WILEY VCH

Vincenzo Balzani, Paola Ceroni, and Alberto Juris

Photochemistry and Photophysics

Concepts, Research, Applications

Second Edition

Photochemistry and Photophysics

Photochemistry and Photophysics

Concepts, Research, Applications

Second Edition

Vincenzo Balzani, Paola Ceroni, and Alberto Juris

WILEY-VCH

Authors
Prof. Vincenzo Balzani
University of Bologna
Department of Chemistry Giacomo Ciamician
via Selmi 2
Bologna
IT, 40126

Prof. Paola Ceroni
University of Bologna
Department of Chemistry Giacomo Ciamician
Via Selmi 2
Bologna
IT, 40126

Prof. Alberto Juris
University of Bologna
Department of Chemistry Giacomo Ciamician
Via Selmi 2
Bologna
IT, 40126

Cover: © agsandrew/Shutterstock

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-35276-0
ePDF ISBN: 978-3-527-84407-4
ePub ISBN: 978-3-527-84408-1

Typesetting Straive, Chennai, India

To Carla, Carlo, and Teresa

Contents

From the Preface to the First Edition

And God said: "Let there be light";
And there was light.
And God saw that the light was good.
(Genesis 1, 3-4)

Photochemistry and photophysics are natural phenomena as old as the world. Our life depends on photosynthesis, a natural photochemical and photophysical process. We get information about the surrounding space by photochemical and photophysical processes that occur in our eyes.

Currently, photochemistry and photophysics represent a modern branch of science, at the interface between light and matter and at the crossroads of several disciplines including chemistry, physics, materials science, ecology, biology, and medicine. In our day life, we are surrounded by products obtained with the aid of photochemistry and photophysics and by devices that exploit photochemical and photophysical processes to perform useful functions in various places, from industries to hospitals.

We are moving toward a future in which energy and information will be the dominant features of civilization. We will be forced to exploit sunlight as our ultimate energy source, converting it into useful energy forms by photochemical and photophysical processes. We will continue to miniaturize devices for information and communication technology down to the molecular level and we will use, more and more, light signals to transfer, store, and retrieve information.

The number of researchers working in the area of light-matter interaction is increasing, but several of them did (and still do) not receive an appropriate training. Light is often used in chemical laboratories as a silver bullet reactant to obtain products unavailable by thermal activation. In general, however, researchers lack the basis to fully understand how photochemical and photophysical processes can be exploited for novel, unusual, and unexpected applications in fields of energy conversion, information technology, nanotechnology, and medicine.

Preface to the Second Edition

In the past 10 years, several textbooks and reference books on photochemistry have been published. However, most of them essentially focus on the photoreactions of organic molecules. In some textbooks, the fundamental bases of excited-state properties are confined in a few pages; in others, theoretical aspects are presented in too much detail, including boring and unnecessary mathematical treatments. Most of the available books ignore, or barely mention, the photochemical and photophysical properties of metal complexes, a class of molecules that is attracting increasing theoretical and applicative interest. No textbook emphasizes the most recent trends in photochemistry and photophysics, such as information processing by reading, writing, and erasing molecules with light signals, the capability of powering and controlling molecular machines by light, the conversion of sunlight into electrical energy by inorganic and organic solar cells, the recent developments in the field of light-emitting diodes, and the first achievements along the road toward artificial photosynthesis.

For all these reasons, we felt there was the need for a book capable of (i) presenting a clear picture of the concepts required to understand the excited-state properties of the most important types of molecules, (ii) showing recent applications concerning photochemistry and photophysics, and (iii) opening the eyes of young researchers toward forefront developments or even futuristic visions of the light–matter interaction. The usefulness of the first edition of this book was testified by the prompt publication of a Chinese edition in 2015. In the following years, the frontiers of photochemistry and photophysics continued to expand with the development of new molecules, new materials, and new processes. There is no doubt that photochemistry and photophysics will play an increasingly important role in the development of science and technology.

Although the organization of this second edition is essentially the same as that of the first edition, several chapters have been revised considerably, others have been almost entirely rewritten, a number of schemes and figures have been added, and the reference list at the end of each chapter has been extended and updated.

We believe that this book, which originates from our long experience in teaching photochemistry and photophysics at the University of Bologna, can be a basic text for graduate and postgraduate courses because of its balanced content. We feel that it can also be useful for scientists who desire to enter photochemistry and photophysics research even if they did not have a chance, during their university training, to get the fundamental bases of this field. Scientist already active in photochemical and photophysical research can find suggestions to undertake novel scientific adventures.

