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PHOTOCHEMISTRY OF COORDINATION COMPOUNDS: A GLANCE AT PAST, PRESENT, AND FUTURE

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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)

SUMMARY

After an induction period lasted up to the early 1960s, the photochemistry of coordination compounds has exhibited an autocatalytic development for about two decades and continues to be a rapidly growing field. In the past fifteen years there has been a progressive displacement of interest from intramolecular photoreactions (e.g., ligand photosubstitution and photoredox decomposition) towards intermolecular processes (e.g., energy and electron transfer). Presently there is a growing interest towards the study of supramolecular systems, and it seems likely to expect that in the next few years there will be a strong development in investigations concerning photonic molecular devices (i.e., assemblies of molecular components capable of performing valuable light-induced functions).

INTRODUCTION

Photochemistry 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. But before being a branch of modern science, photochemistry was, and still is, an extremely important natural phenomenon. Since God said: "Let there be light", photochemistry began to operate helping God to create the world as now we know it. Photochemistry was likely the key for the origin of life on the earth, played a fundamental role in life evolution, and it is responsible, through the photosynthetic process that takes place in green plants, for the maintenance of all living organisms. Photochemistry caused the accumulation in the geological past 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.

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Photochemistry as a science is quite young since, as it will be shown later, we only need to go back less than one century to find its early pioneers. In an attempt to have a look at past, present, and future of the photochemistry of coordination compounds, we have arbitrarily divided the period examined into eight ages: 1) earlier observations (before 1900); 2) realization of the potential of photochemistry (1900-1920); 3) the concept of quantum yield (1920-1950); 4) renaissance: spectroscopic-photochemical relationships (1950-1965); 5) intramolecular photochemistry (1965-1975); 6) intermolecular photochemistry (1975-1985); 7) towards a supramolecular photochemistry (1985-1989); 8) future trends.

It should be pointed out that this overview is by no means exhaustive. It is, in fact, a short glance on a broad research field. A glance which reflects, of course, the authors' interest and thus is mainly focussed on classical coordination compounds in homogeneous solution. Organometallic complexes and heterogeneous systems, in spite of their great importance, are largely ignored.

EARLIER OBSERVATIONS (BEFORE 1900)

The first paper exhibiting some scientific character is that of Scheele (1772) on the effect of light on AgCl, and photography was becoming established in several countries in the 1830's (ref. 1). The light sensitivity of other metal complexes (particularly, $Na_4[Fe(CN)_6]$), was also observed very early (ref. 2), but in papers of very limited scientific meaning. The so-called first law of photochemistry (only light absorbed by the reacting system can induce a photochemical change) was put forward by Grotthus in 1817 and then by Draper in 1841 (ref. 2).

Before the end of the last century electric lamps were already available for house lightening, but their light was too faint and too "red" to be effective for photoexcitation. Therefore, the only light source available for photochemical investigations was the sun, as shown by the very famous picture of one of the first photochemical laboratories, that was situated on the roof of the Chemical Institute at the University of Bologna (ref. 3). As a consequence, the progress of photochemistry was strictly dependent on the weather conditions. This clearly appears from a series of papers published by a French scientist, G. Lemoine, on the photochemistry of ferric oxalate (ref. 4). He complained of the bad climate of Paris

> "J'ai dû me contenter de la lumière solaire; comme sous le climat de Paris le belles journées son tres rares, ces recherches on été tres laborieuses et tres longues".

and eventually moved to the Swiss Alps to find more intense (and ultraviolet) light. The experimental sections of Lemoine's papers report detailed meteorological information, e.g.,

> "31 août 1886: ciel très pur: l'une des plus belles journées et la plus chaude de l'année. Temperature maxima l'après-midi 33°,5."

but no useful photochemical result.

REALIZATION OF THE POTENTIAL OF PHOTOCHEMISTRY (1900-1920)

At the beginning of this century the importance of photochemistry both as a natural phenomenon and as a science became more widely recognized. This was mainly due to the work and the ideas of Giacomo Ciamician, professor of Chemistry at the University of Bologna from 1889 to 1922. Ciamician worked essentially on organic molecules, but his ideas were fundamental for the development of the whole photochemical research. Ciamician realized that an important difference between natural and artificial chemical synthesis was the much milder conditions of natural synthetic processes, due to the ability of plants to make use of solar light which is a form of energy much more effective and "noble" than heat. As a consequence, he decided to carry out systematic investigations to reproduce natural photochemical reactions "in vitro" (see, e.g., ref. 5). He also realized the wide scope of photochemistry and the great importance of a correct exploitation of solar energy. Most of his brilliant ideas were presented in a famous lecture entitled "The Photochemistry of the Future" (ref. 6), delivered in New York at the VIII International Congress of Applied Chemistry (1912). In that lecture, Ciamician discussed in detail the problem of the utilization of solar energy and pictured, at the time of the apex of coal technology, a future society based on the sun as direct energy source:

> "So far, human civilization has made use almost exclusively of <u>fossil</u> solar energy. Would it not be advantageous to make better use of radiant energy?"

