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# PERSPECTIVES IN PHOTOCHEMISTRY

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## Abstract

Some brief remarks, at the conclusion of the symposium, outline a few areas of current interest and possible perspectives in photochemistry research with particular regard to photocatalysis, organometallic and coordination photochemistry, polymers processes, bioinorganic photochemistry, supramolecular photochemistry, microheterogeneous or organized systems, atmospheric photochemistry.

## 1. INTRODUCTION

The meeting, which has seen gathered in Ferrara some among the leading scientists in photochemistry, has stimulated several suggestions about the future directions in photochemical research. Basically, the question is: where is photochemistry going? What are the perspectives?

The answer is not simple. Personally, I can only express a parochial view of an inorganic chemist about a few topics which I consider important branches of the research. This is by no means meant to be a comprehensive review but rather some reflections on the state of the art of photochemistry and its possible developments.

First of all some general remarks:

-advances in photophysics - properties of excited states, radiative and non-radiative decay channels, intramolecular and intermolecular processes after excitation, time-resolved spectra, transients, theoretical approaches, etc. - are obviously of determining importance to photochemistry;

-as a matter of fact development of new experimental techniques and, in particular, in situ instrumentation controls the scientific advancement in laboratories suitably financed;

-several biophysical processes take place over the ps to ns time scale: this makes photophysics a powerful tool for understanding processes and mechanisms in biochemistry;

-in the field of photophysics and photochemistry of coordination compounds, excited states spectra, luminescence processes, ultrafast electron transfer, are active areas of research; photochemistry has reached by now the stage of maturity and we possess a relatively high level of knowledge on the photochemical behavior

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of coordination compounds, however, studies on novel families of molecules are helpful;

-much work on photochemistry of coordination compounds appear today in other areas: photocatalysis, photogalvanic cells (coordination compounds as sensitizers on semiconductors), supramolecular photochemistry, photochemical recording of information, etc.;

-in the field of organic compounds we have a knowledge of the various photochemical reactions; some perspectives can be envisaged: research on the excited states partition between the different reaction pathways will continue; incorporation of photochemical steps into multistep syntheses of complex organic molecules such as those of natural compounds; photoinduced generation of reactive species, such as radicals and radical ions in opening new synthetic routes under mild and selective conditions; oxygen photofunctionalization as a synthetic tool; syntheses of industrial relevance aiming to obtain pollution-free processes;

-much fundamental organic research is correlated with various application fields such as polymers.

## 2. PHOTOCATALYSIS.

Much research work continues to be done in the field of photocatalysis.

In the photocatalysis by semiconductors the research focused on the characterization of phenomena and intimate mechanisms at the semiconductor/electrolyte interface by a variety of methods, advanced techniques in surface investigations, new synthetic routes, degradation and abatement processes of environmental interest, design and modelling of suitable photoreactors.

Other lines of perspective can be developed on the new photocatalysts: composite catalysts, inorganic membranes, surface confined biomimetic photocatalysts. More generally many microheterogeneous systems are potentially new materials of high catalytic ability which can be explored.

Moreover, organometallic compound - containing polymers, as photocatalysts, are attractive: binding homogeneous catalysts onto polymers generates heterogeneous catalysts of high interest.

Organic, inorganic and organometallic chemistry offer stimulating research problems in the field of homogeneous catalysis. Examples are photoactivation of small molecules, photofunctionalization of C-H bonds of hydrocarbons, catalysis by metallo-fragments [1,2].

## 3. ORGANOMETALLIC PHOTOCHEMISTRY

Organometallic photochemistry is a powerful source of inorganic chemistry, where several research perspectives can be visualized (preparative photochemistry, photoassisted processes, photochemical production of reactive organometallics for synthesis and catalysis).

Moreover wide varieties of structures can be created in the area of molecular materials, such as stacks and charge transfer complexes with magnetic or conducting properties, metal-containing polymers, as semiconductors, one- or two-dimensional conductors, photoassisted selective transport membranes.

Photochemistry of organometallic compounds plays an essential role in technological processes which sustain the modern microelectronic industries, that is to say in microlithographic preparation of the very large scale integrated circuits (VLSI), by photochemical vapor deposition of metals, semiconductors and insulators, particularly laser photochemical vapor deposition (LPCVD).