Chapters 1–4 of this book deal with fundamental concepts concerning the nature of light, the principles that govern its interaction with matter, and the formation, electronic structure, properties, chemical reactivity, and radiative and nonradiative decay of excited states. Each concept is illustrated making reference to important classes of molecules. The notion that an excited state is a new chemical species with its own chemical and physical properties compared with the ground state is underlined, leading to the conclusion that photochemistry is a new dimension of chemistry.

Chapter 5 extends the above concepts from molecules to supramolecular (multicomponent) systems where a fundamental role is played by structural organization and component interactions.

Chapter 6 illustrates the fundamental concepts and the theoretical approaches concerning the two most important photochemical and photophysical processes, namely, energy transfer and electron transfer.

Chapters 7 and 8 deal with the photochemical and photophysical properties of organic molecules and metal complexes, respectively. The peculiar light absorption/emission spectra and the photochemical properties of the various families of organic molecules are illustrated by detailed discussions of several examples. For metal complexes, the discussion of the relationship between structure and photochemical and photophysical properties is underlined, with particular emphasis on the nature of the metal(s) involved, the outstanding luminescence properties of some classes of these compounds, and the relationships between luminescence and electrochemical properties.

Chapter 9 offers a detailed presentation of equipment, techniques, procedures, and reference data concerning photochemical and photophysical experiments, including warnings to avoid mistakes and misinterpretations.

Chapter 10 describes the relationships between photochemical, photophysical, and electrochemical properties of molecules that can be exploited for the interconversion between light and chemical energy.

Chapter 11 deals with the mechanisms of homogeneous and heterogeneous photocatalytic processes based on electron and hydrogen transfer reactions, including two-photon-driven photoredox catalysis and applications of photocatalysis for environmental protection.

Chapter 12 concerns the hot topic of light-powered molecular devices and machines. The concepts of exploiting the interaction between molecules and light to read, write, and erase information are illustrated, together with their application in the field of molecular logics. Various molecular devices (e.g., wires, switches, extension cables, pumps, and light-harvesting antennas) based on energy transfer, photoinduced electron transfer, or photoisomerization processes are described and important examples of light-powered molecular machines (e.g., linear and rotary motors) are discussed.

Chapter 13 illustrates in detail the reactions taking place in the natural photosynthetic processes of bacteria and green plants and describes the first achievements along the road toward photochemical water splitting by photocatalytic semiconductor nanoparticles and photoelectrochemical cells.

Chapter 14 illustrates the relationships between light and life, starting from vision and including damages caused by exposure to UV light, benefits deriving from light-based therapeutic processes, fluorescent sensors and their applications, and a brief description of bioluminescence processes.

Chapter 15 deals with applications of photochemistry and photophysics, covering various topics: photochromic compounds, luminescent sensors (including their use in fields as diverse as wind tunnel, thermometers, measuring blood analytes, detecting explosives, and warfare chemical agents), optical brighteners, atmospheric photochemistry, solar cells (PV, OSC, DSSC), electrochemiluminescent materials (LED, OLED, LEC), numerous applications concerning the interaction between polymers and light (e.g., photodegradation, photostabilization, photolitography, and stereolitography), and the photochemical syntheses of industrial products.

After having presented the fundamental concepts of photochemistry and photophysics and described the most important natural and artificial photochemical and photophysical processes, in Chapter 16, we offer the reader the opportunity to make acquaintance with forefront research through the discussion of selected topics taken from recent literature. The choice of the examples has been based not only on their intrinsic interest, but especially on their educational capacity to illustrate connections among fundamental photochemical and photophysical concepts.

In several chapters, additional information on specific topics is presented in boxes interlaced with the text. An important feature of the book is the abundance of illustrations that are essential for an easier understanding of the concepts discussed. References have been updated up to December 2023.

Before closing, we express our feeling concerning science, society, and Earth, the place on which we live. Planet Earth is a very special spaceship that cannot land or dock anywhere for being refueled or repaired. We can only rely on the limited resources available on the spaceship and the energy coming from the Sun. We are concerned about the increasing consumption of natural resources [1], the climate change [2], the energy crisis [3], and the degradation of the environment [4–6], which is accompanied by an increased social disparity. As Pope Francis warns [7–9], we are faced with a complex crisis that is both social and environmental. Strategies for a solution demand an integrated approach to combating poverty and protecting nature.

