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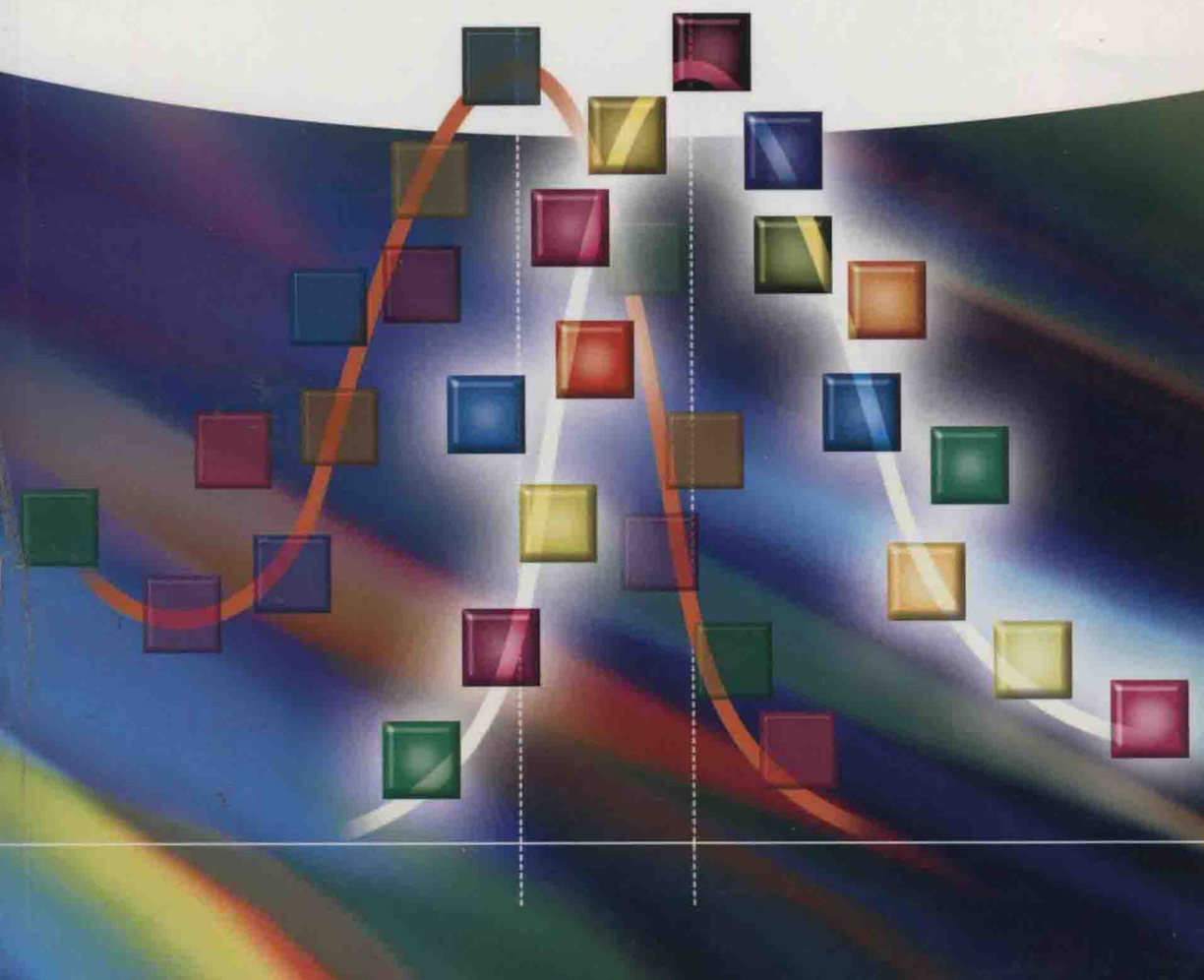
Photochemistry and Photophysics

Concepts, Research, Applications



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To Carla, Carlo, and Teresa

List of Boxes

Preface

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, material science, ecology, biology, and medicine. In our daily 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 a variety of 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 current scientific literature shows that the frontiers of photochemistry and photophysics continue 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.

