cause substantial modifications in the chemical and physical properties of a molecule. Among these properties the energy, molecular geometries, polarizability, dipole and magnetic moments, and related redox and acid-based properties can change on passing to excited states [44]. Over the past decades inorganic photochemistry, which extends from simple Werner transition-metal complexes through supramolecular and multimetallic systems to homogeneous and heterogeneous nanoassemblies, has attracted increasing interest in various fields of science and technology, including bioscience and biotechnology [2–4, 11, 12, 16–36, 45–62]. One of the tremendous advantages of photochemical activation of transition-metal complexes is the generation of electronic excited states with moderate energy consumption. Transition-metal complexes distinguish themselves from organic compounds by both the number of accessible electronic excited states and their spin multiplicity. Consequently, depending on the wavelength (energy) of irradiation, optical excitation leads to various electronic excited states of different reactivity. In some favourable circumstances this behaviour allows tuning of photochemical reactivity and switching between various pathways such as electron transfer (preferably due to the population of diverse charge transfer states – CT), dissociation/substitution/rearrangement reactions (caused by excited metal-centred states – MC), and ligand-centred reactivity caused by the population of intraligand states (ligand centred – LC).

The great variety of available electronic excited states may be used for photogeneration of coordinatively unsaturated species, transition-metal compounds with changed formal oxidation numbers, as well as free ligands and ligand radicals. Such species generated photochemically not only can take part in stoichiometric processes but also open new pathways into both light-induced catalytic reactions and chain processes [21, 52]. Two limiting cases of photocatalysis, photoinduced catalytic and photoassisted reactions, can be distinguished. Photoinduced catalysis is the photogeneration of a catalyst that subsequently promotes a catalyzed reaction. Photoassisted reactions enable conversion of solar energy into useful energy. The activation of transition-metal complexes by visible and UV light provides definite advantages compared with the usual thermal activation. Catalysts usually have unique properties and are generated with high selectivity. The strategic synthetic

design of transition-metal complexes or organometallic compounds, as well as the choice of the irradiation wavelength (ligand field, charge transfer, and intraligand excitation), allows modelling of photoinduced catalytic or photoassisted reactions. Photocatalytic reactions can be carried out at ambient temperature and pressure. To utilize the broadband solar energy spectrum it is necessary to involve some spectral sensitization [21, 52].

Application of inorganic photophysics generates challenging new areas in bio-science and biotechnology. Optical and, especially, fluorescence spectroscopy are widely used research tools in biochemistry, molecular biology, and environmental studies [31, 63]. Fluorescence has also become the dominant method enabling the revolution in medical diagnostics, DNA sequencing, and genomics. To date, all fluorescence observables, including spectral shifts, anisotropies, quantum yields, and lifetimes, have found both scientific and analytical applications [31]. New opportunities in fluorescence and radiation decay engineering, eg modification of fluorophore emissions by changing non-radiation decay rates has been described [32]. Transition-metal complexes have many potential advantages including numerous excited states of long lifetimes and high luminescence quantum yields [32, 33, 58–60, 64]. Luminescent polynuclear transition-metal complexes containing multichromophoric ligands with extended conjugation have been extensively studied in recent years, partly because of their potential use as sensors, labels, and probes in (bio)chemical systems [13, 35, 58, 65–70]. Many of them are easily excited by visible light with low-cost light-emitting diodes (LEDs) or inexpensive diode lasers. They show large spectral shifts between the excitation and emission bands that minimize the difficulty of isolating the excitation and emission wavelengths. Long lifetimes allow efficient time discrimination from the ubiquitous background fluorescence. Importantly, the longer lifetimes also allow the excited state ample time to sample its environment, making these materials particularly sensitive reporters [27, 33, 59, 60].

Supramolecular systems are constituted of a number of discrete molecular components with definite individual properties held together by various interactions. In natural systems the molecular components are frequently assembled by intermolecular forces (hydrogen bonds, donor–acceptor interactions, van der Waals' forces, etc), whereas in artificial systems covalent or coordination bonds are used to achieve a better control of the supramolecular structure [12, 16, 30, 40, 42, 56, 71–73]. Supramolecular systems began the concept of molecular devices, assemblies of molecular components designed to achieve specific functions, such as photoinduced electron and energy transfer in solar energy conversion, electron collection, photosensitization, antenna effect, photoswitching of electric signals, light-energy conversion, and photoinduced structural changes in switch on/off applications (photoisomerizable systems, molecular wires, and sensors) [12, 16, 17, 21, 29, 71].