If we want to continue living on Earth, we must achieve the goals of ecological and social sustainability by implementing three transitions: from fossil fuels to renewable energies, from a linear to a circular economy, and from consumerism to sobriety [10], but we also need to create new resources. In principle, this is possible by exploiting the only abundant, inexhaustible, and well-distributed resource on which we can rely: solar energy. Starting from seawater, the fundamental components of our atmosphere, and mineral resources, by means of sunshine, we need to "fabricate" fuels, electricity, pure water, polymers, food, and other things we need [11].

Until now, humankind has taken from spaceship Earth enormous amounts of resources [12]. Hopefully, future generations will pay back Earth with a capital produced from human intelligence. Photochemistry and photophysics can help. Indeed, science can greatly benefit humankind, but science and technology alone will not take us where we need to go: a fair, open, responsible, friendly, united, and peaceful society. Responsible scientists, while creating, with the greatest moral care, new science and technology, should also play an important role as authoritative, informed, and concerned citizens of Earth [13]. They should teach their students not only to make science but also to distinguish what is worth making with science. As pointed out by Albert Einstein, "*Concern for man himself and his fate must always constitute the chief objective of all technological endeavors … never forget this in the midst of your diagrams and equations*." We need scientists watching that science and technology are used for peace, not for war; for alleviating poverty, not for maintaining privileges; for reducing, not for increasing the gap between developed and underdeveloped countries; for protecting, not for destroying our planet that, beyond any foreseeable development of science, will remain the only place where mankind can live. Science, but also consciousness, responsibility, compassion, and care must be the roots of a new knowledge-based society.

References

1 Richardson, K., Steffen, W., Lucht, W., Bendtsen, J., Cornell, S. E., Donges, J. F., Drüke, M., Fetzer, I., Bala, G., von Bloh, W., et al. (2023) Earth beyond six of nine planetary boundaries. *Sci. Adv.*, **9**, eadh2458.

2 Masson-Delmotte, V., Zhai, P., Pirani, S., Connors, C., Péan, S., Berger, N., Caud, Y., Chen, L., et al. (2023) Summary for policymakers in *Climate Change 2021 – The Physical Science Basis*, Cambridge University Press, pp. 3–32.

3 Armaroli, N. and Balzani, V. (2010) *Energy for a Sustainable World: From the Oil Age to a Sun-Powered Future*, Wiley-VCH, Weinheim.

4 Wilson, E. O. (2006) *The Creation: An Appeal to Save Life on Earth*, Norton, New York.

5 Brown, L. R. (2011) *World on the Edge: How to Prevent Environmental and Economic Collapse*, Norton, New York.

6 Ehrlich, P. R. and Ehrlich, A. H. (2013) Can a collapse of global civilization be avoided? *Proc. R. Soc. B Biol. Sci.*, **280**, 20122845.

7 Pope Francis (2015) *On Care for Our Common Home, Laudato si'*, https://www.vatican.va/content/francesco/en/encyclicals/documents/papa-francesco_20150524_enciclica-laudato-si.html (3 October 2023).

8 Pope Francis (2020) *Fratelli Tutti*, https://www.vatican.va/content/francesco/en/encyclicals/documents/papa-francesco_20201003_enciclica-fratelli-tutti.html (1 December 2023).

9 Pope Francis (2023) *Apostolic Exhortation Laudate Deum of The Holy Father Francis To All People of Good Will on the Climate Crisis*, https://press.vatican.va/content/salastampa/it/bollettino/pubblico/2023/10/04/0692/01509.html#inglese (10 October 2023).

10 Balzani, V. (2019) Saving the planet and the human society: renewable energy, circular economy, sobriety. *Substantia*, **3**, 9–15.

11 Jacobson, M. Z. (2023) *No Miracles Needed: How Today's Technology Can Save Our Climate and Clean Our Air*, Cambridge University Press, Cambridge.

12 Krausmann, F., Erb, K.-H., Gingrich, S., Haberl, H., Bondeau, A., Gaube, V., Lauk, C., Plutzar, C., Searchinger, T. D. (2013) Global human appropriation of net primary production doubled in the 20th century. *Proc. Natl. Acad. Sci.*, **110**, 10324–10329.

13 Balzani, V., Credi, A., Venturi, M. (2008) The role of science in our time in *Molecular Devices and Machines: Concepts and Perspectives for the Nanoworld*, Wiley-VCH, Weinheim.

Acknowledgments

In 1675, Isaac Newton in a letter to Hooke wrote: *If I have seen further, it is by standing on the shoulders of Giants*. This aphorism can be applied to any scientific paper and especially to any scientific book. Therefore, first of all we thank the thousands of authors whose papers have allowed us to gain a deeper understanding of the topics we have tried to illustrate and discuss in this book. We also thank a number of colleagues encountered at international meetings and in other occasions for enlightening discussions that have contributed to better focus the basic role played by photochemistry and photophysics in modern science and technology.

