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**Volume Editors** V. Balzani · S. Campagna

# Photochemistry and Photophysics of Coordination Compounds I

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# Photochemistry and Photophysics of Coordination Compounds I

Volume Editors: Vincenzo Balzani · Sebastiano Campagna

With contributions by

G. Accorsi · N. Armaroli · V. Balzani · G. Bergamini · S. Campagna  
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## Preface

Photochemistry (a term that broadly speaking includes photophysics) is a branch of modern science that deals with the interaction of light with matter and lies at the crossroads of chemistry, physics, and biology. However, before being a branch of modern science, photochemistry was (and still is today), an extremely important natural phenomenon. When God said: "Let there be light", photochemistry began to operate, helping God to create the world as we now know it. It is likely that photochemistry was the spark for the origin of life on Earth and played a fundamental role in the evolution of life. Through the photosynthetic process that takes place in green plants, photochemistry is responsible for the maintenance of all living organisms. In the geological past photochemistry caused the accumulation of the deposits of coal, oil, and natural gas that we now use as fuels. Photochemistry is involved in the control of ozone in the stratosphere and in a great number of environmental processes that occur in the atmosphere, in the sea, and on the soil. Photochemistry is the essence of the process of vision and causes a variety of behavioral responses in living organisms.

Photochemistry as a science is quite young; we only need to go back less than one century to find its early pioneer [1]. The concept of coordination compounds is also relatively young; it was established in 1892, when Alfred Werner conceived his theory of metal complexes [2]. Since then, the terms coordination compound and metal complex have been used as synonyms, even if in the last 30 years, coordination chemistry has extended its scope to the binding of all kinds of substrates [3, 4].

The photosensitivity of metal complexes has been recognized for a long time, but the photochemistry and photophysics of coordination compounds as a science only emerged in the second half of the last century. The first attempt to systematize the photochemical reactions of coordination compounds was carried out in an exhaustive monograph published in 1970 [5], followed by an authoritative multi-authored volume in 1975 [6]. These two books gained the attention of the scientific community and certainly helped several inorganic and physical chemists to enter the field and to enrich and diversify their research activities. Interestingly, 1974 marked the beginning of the series of International Symposia on the Photochemistry and Photophysics of Coordi-

nation Compounds. The venue of the 17th symposium of this series is Dublin and will be held in June 2007.

Up until about 1975, most activity was focused on intramolecular photochemical reactions. Subsequently, due partly also to the more diffuse availability of flash techniques, the interest of several groups moved to investigations of luminescence and bimolecular energy and electron transfer processes. In the last decade of the past century, with the development of supramolecular chemistry, it was clear that photochemistry would play a very important role in the achievement of valuable functions, such as charge separation, energy migration and conformational changes [7], related to applications spanning from solar energy conversion to signal processing and molecular machines [8, 9]. In the last few years, an increasing number of scientists have become involved in these fields. Because of their unique ground and excited state properties, metal complexes have become invaluable components of molecular devices and machines exploiting light (often sunlight) to perform useful functions [8, 9, 10]. The photochemistry of coordination compounds can also contribute to solving the energy crisis by converting sunlight into electricity or fuel [11]. In the meantime, the basic knowledge of the excited state properties of coordination compounds of several metal ions has increased considerably. However, this has resulted in an unavoidable loss of general knowledge and an increase in specialization. Currently, all scientists working in the field of the photochemistry and photophysics of coordination compounds have their own preferred metal. There is, therefore, an urgent need to spread the most recent developments in the field among the photochemical community. To write an exhaustive monograph like [5], however, would now be an impossible enterprise. For this reason, we decided to ask experts to write separate chapters, each one dealing with a specific metal whose complexes are currently at the frontier of research. It has been a delight as well as a privilege to work with an outstanding group of contributing authors and we thank them for all their efforts. We would also like to thank all the members of our research groups for their support.