The development of supramolecular chemistry has allowed construction of structurally organized and functionally integrated chemical systems capable of elaborating energy and information input photons so that they can perform complex functions [40, 41, 72, 74–83]. Over the past decade research on transition metal supramolecular systems has experienced extraordinary progress. In terms of bonding strength, the moderate coordination bonds between transition metals and ligands

are between strong covalent bonding in carbon-based systems and weak interactions in biological systems. Some advantages of employing transition metals to build supramolecular systems include the following [30, 44, 58, 84]:

- Involvement of *d* orbitals, which offer more bonding modes and geometric symmetries than simple organic molecules
- A range of electronic and steric properties that can be fine-tuned by employing various ancillary ligands
- Easily modified size of the desired supermolecules by utilizing various lengths of bridging ligands
- Incorporation of their distinct spectral, magnetic, redox, photophysical, and photochemical properties.

Moreover, the diverse bonding angles imported by the transition-metal centres and the high directionality of the bonding between the ligands and metals also provide superior features over weak electrostatic, van der Waals', and π - π interactions. Another interesting aspect is that thermodynamically driven spontaneous self-assembly of individual molecular components into well-defined molecular structures in solution is expected to be rather similar for both coordination chemistry and biology, and this enables transition metal complexes to be valuable mimics of the more complicated biological systems [58, 71].

Recently, nanoscience and nanotechnology, which involve research on materials and species at length scales between 1 to 100 nm, have been revolutionizing important areas in environmental protection and biomedical photonics, especially diagnostics and therapy at the molecular levels [13, 16, 85–87]. The combination of photonics and nanotechnology has already led to new generation of methods and devices for probing the cell machinery and elucidating intimate life processes occurring at the molecular level. This will open the possibility of detecting and manipulating atoms and molecules using nanodevices, which have the potential for a wide variety of medical uses at the cellular level.

Colloidal-metal nanoparticles have found use in biology and medicine in the last 20 years, but semiconductor nanocrystals have only recently been used for biological labelling [13, 88–90].

A great trend in biotechnology is the development of multiplex sensing and ultrasensitive imaging technologies for the rapid molecular profiling of cells, tissues, and organs. These probes are traditionally based on organic dyes conjugated to biomolecules. As a result of their complex molecular structures, however, organic fluorophores often exhibit unfavourable absorption and emission properties such as photobleaching, environmental quenching, broad and asymmetric emission spectra, and the inability to emit various colours at a single wavelength excitation. These problems can be overcome by exploiting the unique optical properties of metal and semiconductor nanoparticles. The ongoing research attempts on bio-conjugation of quantum dots to peptides, proteins, oligonucleotides and other biomolecules have demonstrated their applications in assembling new materials, in homogeneous bioassays, and multicolour fluorescence imaging and detection [13, 88, 91–93].

Nanostructured materials offer many new opportunities to study fundamental processes in a controlled manner, and this in turn leads to fabrication of numerous photonic and optoelectronic devices [13, 16, 17, 87, 94–98]. The design of photochemical molecular devices requires the ability to organize molecules on a nanometric scale with the fine control of their arrangement/distribution, mobility, and spectral and redox properties. Several types of heterogeneous multiphase systems have been proposed and tested. Mesoporous membrane-type films with a large surface area can be prepared from nanosized colloidal semiconductor dispersions. Nanocrystalline oxide or chalcogenide semiconductor thin films and particles such as TiO_2 , ZnO , ZnS , CdS , and CdSe have been used for that purpose [13, 17, 85, 99, 100]. By suitable molecular engineering the metal complexes can be readily attached to the surface. These films with anchored photoactive complexes find increasing use in energy-conversion devices such as optical sensors [17, 54, 55]. For biophotonic applications the photoactive component has to meet several stringent requirements: the first is the intensity and spectral range of light absorption in the UV, visible, and near-infrared (IR) regions; the second is tunability of the absorption band; the third are photo-physical properties: types and number of accessible excited states and their lifetimes and quantum yields of radiative and non-radiative decays; and the fourth are redox properties of the ground and excited states. For redox sensitizers or redox mediators there are further requirements of stability of both the redox forms and the reversibility of the redox processes. The interaction with biomatter is of primary importance. In all cases transition-metal complexes with polypyridines or polypyrrolic macrocycles as ligands come out clearly as the sensitizers of preferred choice [1, 13, 17].