Organometallic compounds are the starting materials in LPCVD, but the available data are still limited. So the needs of technology open various perspectives on: absorption spectral data of organometallic compounds, both in gaseous phase and in adsorbed state on solid surfaces; photodissociation reactions of compounds with metal-carbon bonds and exact steps in reaction mechanisms; development of knowledge, by a variety of techniques, on radicals, intermediates and reactive molecular fragments; photophysics and spectroscopy of excited states; design of new suitable organometallic molecules [2 - 5].

## 4. POLYMER PHOTOCHEMISTRY.

Here, academic and industrial interest are often intimately bound. Enormous progress has been achieved on polymer photochemistry, but a valuable work still can be spend because some basic mechanisms of photochemical reactions are not completely understood.

Furthermore, many technological properties of polymeric materials such as printability, dyeability, paintability, wettability, adhesivity, biocompatibility, surface hardness, scratch resistance, gloss, etc., are not determined by bulk but by surface properties.

Polymer surface can be modified by some photochemical processes such as photografting, photocrosslinking and others, in order to obtain basic surface characteristics correlated to various surface functionalities.

Large scale applications appear still limited to UV curing of surface coatings, screen printing and reactive photoresists. However, polymer photoassisted processes are very promising for modern application, e.g. photografting onto a variety of macromolecules, included inorganic polymers and cellulosic materials, and photoproduction of new materials (composites, membranes, etc.).

The need for polymer materials has caused the design and generation of functional materials beside structural materials; molecules which exhibit photoinduced structural changes suitably linked to polymer chains, can provide light control of various physical properties and chemical functions. The optical and luminescence properties of polymers maintain a noticeable interest.

Special photochemical techniques for polymerization catalysis of pyrrole and other monomers are investigated for the development of interesting metal-containing photoconductive polymers.

Research on the natural degradation of polymers by UV radiation continues to be a subject of relevant fundamental and practical importance, with the aim of explanation of oxidative mechanisms by refined techniques, and the investigations of new polymeric materials of high resistance to the UV damage, by preparation of blends where the classical way of hindered piperidine light stabilizers is not effective.

Finally, in comparing lasers to the incoherent light sources utilized in polymer technology, the advantages of the former (intensity, spectral purity, spatial and temporal behavior) must be recognized.

In spite of the optical advantages of the lasers, they have not had a larger impact depending on factors such as complexity, technical expertise, expense (capital investment): in the next future lasers will play an increasing role if advancement of current technical level and decrease of cost will occur [6 -11].

## 5. BIOPHOTOCHEMISTRY.

Hemoproteins and their model systems remain stimulating research subjects in the field of bioinorganic chemistry.

Redox processes induced by light are of interest both in the understanding of enzymatic reaction mechanisms and photoassisted synthesis or catalysis.

In the elucidation of enzymatic reaction mechanisms research focuses on photoinduced electron transfer processes in cytochromes, and structure-activity relationships via modifications of the polypeptidic chain, with the perspective of extension of the photochemical investigation to peroxidase and catalase.

In photoassisted synthesis and catalysis, models of hemoproteins concerned with biomimetic processes of electron transfer and molecular oxygen activation are investigated with the aim to develop efficient oxidation catalysts of organic compounds.

Biomimetic systems based on Fe(III) or Mn(III)-porphyrins are able to perform selective oxidation of alkanes by mechanisms of the monoxygenase type; moreover recent results have shown that photoactivated Fe(III)-porphyrins are able to insert the two O atoms of $O_2$ into alkane molecules by a "dioxygenase-type" mechanism.

In homogeneous catalysis, metalloporphyrin complexes of high resistance to degradation and with the ability to control the selectivity of photocatalytic processes can be designed, prepared and characterized. In addition the so-called "inorganic porphyrins", such as polyoxometallates, are interesting candidates.

In heterogeneous catalysis, metalloporphyrins bonded in different ways to surfaces of different nature are very promising: novel global reactivity can be showed by these organized systems (anchored, entrapped, dispersed).

Another subject discussed in this symposium deals with mechanisms of sensitization in biological systems, due to the light absorption by exogeneous agents (drugs). The interest of photochemists resides in the variety of the mechanisms of energy or electron transfer processes via excited states, and the protective activity of inorganic complex systems.