He also realized that a civilization based on solar energy could reequilibrate the economic gap, already existing at that time, between northern and southern regions of the world:

> "Solar energy is not evenly distributed over the surface of the earth..... The tropical countries would be conquered by civilization which would in this manner return to its birth-place. Even now the strongest nations rival each other in the conquest of the lands of the sun,

> as though unconsciously foreseeing the future.... On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."

The final, very famous sentence of that paper presents a concept quite meaningful even today:

> "If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to the progress and to the human happiness."

Ciamician was indeed a broad-minded photochemist. He predicted the use of photosensitizers (that he called catalyzers),

> "By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes."

the construction of photoelectrochemical batteries,

> "It is conceivable that we might make photoelectrical batteries or batteries based on photochemical processes...."

the important role of photoinduced electron transfer processes,

> "The action of light is especially favorable to processes of oxidation and reduction...."

the use of photochemistry in industrial processes,

> "The reactions caused by light are so many that it should not be difficult to find some which are of practical value. Many syntheses might become the object of industrial photochemical processes."

and also the use of phototropic (photochromic) substances for fashion purposes:

> "Phototropic substances might well attract the attention of fashion.... The dress of a lady, so prepared, would change its color according to the intensity of light. Passing from darkness to light the colors would brighten up, thus conforming automatically to the environment: the last word of fashion for the future."

"The Photochemistry of the Future" had an extremely large echo among chemists from all over the world and marked the beginning of systematic photochemical studies, especially in the field of organic chemistry.

In the same period, most eminent scientists like Planck and Einstein elaborated the quantum model of light which, a few years later, allowed photochemistry to emerge from its empirical stage to answer the question "how has it occurred?" that Ciamician could not tackle.

THE CONCEPT OF QUANTUM YIELD (1920-1950)

The first fundamental concept introduced into photochemistry by modern physics was that light absorption corresponds to the "capture" of a photon by a molecule. With this concept in mind, Stark (1908-12) and Einstein (1912-13) proposed that there should be a 1:1 equivalence between the number of molecules decomposed and the number of quanta absorbed (second law of photochemistry). On this hypothesis, the quantum yield of a photochemical reaction obeying the "one molecule per photon" law should be unity. With the aim of testing this hypothesis, several scientists undertook the experimental determination of the quantum yields of many photoinduced reactions: the results spread from 10^{-2} to 10^{+6}. Then Bodestein realized that the absorption of a photon could be followed by secondary chemical reactions and proposed that the photo-processes should be termed "primary", while any subsequent chemical reaction initiated by the primary photo-products should be termed "secondary" (ref. 7). A few years later, the concept of electronically excited state began to be used by photochemists. After these discoveries, the attention of most scientists was mainly attracted by the measurement and the understanding of quantum yields, especially upon photofragmentation of small molecules. Mercury lamps, equipped with monochromators or light filters, became the usual source for light excitation.

In this period the main studies in the field of the photochemistry of coordination compounds concerned Fe^{3+} and UO_2^{2+} complexes because of their interest as chemical actinometers (see, e.g., ref. 8). Several quantitative works also appeared on the photochemical behavior of $Fe(CN)_6^{4-}$ and Co(III)-amine complexes (ref. 2). The lack of a theory on the absorption spectra and on the nature of the excited states prevented any mechanistic interpretation of the results obtained. Some isolated study on the luminescence of metal complexes began to appear, but this field developed only several years later.

RENAISSANCE: SPECTROSCOPIC-PHOTOCHEMICAL RELATIONSHIPS (1950-1965).