The number of researchers working in the area of light–matter interaction is increasing, but several of them did (and still do) not receive 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 such as energy conversion, information technology, nanotechnology, and medicine.

In the past 5 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 devices, 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 states 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.

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 entering photochemistry and photophysics research even if they did not have a chance, during their university training, to get the fundamental bases of this field. Scientists already active in photochemical and photophysical research may 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-mentioned concepts 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 photoinduced electron transfer. Chapter 7 deals with molecular organic photochemistry, illustrating the main types of reactions of the various families of organic compounds. Chapter 8

is dedicated to the photochemistry and photophysics of metal complexes, with particular emphasis on the outstanding luminescence properties of some classes of these compounds. Chapter 9 describes the relationships between photochemical, photophysical, and electrochemical properties of molecules and shows how these properties can be exploited for the interconversion between light and chemical energy. Chapter 10 deals with 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. A variety of molecular devices (e.g., wires, switches, extension cables, 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 illustrated. Chapter 11 describes the photochemical and photophysical processes taking place in the natural photosynthetic process and the approaches developed toward artificial photosynthesis, with particular focus on the photosensitized water splitting process. Chapter 12 offers a detailed presentation of equipment, techniques, procedures, and reference data concerning photochemical and photophysical experiments, including warnings to avoid mistakes and misinterpretations.

Chapters 13–16 deal with topics of great current interest. Chapter 13 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, photocatalysis for environmental protection, fluorescence for labeling biomolecules, and a brief description of bioluminescence processes. Chapter 14 deals with applications of photochemistry and photophysics, covering a variety of topics: photochromic compounds, luminescent sensors (including, e.g., 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, photolithography, and stereolithography), and the photochemical syntheses of industrial products. Chapter 15 illustrates the use of light as an ideal reagent for green chemical synthesis; also described is the extensive use of homogeneous and heterogeneous photocatalysis for taking advantage of sunlight in laboratory processes as well as practical applications such as pollution remediation.

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 10 selected topics taken from the 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 some particular 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. Several papers reported in the recent literature (up to mid-2013) have been cited.

Before closing, we would like to express our feeling concerning science, society, and Earth, the spaceship on which we live. 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]. Until now, mankind has taken from spaceship Earth enormous amounts of resources [7]. We need to reverse this trend [8]. We 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 and the fundamental components of our atmosphere (nitrogen, oxygen, and carbon dioxide), by means of sunshine, we need to "fabricate" fuels, electricity, pure water, polymers, food, and other things we need [9]. Photochemistry and photophysics can help. Maybe future generations will pay back the Earth with a capital created by human intelligence. We should not forget, however, that our society is affected by a thread more dangerous than ecological unsustainability, namely, social unsustainability, which results from the continuously increasing disparities among people living on different nations as well as within each nation. Indeed, science can greatly benefit mankind, 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 planet Earth [10]. 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.

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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 on 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 daily discussions over several years of friendly research activity. We warmly thank Professor Nick Serpone, Concordia University, Montreal, for careful reading all the manuscript; he has corrected errors, improved language, and made a number of clever suggestions that have improved precision and clarity. We also thank our colleagues Luca Moggi, Alberto Credi, Giacomo Bergamini, Serena Silvi, Giorgio Orlandi, Fabrizia Negri, and the PhD student Massimo Sgarzi (University of Bologna), Nicola Armaroli, Lucia Flamigni, Ilse Manet, Sandra Monti (ISOF Research Institute, CNR, Bologna), Maria Teresa Indelli and Franco Scandola (University of Ferrara), Angelo Albini and Maurizio Fagnoni (University of Pavia), Sebastiano Campagna (University of Messina), and A. Prasanna de Silva (University of Belfast) who have read some chapters of the manuscript, corrected errors, and suggested improvements at various levels.

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Bologna, September 2013

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