Some specific aspects of light and inorganic compound interactions in bioscience and biotechnology have been reviewed [1, 12, 19, 22–28, 32–34, 36, 58–60]. Future perspectives of bioinorganic photochemistry will depend on both development of bioinorganic solar photochemistry and progress in understanding, as well as application of artificial light interaction with biomatter.

References

1. Szaciłowski K, Macyk W, Drzewiecka-Matuszek A, Brindell M, Stochel G. Bioinorganic photochemistry: Frontiers and mechanisms. *Chem Rev* 2005;**105**:2647–94.
2. Milgrom LR. *The Colours of Life*. Oxford: Oxford University Press, 1997.
3. Wolken JJ. *Light and Life Processes*. New York: Van Nostrand Reinhold Co., 1998.
4. Suppan P. *Chemistry and Light*. Cambridge: Royal Chemical Society (RSC), 1994.
5. Renger G. *Primary Processes of Photosynthesis* – Part 1. Cambridge: RSC, 2008.
6. Renger G. *Primary Processes of Photosynthesis* – Part 2. Cambridge: RSC, 2008.
7. Batschauer A. *Photoreceptors and Light Signalling*. Cambridge: RSC, 2003.
8. Frausto da Silva JJR, Williams RJP. *The Biological Chemistry of the Elements. The inorganic chemistry of life*. Oxford: Oxford University Press, 2001.
9. Blankenship R. *Molecular Mechanisms of Photosynthesis*. St Louis, MO: Washington University, 2002.
10. Sarna T, ed. *Advanced Course in Photobiology and Photomedicine*. Kraków: UJ Press, 1999.
11. Bonnett R. Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy. *Chem Soc Rev* 1995;**24**:19.