A true growth of the research on the photochemistry of coordination compounds could not take place until some rationalization was achieved concerning thermal reactivity and spectroscopy. After the second world war, an intense activity began in both such related fields and, by the late 1950s, a reasonably large number of substitution, isomerization, and redox reactions of "robust" coordination compounds had been studied and some general principles governing such processes became available (refs. 9-11). At the same time, the interpretation of the electronic absorption spectra started, thanks to the development of the Ligand Field theory (refs. 12-13) and the first attempts to rationalize the charge transfer bands (refs. 13-14). Following these developments, the photochemistry of coordination compounds could move its first steps as a modern science, and in a time span of two years four important laboratories published their first photochemical paper (refs. 15-18). Much of the attention was initially focussed on Cr(III) complexes, whose luminescence was also investigated in some detail (ref. 19). Later, Co(III) complexes attracted a great deal of interest because their photochemical behavior was found to change drastically with excitation wavelength (refs. 20-21). In the best photochemical papers of that period, the aims of the research were well defined (elucidation of the photochemical mechanisms and of the role played by the excited states), a variety of analytical techniques were used, both the nature and the quantum yield of the photoreaction(s) were investigated on excitation with light corresponding to the various absorption bands, and the results were discussed on the basis of kinetic and spectroscopic theories. Some isolated flash photolysis investigations also appeared (see, e.g., refs. 22 and 23), but this technique remained not available to most inorganic photochemists for several years. An intense activity in the field of carbonyl complexes began, mainly for preparative purposes (see, e.g., ref. 24).

INTRAMOLECULAR PHOTOCHEMISTRY (1965-1975)

An autocatalytic growth of research on the photochemistry and photophysics of coordination compounds took place during that decade. The main reasons for such a growth were: i) the full realization that electronically excited states are new chemical species since they exhibit different chemical properties compared to the corresponding ground state molecules (refs. 25,26); ii) the success of the "localized" molecular orbital approach to describe the electronic structure of the ground and excited states of coordination compounds (refs. 2,27); iii) the increasing consciousness that photochemistry and luminescence give complementary pieces of information concerning the excited state behavior (ref. 28); iv) the great development of photochemical and luminescence studies in the field of organic chemistry, with the consequent publication of several books which illustrated fundamental photochemical concepts (see, e.g., refs. 29-32).

An exhaustive monograph on the "Photochemistry of Coordination Compounds" (ref. 2) was published in 1970 and presumably helped several inorganic and physical chemists to enter the field and to enrich and diversify the research activities. An authoritative multi-author book on "Inorganic Photochemistry" also appeared a few years later (ref. 33). Looking at such two books, the following picture emerges of the 1965-1975 decade:

1. Most of the interest was focussed on intramolecular reactions, i.e. ligand photosubstitution reactions, photoredox decomposition reactions, and photoisomerization reactions.

2. The use of quenching and sensitization techniques (almost exclusively via an energy transfer mechanism) became extended, aiming at the identification of the excited state responsible for the observed photoreaction.

3. The complexes most extensively studied were those of cobalt (48 pages in the above quoted monograph), chromium (38 pages), and iron (30 pages), whereas ruthenium complexes were scarcely investigated (together with osmium complexes, 1 page only).

4. Available information concerning luminescence was rapidly increasing, particularly for Cr(III) complexes.

5. The availability of a large number of experimental results concerning homogeneous families of complexes encouraged the first attempts to systematize and predict the photochemical behavior (e.g., Adamson's rules) and to identify the excited state responsible for the observed photoreaction (e.g. doublet vs quartet excited state in Cr(III) complexes).

This picture, however, was destined to change profoundly in a few years, following the first observation of electron transfer quenching of the luminescent excited state of $Ru(bpy)_3^{2+}$ by Gafney and Adamson (ref. 34), the growing interest towards intermolecular processes (ref. 35), and the beginning of research on photochemical conversion of solar energy (ref. 36).

We would also like to note that 1974 marks the beginning of the series of the International Symposia on the Photochemistry and Photophysics of Coordination Compounds.

INTERMOLECULAR PHOTOCHEMISTRY (1975-1985)

The previously mentioned report on the electron transfer quenching of the luminescent excited state of $Ru(bpy)_3^{2+}$ by pentaammine Co(III) complexes (ref. 34) was followed in a few years by a series of papers from different laboratories which gave definitive evidence of the reducing and oxidizing properties of $^*Ru(bpy)_3{}^{2+}$. In the meantime, the extensive work carried out by several research groups on the luminescence of coordination compounds (refs. 37-39) showed that the lowest excited state of a number of Cr(III), Ru(II), and Os(II) complexes exhibits a sufficiently long excited state lifetime in fluid solution (micro- to nano-second time scale) to be able to intervene as a reactant in bimolecular processes. Energy and electron transfer processes involving electronically excited states had already been the object of numerous studies in the field of organic chemistry (ref. 40), but the use of coordination compounds led to an outstanding development in this field. In particular, it was soon realized that Ru(II) and Os(II) polypyridine complexes, because of their reversible redox behavior, are excellent reactants and/or mediators in light induced (refs. 41-45) and light generating (refs. 45-46) electron transfer processes.