Bologna and Messina, March 2007

Vincenzo Balzani  
Sebastiano Campagna

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# Photochemistry and Photophysics of Coordination Compounds: Overview and General Concepts

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And God said: “Let there be light”;  
 And there was light.  
 And God saw that the light was good.  
 (*Genesis, 1, 3–4*)

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**Abstract** Investigations in the field of the photochemistry and photophysics of coordination compounds have proceeded along several steps of increasing complexity in the last 50 years. Early studies on ligand photosubstitution and photoredox decomposition reactions of metal complexes of simple inorganic ligands (e.g.,  $\text{NH}_3$ ,  $\text{CN}^-$ ) were followed by accurate investigations on the photophysical behavior (luminescence quantum yields and lifetimes) and use of metal complexes in bimolecular processes (energy and electron transfer). The most significant differences between Jablonski diagrams for organic molecules and coordination compounds are illustrated. A large number of complexes stable toward photodecomposition, but capable of undergoing excited-state redox processes, have been used for interconverting light and chemical energy. The rate constants of a great number of photoinduced energy- and electron-transfer processes involving coordination compounds have been measured in order to prove the validity and/or extend the scope of modern kinetic theories. More recently, the combination of supramolecular chemistry and photochemistry has led to the design and construction of supramolecular systems capable of performing light-induced functions. In this field, luminescent and/or photoredox reactive metal complexes are presently used as essential components for a bottom-up approach to the construction of molecular devices and machines. A few examples of molecular devices for processing light signals and of molecular machines powered by light energy, based on coordination compounds, are briefly illustrated.

**Keywords** Coordination compounds · Electron transfer · Energy transfer · Excited-state properties · Photochemistry · Supramolecular photochemistry

## 1

### Early History

The photosensitivity of metal complexes has been known for a long time. The first paper exhibiting some scientific character was that of Scheele (1772) on the effect of light on  $\text{AgCl}$ , and photography was becoming established in several countries in the 1830s [1]. The light sensitivity of other metal complexes (particularly  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ ) was also observed very early [2]. At the beginning of the last century the importance of photochemistry became more widely recognized, mainly due to the work and the ideas of Giacomo Ciamician [3], Professor of Chemistry at the University of Bologna. In the same period (1912–1913), modern physics introduced the concept that light absorption corresponds to the capture of a photon by a molecule. This concept, and the distinction (sometimes difficult) between primary and secondary photoprocesses, led to the definition of quantum yield. In the following years, investigations on  $\text{Fe}^{3+}$  and  $\text{UO}_2^{2+}$  complexes were performed in looking for useful chemical actinometers (see, e.g., [4]). Several quantitative works also appeared on the photochemical behavior of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{Co(III)}$ –amine complexes in aqueous solution [2]. The lack of a theory on the absorption spectra and on the nature of the excited states, however, prevented any mechanistic interpretation of the observed photoreactions as well as of the few scattered reports on luminescent complexes.

After the Second World War, the interpretation of the absorption spectra started thanks to the development of the ligand field theory [5, 6] and the first attempts to rationalize the charge-transfer bands [7, 8]. Following these developments, the photochemistry of coordination compounds could take its first steps as a modern science and in a time span of 2 years four important laboratories published their first photochemical paper [9–12]. Much of the attention was focused on Cr(III) complexes, whose luminescence was also investigated in some detail [13]. Later, Co(III) complexes attracted a great deal of attention since their photochemical behavior was found to change drastically with excitation wavelength [14, 15]. A few, isolated flash photolysis investigations began to appear, but this technique remained unavailable to most inorganic photochemists for several years.

Since the late 1960s, the great development of photochemical and luminescence investigations on organic compounds led to the publication of books [16–19] illustrating fundamental photochemical concepts that were also quickly exploited for coordination compounds [2]. From that period, it became common to discuss the photochemical and photophysical behavior of a species (be it an organic molecule or a charged metal complex) on the basis of electronic configurations, selection rules, and energy level diagram, as we do today.