12. Balzani V, Credi A, Venturi M. Photoprocesses. *Curr Opin Chem Biol* 1997;**1**:506–13.
13. Vo-Dinh T. *Biomedical Photonics Handbook*. New York: CRC Press, 2003.
14. Kraatz H-B, Metzler-Nolte N, eds. *Concepts and Models in Bioinorganic Chemistry*. Weinheim: Wiley, 2006.
15. Saleh BEA, Teich MC. *Fundamentals of Photonics*. New York: John Wiley & Sons, Inc., 1991.
16. Balzani V, Venturi M, Credi A. *Molecular Devices and Machines – A journey into nano-world*. Weinheim: Wiley-VCH, 2003.
17. Kalyanasundaram K, Grätzel M. Applications of functionalized transition metal complexes in photonic and optoelectronic devices. *Coord Chem Rev* 1998;**77**:347–414.
18. Nalwa HS, ed. *Handbook of Photochemistry and Photobiology*, Vol 4. *Photobiology*. New York: American Scientific Publishers, 2003.
19. Litter MI. Heterogeneous photocatalysis. *Appl Catal B: Environ* 1999;**23**:89–114.
20. Balzani V, Scandola F. *Photochemical and Photophysical Devices*. Oxford: Pergamon Press, 1996.
21. Kalyanasundaram K, Grätzel M, eds. *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*. Dordrecht: Kluwer Academic Press, 1993.
22. Schance KS, Schmehl RH. Applications of inorganic photochemistry in the chemical and biological sciences. *J Chem Educ* 1997;**74**:633–5.
23. Bonnett R. Metal complexes for photodynamic therapy. In: McCleverty JA, Meyer TJ, eds. *Comprehensive Coordination Chemistry II*. Amsterdam: Elsevier, 2003: 945.
24. Faulkner S, Matthews JL. Fluorescent complexes for biomedical applications. In: McCleverty JA, Meyer TJ, eds. *Comprehensive Coordination Chemistry II*. Amsterdam: Elsevier 2003: 913.
25. Stochel G, Wanat A, Kuliš E, Stasicka Z. Light and metal complexes in medicine. *Coord Chem Rev* 1998;**171**:203–20.
26. Stochel G, Drzewiecka A, Kuliš E, et al. Photochemistry and photophysics of coordination compounds in medicine. In: Melnik M, Sirota A, eds. *Challenges for Coordination Chemistry in the New Century*. Bratislava: Slovak Technical University Press, 2001: 301–6.
27. Yam VW-W, Lo KK-W. Recent advances in utilization of transition metal complexes and lanthanides as diagnostic tools. *Coord Chem Rev* 1998;**184**:157–240.
28. Ali H, van Lier JE. Metal complexes as photo- and radiosensitizers. *Chem Rev* 1999;**99**:2379–450.
29. Balzani V, Scandola F. *Supramolecular Photochemistry*. New York: Ellis Horwood, 1991.
30. Balzani V, Credi A, Venturi M. Photochemistry and photophysics of coordination compounds. An extended view. *Coord Chem Rev* 1998;**171**:3–16.
31. Lakowicz JR. *Principles of Fluorescence Spectroscopy*. New York: Kluwer Academic/Plenum Publishers, 1999.
32. Lakowicz JR. Radiative decay engineering: biophysical and biomedical applications. *Anal Biochem* 2001;**298**:1–24.
33. Demas JN, DeGraff BA. Application of luminescent transition platinum group metal complexes to sensor technology and molecular probes. *Coord Chem Rev* 2001;**211**: 317–51.
34. Cieřla P, Kocot P, Mytych P, Stasicka Z. Homogeneous photocatalysis by transition metal complexes in the environment. *J Mol Catal A: Chem* 2004;**224**:17–33.
35. Balzani V, Juris A, Venturi M, Compagna S, Serroni S. Luminescent and redox-active polynuclear transition metal complexes. *Chem Rev* 1996;**96**:759.
36. Burdette SC, Lippard SJ. ICC34 – golden edition of coordination chemistry reviews. Coordination chemistry for the neurosciences. *Coord Chem Rev* 2001;**216–217**:333–61.
37. McCleverty JA, Meyer TJ, eds. *Comprehensive Coordination Chemistry II*. Amsterdam: Elsevier, 2003.
38. Balzani V, Campagna S, eds. *Photochemistry and Photophysics of Coordination Compounds*. Berlin: Springer-Verlag GmbH, 2007.