It should also be noted that the energy crisis of the early 1970s led several photochemists to become involved in the problem of solar energy conversion and storage. Particular interest arose around the photosensitized water splitting (refs. 47-51) and it was soon realized (ref. 52) that $Ru(bpy)_3{}^{2+}$ and related complexes, because of their excited state redox properties, might function as photocatalysts for such a process.

The profound change occurred in those years appears clearly on comparing the contents of the previously mentioned multi-author book of 1975 (ref. 33) with the special issue on inorganic photochemistry published by the Journal of Chemical Education in 1983 (ref. 53). While in the 1975 book much of the chapters concern intramolecular processes, in the 1983 J. Chem. Educ. issue many articles are (directly or indirectly) dealing with energy and electron transfer processes and an entire article is dedicated to $Ru(bpy)_3{}^{2+}$, which was certainly the most studied compound of that decade.

A few figures are sufficient to understand the revolution occurred in that period: (i) a review article (updated to middle 1986) on the photochemistry and photophysics of Ru(II)-polypyridine complexes (ref. 54) is about 200 pages long (compare with the single page dedicated to ruthenium and osmium in ref. 2), covers more than 300 references, and lists the properties of more than 300 complexes; (ii) a compilation (updated to 1986) of rate constants for the quenching of excited states of metal complexes in fluid solution (ref. 55) is 325 pages long, covers about 500 papers, reports data for excited states of 261 complexes of 26 metals quenched by more than 400 inorganic and 600 organic quenchers.

It should be pointed out that in that decade an extensive use began to be made of pulsed techniques (for a history of photochemistry from the point of view of flash techniques, see ref. 56). Such techniques were needed to determine the rate constants of bimolecular processes as well as to identify the nature of the transient products generated by photoinduced electron transfer processes.

The high exergonicity of excited state electron transfer reactions (or of their back reactions) offered a unique opportunity to investigate some fundamental aspects of electron transfer theories (refs. 57,58), with particular attention to the problem of the Marcus inverted region (see, e.g., ref. 59). The growing knowledge in the fields of luminescence and electron transfer also led to a noticeable development of investigations on chemi- and electrochemi-luminescence (see, e.g., refs. 60,61).

Again related to the problem of water splitting, and more generally of solar energy conversion and storage, extensive investigations were carried out on photochemical processes involving semiconductors (refs. 62-63) and micro-heterogeneous systems (ref. 64). Other rapidly growing fields were photochemistry (refs. 65,66) and luminescence (ref. 67) of organometallic complexes, and theoretical treatments of excited state reactivity (refs. 68,69).

TOWARDS A SUPRAMOLECULAR PHOTOCHEMISTRY (1985-1989)

Some traditional topics of inorganic photochemistry, such as the ligand substitution reactions of Cr(III) complexes (see, e.g., refs. 70-72), have continued to attract the attention of several research groups because investigations on suitable designed complexes have always revealed new interesting facets. However, there has been an increasing interest towards processes taking place between excited states and appropriate reaction partners. Numerous and very accurate investigations have been performed on suitably chosen families of complexes with the aim to obtain the parameters which govern the electron transfer processes (ref. 73). Detailed studies on the luminescent properties (particularly, on their temperature dependence) of several complexes have also been reported (see, e.g., refs. 74-76). The extensive use of complexes as luminescent species, electron transfer photosensitizers, and chemiluminescence inducers has evidenced the need for compounds that, while exhibiting the desired spectroscopic properties, do not undergo dissociation when they are photoexcited, oxidized, and/or reduced. Much effort has therefore been devoted to build up luminescent and/or redox active cage-type complexes (refs. 76-79). While attempts aimed at the splitting of water by solar light have continued with limited success (refs. 73,80), much attention has been devoted to the photoreduction of carbon dioxide (ref. 81).

The most noticeable trend in current years is a progressive displacement of interest from <u>intra</u>- and <u>inter</u>-molecular photochemical processes towards processes occurring in <u>supra</u>molecular systems (i.e., assemblies of two or more molecular components) (refs. 82,83). This has been made possible by the extraordinary progress of chemical synthesis and the extensive knowledge reached in the field of molecular photochemistry.