Finally, photosynthesis and other natural systems are a very large subject of course, with several perspectives [12 -14].

Now, no system designed by photochemists can have the complexity or functionality of these natural assemblies, but approaches to similar principles are the goals of active research in:

-artificial photosynthesis and photoconversion, both mimicking nature and speculating into new directions;

-topo-photochemistry;

-supramolecular photochemistry and molecular devices.

## 6. SUPRAMOLECULAR PHOTOCHEMISTRY.

At the present time there is a rapid growth of research in this field, about the concept of supramolecular system, made of a number of discrete molecular components held together by chemical interactions: covalent bonds, electrostatic interactions, hydrogen bonds, and other intermolecular forces.

The general perspectives are in the fields: properties related to each molecular component in the assembly, properties related to intercomponent processes, combination, in a wide variety of structures, of organic and inorganic chemistry, relations with properties of solid state.

The concept of supramolecular system opens the concept of molecular device, as an assembly of molecular components designed to achieve specific functions, such as:

-photoinduced electron transfer in light energy conversion, electron collection, remote photosensitization, photoswitching of electric signals;

-photoinduced electronic energy transfer over a more or less long distances in spectral sensitization, antenna effect, remote photosensitization, light-energy up conversion;

-photoinduced structural changes in switch on/off applications (photoisomerizable systems) [15,16].

## 7. TOPO-PHOTOCHEMISTRY.

During this symposium we have encountered a few examples of an elegant field of photochemistry which appeared under many titles, as photochemistry in organized media, in microheterogeneous systems, in integrated systems, in confined media, and so on.

Structurally different systems, such as silica, alumina, semiconductors, cyclodextrins, polymers, clays, etc., used as heterogeneous micro-environments, have the common ability of restricting the rotational and translational molecular freedom of the guest, by interfacial interactions of a micropolyphasic system.

Polyphasic surfaces of microheterogeneous systems can induce significant variations on the substrate behavior during the time scales of the photochemical processes, including interesting abilities in terms of selectivity. Due to the properties of the microenvironment, excited states often seem to compete more efficiently with deactivation processes. Here the microheterogeneous character seems to be essential in determining the conditions of the single organizing microevents.

Several types of host have been utilized: depending on it three general systems can be showed in principle: i) one-dimensional interaction on a surface, ii) guest intercalation (layered media), and iii) three-dimensional interactions (inclusion complexes, incorporated systems, membranes, etc.) [17].

Some examples:

-surface modified semiconductors as photocatalysts: composite redox catalysts consisting of iron(III)porphyrins, covalently linked to $TiO_2$ particles via triethoxyaminopropylsilane are able to functionalize hydrocarbons, by a novel cooperative reactivity [18];

-surface modified semiconductors as photovoltaic devices: a ruthenium trinuclear cyano-bridged complex has been used as antenna-sensitizer adsorbed onto $TiO_2$ surface to increase the light harvesting efficiency of sensitized semiconductors [19];

-inorganic layered materials, intercalation host-guest systems with modified properties:

-photocatalytic processes in a constrained shape-selective environment by semiconductors (CdS, ZnS, CdSe, ZnO, $TiO_2$) on clays, with change in energy-band structure [20];

-photophysical properties: a wide range of flexible luminescent materials, photochromism [21];

-cyclodextrins possess the ability to admit a variety of guests of appropriate size and characteristics into their cavity, with formation of inclusion complexes, and offer the opportunity of a variety of selective photoreactions [15];

-membranes: semiconductors particles (e.g. $TiO_2$, CdS) incorporated in nonconducting polyurethane or Nafion membranes, as redox photocatalysts [22,23];

-membranes: vesicles by photopolymerization of surfactants as hosts of colloidal catalysts (noble metal or semiconductors) in redox reactions [24];

-membranes: iron(III)porphyrins caged inside 2-4% crosslinked polystyrene matrix, as photocatalyst for alkane and alkene oxygenation by $O_2$: the selectivity is governed by the size of the path and the size of the path is controlled by the swelling properties of solvents [25];