39. Balzani V, Credi A, Venturi M. *Molecular Devices and Machines. Concepts and perspectives for the nanoworld*. Weinheim: Wiley-VCH 2008.
40. Balzani V, Credi A, Venturi M. Molecular machines working on surfaces and at interfaces. *ChemPhysChem* 2008;**9**:202–20.
41. Balzani V, Credi A, Venturi M. Processing energy and signals by molecular and supramolecular systems. *Chem Eur J* 2008;**14**:26–39.
42. Balzani V, Credi A, Venturi M. Photochemical conversion of solar energy. *ChemSusChem* 2008;**1**:26–58.
43. Vos JG, Forster RJ, Keyes TA, eds. *Interfacial Supramolecular Assemblies*. Chichester: John Wiley & Sons Ltd, 2003.
44. Turro NJ. From molecular chemistry to supramolecular chemistry to superdupermolecular chemistry. Controlling covalent bond formation through non-covalent and magnetic interactions. *Chem Commun* 2002:2279–92.
45. Balzani V, Carassiti V. *Photochemistry of Coordination Compounds*. London: Academic Press, 1970.
46. Adamson AW. *Concepts of Inorganic Photochemistry*. New York: Wiley-VCH, 1975.
47. Fox MA. *Photoinduced Electron Transfer*. Amsterdam: Elsevier, 1988.
48. Sykora J, Sima J. Photochemistry of coordination compounds. *Coord Chem Rev* 1990;**107**:1.
49. Ramamurthy V, Schance KS. *Multimetallic and Macromolecular Inorganic Photochemistry*. New York: Marcel Dekker, 1999.
50. Nalwa HS, ed. *Handbook of Photochemistry and Photobiology*, Vol 1. *Inorganic Photochemistry*. Stevenson Ranch: American Scientific Publishers, 2003.
51. Roundhill DM. *Photochemistry and Photophysics of Metal Complexes*. New York: Plenum Press 1994.
52. Hennig H. Homogeneous photocatalysis by transition metal complexes. *Coord Chem Rev* 1999;**182**:101–23.
53. Grätzel M. *Energy Resources through Photochemistry and Catalysis*. New York: Academic Press, 1983.
54. Coleman JP, Lynch AT, Madhukar P, Wagenknecht JH. Printed, flexible electrochromic displays using interdigitated electrodes. *Sol Energy Mater Sol Cells* 1999;**56**:395–418.
55. Bonhôte P. Nanocrystalline electrochromic displays. *Displays* 1999;**20**:137–44.
56. Nalwa HS, ed. *Handbook of Photochemistry and Photobiology*, Vol 3. *Supramolecular Photochemistry*. New York: American Scientific Publishers, 2003.
57. Bonnett R. *Chemical Aspects of Photodynamic Therapy*. Amsterdam: Gordon Science Publishers, 2000.
58. Sun S-S, Lees AJ. Transition metal based supramolecular systems: synthesis, photophysics, photochemistry and their potential applications as luminescent anion chemosensors. *Coord Chem Rev* 2002;**230**:171–192.
59. Bergonzi R, Fabbri L, Licchelli M, Mangano C. Molecular switches of fluorescence operating through metal centred redox couples. *Coord Chem Rev* 1998;**170**:31–47.
60. Valeur B, Leray I. Design principles of fluorescent molecular sensors for cation recognition. *Coord Chem Rev* 2000;**205**:3–40.
61. Ariga K, Kunitake T. *Supramolecular Chemistry – Fundamentals and Applications*. Heidelberg: Springer Verlag, 2006.
62. Strosio MA, Dutta M, eds. *Biological Nanostructures and Applications of Nanostructures in Biology*. New York: Kluwer Academic Publishers.
63. Valeur B. *Molecular Fluorescence. Principles and applications*. Weinheim: Wiley-VCH, 2002.
64. Vogler A, Kunkely H. Luminescent metal complexes: Diversity of excited states. *Top Curr Chem* 2001;**213**:143–82.
65. de Silva AP, Eilers J, Zlokarnik G. Emerging fluorescence sensing technologies: from photophysical principles to cellular applications. *Proc Natl Acad Sci USA* 1999;**96**:8336–7.