A prominent research line in the field of supramolecular photochemistry is that concerning luminescent and/or redox active polymetallic complexes, where the various molecular components are assembled to obtain vectorial electron or energy migration. The most common "building blocks" to design such polynuclear systems are polypyridine complexes of Ru^{2+}, Os^{2+}, and Cr^{3+}, while the bridging ligands may range from simple anions like CN^- to multichelating aromatic-type molecules (for details, see refs. 83 and 84, and references therein).

The field of supramolecular photochemistry includes another important research line. In several problems of practical interest, there is a need to modify the excited state behavior of a molecule. This can be done by perturbing the molecule via appropriate nuclear and/or electronic mechanisms (ref. 85). In most cases, such a perturbation can be performed by assembling the molecule with a perturber in appropriate supramolecular structures via ion-pairing (refs. 85-87), second-sphere coordination (refs. 85,88), and host-guest interaction (refs. 78,89,90).

Several other branches of inorganic photochemistry and photophysics continue to attract increasing interest. These include photochemistry of clusters (see, e.g., ref. 91), photochemistry on semiconductors (refs. 80,92), detailed luminescence problems (see, e.g., refs. 93-95), photochemistry in liquid xenon (see, e.g., ref. 96), pressure effects on photochemical reactions (ref. 97), photochemistry in liquid membranes (ref. 98), picosecond time resolution (ref. 99), and application of enzymes in artificial photosynthetic systems (see, e.g., ref. 100). Particularly worth mentioning are the targeting and the selective photocleavage of DNA by intercalation of luminescent and/or photoreactive complexes (see, e.g., ref. 101).

FUTURE TRENDS

The preceding sections have shown the extraordinary quantitative development as well as the profound qualitative changes occurred from time to time in the field of the photochemistry and photophysics of coordination compounds. In such a rapidly growing field, future trends are difficult to predict. In 1970 no one would have predicted the dramatic change occurred a few years later following the discovery of excited state electron transfer reactions.

Investigations on the excited state properties of simple coordination compounds will certainly continue, to arrive at a better understanding of the factors that control the photochemical behavior. All the research lines mentioned in the previous section (particularly, the use of luminescent and/or photoreactive complexes as labels and probes in biological problems) will also develop. We believe, however, that most of the activity in the next few years will be concentrated on supramolecular species with the dual aim of making progress towards the elucidation of photobiological processes and the construction of artificial photochemical systems capable of performing useful functions. Along these ways, we expect that much effort will be concentrated on the design, synthesis, and characterization of photonic molecular devices (PMDs), i.e. assemblies of molecular components capable of performing valuable light-induced functions such as charge separation, energy migration, and conformational changes (refs. 102,103). Some examples of PMDs have already begun to appear (refs. 82,83,102-105). Ranges of possible applications span from solar energy conversion to signal processing, from spectral sensitization to photocontrolled membrane permeability, etc.

PMDs are present, of course, in nature where they perform functions essential to life as photosynthesis and vision. Examination of natural PMDs shows that they are extremely complex systems where the various molecular components are suitably organized in the dimensions of space, energy, and time. Artificial PMDs do not need to (and cannot) be as complex as the natural ones; their molecular components, however, must be suitably chosen and connected so as to yield the space-energy-time organization which allows a correct elaboration of the photon input (refs. 102,103).

The development of PMDs is strictly related the problem of their utilization. In most cases, utilization of PMDs will require scaling-up by several orders of magnitude to pass from molecular (or supramolecular) dimensions to the dimensions of microdevices of the macroscopic world. The solution to this problem, which is also encountered in the small-upward approach of microelectronics (ref. 106), requires the assembly of a great number of supramolecular species in ordered arrays that can be handled and interfaced with electrodes or other terminals (e.g., heterogeneous catalysts) capable of collecting, and making use of, the energy and/or signals generated by light. This is indeed a very difficult task that will require a largely interdisciplinary effort. Current approaches to the macro-to-molecular connections include (i) the use of the Langmuir-Blodgett technique to produce molecular layers of controlled composition and thickness (ref. 107), (ii) self-organization of special types of chain molecules around metal ions (ref. 78), (iii) electrode derivativization (ref. 104), and (iv) fabrication of microelectrochemical devices (ref. 108). For a successful utilization of PMDs all these techniques need to be greatly developed and hopefully new ones have to be discovered.

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