We are profoundly grateful to all the members of the photochemistry research group of the *Giacomo Ciamician* Department of Chemistry of the University of Bologna for several years of friendly research activity. In particular, we thank Alberto Credi, Giacomo Bergamini, and Serena Silvi for many helpful discussions. We also thank Nicola Armaroli and other colleagues of the Istituto ISOF/CNR of Bologna, Mirco Natali, Stefano Caramori and the late Franco Scandola (University of Ferrara), Sebastiano Campagna (University of Messina), Maurizio Fagnoni (University of Pavia), Nick Serpone (Concordia University, Montreal), Felix Castellano (North Carolina State University), Fred Brouwer and René Williams (University of Amsterdam), Gerald Meyer (University of North Carolina), and A. Prasanna de Silva (University of Belfast) who suggested improvements at various levels. Last but not least, we are grateful to the students who, over the years, have attended the photochemistry and photophysical courses in our university. They have greatly contributed to clarify our ideas and improve our teaching with their clever questions and punctual observations.

Bologna, January 2024 *Vincenzo Balzani, Paola Ceroni, Alberto Juris*

List of Abbreviations

acac	acetylacetonate
AFM	atomic force microscopy
AIE	aggregation-induced emission
AIQ	aggregation-induced quenching
AO	atomic orbital
AQY	apparent quantum yield
biq	2,2′-biquinoline
BO	Born–Oppenheimer
BODIPY	boron-dipyrromethenes
bpi	1,3-bis(2′-pyridylimino)-isoindoline
bpy	2,2′-bipyridine
bpym	2,2′-bipyrimidine
bpz	2,2′-bipyrazine
btz	3,3′-dimethyl-1,1′-bis(*p*-tolyl)-4,4′-bis(1,2,3-triazol-5-ylidene)
CAAC	cyclic alkyl(amino)carbene
CB	conduction band
CCD	charge-coupled device
CD	circular dichroism
CFC	chlorofluorocarbon
CISS	chirality-induced spin selectivity
ConPeT	consecutive photoinduced electron transfer
CPL	circularly polarized luminescence
CT	charge transfer
CTTS	charge-transfer-to-solvent
ddpd	*N*,*N*′-dimethyl-*N*,*N*′-dipyridine-2-ylpyridine-2,6-diamine
DFT	density functional theory
DHP	dihydrophenanthrene
DLS	dynamic light scattering
4,4′-dm-bpy	4,4′-dimethyl-2,2′-bipyridine
4,4′-dph-bpy	4,4′-diphenyl-2,2′-bipyridine
DMF	*N*,*N*-dimethylformamide
dbp	2,9-di-*n*-butyl-1,10-phenanthroline
dmp	2,9-dimethyl-1,10-phenanthroline

dpc	3,6-di-*tert*-butyl-1,8-di(pyridine-2-yl)-carbazolato
dpp	2,9-diphenyl-1,10-phenanthroline
DSPEC	dye-sensitized photoelectrosynthesis cell
DSSCs	dye-sensitized solar cells
EC	electrolyzer cell
ECL	electrochemiluminescence
en	ethylenediamine
FCS	fluorescence correlation spectroscopy
FRET	Förster-resonance energy transfer or fluorescence resonance energy transfer
GFP	green fluorescent protein
gly	glycine
HAT	hydrogen atom transfer
HCFC	hydrochlorofluorocarbon
HOMO	higher occupied molecular orbital
i-biq	3,3′-biisoquinoline
ic	internal conversion
ICT	interligand charge transfer
IPCE	incident photon-to-current efficiency
isc	intersystem crossing
ITO	indium tin oxide
LAS	light absorption sensitizer
LC	ligand-centered
LCAOs	linear combinations of atomic orbitals
LD	linear dichroism
LEC	light-emitting electrochemical cell
LED	light-emitting diode
LES	light emission sensitizer
LMCT	ligand-to-metal charge transfer
LMT	luminescent molecular thermometer
LUMO	lowest unoccupied molecular orbital
MC	metal-centered
MCP	microchannel plate
MLCT	metal-to-ligand charge transfer
MO	molecular orbital
NHE	normal hydrogen electrode
NIR	near-infrared
NLC	nonlinear crystal
NMI	naphthalimide
OEC	oxygen-evolving complex
OEP	octaethylporphyrin
OLED	organic light-emitting diode
OPA	optical parametric amplifier
OSCs	organic solar cells
PACT	photoactivated chemotherapy