66. de Silva AP, Fox DA, Huxley AJM, McClenaghan ND, Roiron J. Metal complexes as components of luminescent signalling systems. *Coord Chem Rev* 1999;**185–186**: 297–306.
67. de Silva AP, Fox DA, Huxley AJM, Moody TS. Combining fluorescence, coordination chemistry and electron transfer for signalling purposes. *Coord Chem Rev* 2000;**205**:41–57.
68. de Silva AP, Fox DB, Moody TS, Weir SM. The development of molecular fluorescent switches. *Trends Biotechnol* 2001;**19**:29–34.
69. de Silva AP, Gunaratne HQN, Gunnlaugsson T, et al. Signaling recognition events with fluorescent sensors and switches. *Chem Rev* 1997;**97**:1515–66.
70. de Silva AP, McClean GD, Moody TS. Fluorescent sensors. In: *Encyclopedia of Supramolecular Chemistry*. New York: Marcel Dekker, Inc., 2004: 572–8.
71. Lehn J-M. *Supramolecular Chemistry: Concepts and perspectives*. Weinheim: VCH, 1998.
72. Balzani V, Credi A, Venturi M. Light-powered molecular-scale machines. *Pure Appl Chem* 2003;**75**:541–7.
73. Balzani V, Sabbatini N, Scandola F. ‘Second-sphere’ photochemistry and photophysics of coordination compounds. *Chem Rev* 1986;**86**:319–37.
74. Balzani V, Ceroni P, Maestri M, Vicinelli V. Light-harvesting dendrimers. *Curr Opin Chem Biol* 2003;**7**:657–65.
75. Balzani V, Credi A, Raymo FM, Stoddart JF. Machines at the molecular level. *Angew Chem Int Ed* 2000;**39**:3348.
76. Balzani V, Credi A, Silvi S, Venturi M. Artificial nanomachines based on interlocked molecular species: recent advances. *Chem Soc Rev* 2006;**35**:1135–49.
77. Balzani V, Credi A, Venturi M. Molecular logic circuits. *ChemPhysChem* 2003;**3**:49–59.
78. Credi A. Artificial molecular motors powered by light. *Aust J Chem* 2006;**59**:157–69.
79. Credi A. Molecules that make decisions. *Angew Chem Int Ed* 2007;**46**:5472–5.
80. de Silva AP, McClenaghan ND. Molecular-scale logic gates. *Chem Eur J* 2004;**10**:574–86.
81. de Silva AP, Uchiyama S, Vance TP, Wannalorse B. A supramolecular basis for molecular logic and computation. *Coord Chem Rev* 2007;**251**:1623–32.
82. Szaciłowski K. Digital information processing in molecular systems. *Chem Rev* 2008;**108**: 3481–548.
83. Atwood JL, Davies JED, MacNicol DD, Vögtle F, Lehn J-M, eds. *Comprehensive Supramolecular Chemistry*. Oxford: Pergamon, 1996.
84. Balzani V, Bergamini G, Campagna S, Puntoriero F. Photochemistry and photophysics of coordination compounds: overview and general concepts. In: Balzani V, Campagna S, eds. *Photochemistry and Photophysics of Coordination Compounds I*. Berlin: Verlag 2007: 1–36.
85. Ozin GA, Arsenault AC. *Nanochemistry. A chemical approach to nanomaterials*. Cambridge: Royal Chemical Society, 2005.
86. Dupas C, Houdy P, Lahmani M, eds. *Nanoscience. Nanotechnologies and nanophysics*. Berlin: Springer Verlag, 2007.
87. Fahrner WR, ed. *Nanotechnology and Nanoelectronics*. Berlin: Springer Verlag, 2005.
88. Mirkin CA, Taton TA. Semiconductors meet biology. *Nature* 2000;**405**:626–7.
89. Daniel M-C, Astruc D. Gold nanoparticles: assembly, supramolecular chemistry, quantum size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chem Rev* 2004;**104**:293–346.
90. Medintz IL, Clapp AR, Mattoissi H, Goldman ER, Fisher B, Mauro JM. Self-assembled nanoscale biosensors based on quantum dot FRET donors. *Nature Mat* 2003;**2**:630–8.
91. Niemeyer CM. Nanoparticles, proteins and nucleic acids: biotechnology meets material science. *Angew Chem Int Ed Eng* 2001;**40**:4128–58.
92. Mirkin CA. Programming the assembly of two and three-dimensional architectures with DNA and nanoscale inorganic building blocks. *Inorg Chem* 2000;**39**:2258–72.
93. Rosi NL, Mirkin CA. Nanostructures in bionanotechnology. *Chem Rev* 2005;**105**:1547–62.

94. Dragoman M, Dragoman D. *Nanoelectronics. Principles and devices*. Norwood, MA: Artech House, Inc., 2006.
95. Minolli D. *Nanotechnology Applications to Telecommunications and Networking*. Hoboken, NJ: Wiley-Interscience, 2006.
96. Regis E. *Nano: The emerging science of nanotechnology*. Newport Beach, CA: Back Bay Books, 1996.
97. Bhushan B, ed. *Handbook of Nanotechnology*. Berlin: Springer Verlag, 2004.
98. Lyshevski SE, ed. *Nano and Molecular Electronics*. London: CRC Press, 2007.
99. Kamat PV. *Composite Semiconductor Nanoclusters. Studies in surface science and catalysis*. Amsterdam: Elsevier, 1996.
100. Di Ventra M, Evoy S, Heflin JR Jr, eds. *Introduction to Nanoscale Science and Technology*. New York: Kluwer Academic Publishers, 2004.