## 2

### Molecular Photochemistry

Molecules are multielectron systems. Approximate electronic wavefunctions of a molecule can be written as products of one-electron wavefunctions, each consisting of an orbital and a spin part:

$$\Psi = \Phi S = \prod_i \varphi_i s_i. \quad (1)$$

The  $\varphi_i$ s are appropriate molecular orbitals (MOs) and  $s_i$  is one of the two possible spin eigenfunctions,  $\alpha$  or  $\beta$ . The orbital part of this multielectron wavefunction defines the *electronic configuration*.

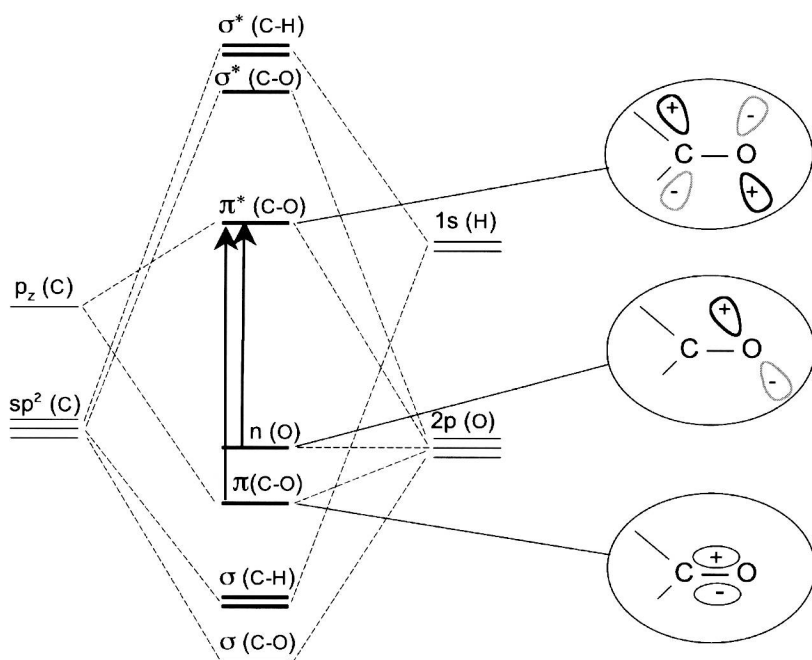
We illustrate now the procedure to construct energy level diagrams, using as examples an organic molecule and a few coordination compounds.

### 2.1

#### Organic Molecules

The MO diagram for formaldehyde is shown in Fig. 1 [20]. It consists of three low-lying  $\sigma$ -bonding orbitals, a  $\pi$ -bonding orbital of the CO group, a non-bonding orbital  $n$  of the oxygen atom (highest occupied molecular orbital, HOMO), a  $\pi$ -antibonding orbital of the CO group (lowest unoccupied molecular orbital, LUMO), and three high-energy  $\sigma$ -antibonding orbitals. The





**Fig. 1** Molecular orbital diagram for formaldehyde. The arrows indicate the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions

lowest-energy electronic configuration is (neglecting the filled low-energy orbitals)  $\pi^2 n^2$ . Excited configurations can be obtained from the ground configuration by promoting one electron from occupied to vacant MOs. At relatively low energies, one expects to find  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transitions (Fig. 1), leading to  $\pi^2 n \pi^*$  and  $\pi n^2 \pi^*$  excited configurations (Fig. 2a).

In a very crude zero-order description, the energy associated with a particular electronic configuration would be given by the sum of the energies of the occupied MOs. In order to obtain a more realistic description of the energy states of the molecule, two features should be added to the simple configuration picture: (1) spin functions must be attached to the orbital functions describing the electronic configurations, and (2) interelectronic repulsion must be taken into account. These two closely interlocked points have important consequences, since they may lead to the splitting of an electronic configuration into several states.

In the case of formaldehyde, the inclusion of spin and electronic repulsion leads to the schematic energy level diagram shown in Fig. 2b: each excited electronic configuration is split into a pair of triplet and singlet states, with the latter at higher energy because electronic repulsion is higher for spin-paired electrons. It can be noticed that the singlet–triplet splitting for the states arising from the  $\pi \pi^*$  configuration is larger than that of the states cor-