-carrier-containing membranes for selective phototransport of gases: cyclopentadienyltricarbonil manganese, upon UV irradiation, looses CO and generates a coordinatively insaturated complex which binds $N_2$ reversibly. The site isolation of the complex in a polymeric chain prevents its decomposition: the membrane will facilitate the transport of $N_2$ by photosubstitution reactions [26,2];

-functional molecule - containing conducting-polymer membranes, with various functionalities, such as electrochromism, photoelectric conversion, electrogenerated luminescence, catalysis; e.g.[27]:

-electrochromism: inorganic units, such as Fe-tris(bathophenanthroline disulfonate), or $PtCl_4^{2-}$, or $AuCl_4^-$, in polypyrrole or polythiophene;

-photoelectric conversion: Zn-tetra(4-sulfophenyl)porphyrin dispersed in polypyrrole, or $Fe_2O_3$ dispersed in Nafion;

-metallophorphyrin films prepared by interfacial polymerization of a pair of reactive comonomers (amine and acid chloride derivatized tetraphenyl metalloporphyrins) display a chemical asymmetry (the opposite surfaces show distinctive differences of functional groups) and develop directional photopotentials: the interfacial polymerization can be carried out at the surface of microporous substrates to provide suitable durability [28];

-inorganic membranes as catalytic materials, e.g., a thin plate of macroporous titanium covered on the opposite surfaces by $TiO_2$ crystals and Nafion membranes: an integrated catalyst for continuous-flow systems; for two solutions, two gaseous phases, or one solution/one gaseous phase; for photo- and/or electro-assisted redox reactions; Nafion membrane can provide electrolytic control [29].

## 8. ATMOSPHERIC PHOTOCHEMISTRY.

The chemistry of atmosphere is all part of a cycle in which photochemical processes play the main role.

The correct way to treat this system is to consider troposphere and stratosphere as an unique photochemical reactor which works at highest efficiency on the transformation and removal of pollutants.

One of the basic objects is the understanding of the integrated mechanisms: here photochemists have provided the most important contribution.

The atmosphere is a complex system: a variety of highly reactive oxidizing species ($^{\bullet}OH$, $HO_2^{\bullet}$, $NO_3^{\bullet}$, $O_3$, $O(^3P)$, $O(^1D)$, $O_2(^1\Delta g)$, etc.), some hundreds of volatile organics which must be oxidized. Moreover, the reactions could proceed in homogeneous or heterogeneous way.

Much work is still need in the area of heterogeneous reactions: while extensive data of rate constants for gas phase reactions of OH and $NO_3$ radicals are available, there are limited data for the rates on aqueous phase of atmospheric droplets and on surfaces of solids, included processes catalyzed by metals.

The knowledge of the rate constant values is essential in order to evaluate the lifetimes of organics in the atmosphere: because of the very high number of organics it is necessary to develop empirical physico-chemical models like the quantitative structure-activity relationships designed for various classes (e.g., alkenes, halogenate alkenes, aromatics, etc.), enabling to estimate the rate constants.

Cooperation between photochemists and physicists on the problem of reaction mechanisms of $O_3$ depletion is very fruitful [30,31].

## 9. CONCLUSION

Well; photochemistry has a determining impact on the Earth's life: natural photochemical processes have performed an unique role in the evolution and preservation of life.

Photosynthesis generates the basic compounds of life, as well as liberating oxygen to the atmosphere.

Moreover, photochemical reactions in the tropospheric and stratospheric reactor maintain the characteristics of the atmosphere and allow it to support life [32].

Limiting our attention to these two natural applications, we can see that they are impressive.

In comparison man's applications of photochemistry, such as photography, organic syntheses, photocatalysis, photoelectrochemistry, solar energy conversion, microlithography, photomedicine, polymer processes, are still relatively scarce.

Moreover, the silver halide photographic emulsion, which represent the most successful man's application, is a microheterogeneous system which splendidly work, in his motor principle, more likely owing to a series of uncommonly fortunate microevents rather than by the conscious intervention of the researchers.

Thus, in my opinion, today there are many opportunities: high performance materials and new generations of high performance materials, catalysis, synthesis, biomimetic chemistry.

There is, in the trend of the modern photochemistry, a novel attention to the aspects suggested by the nature.

It already occurred once that photochemistry resorted to nature in order to impress the right direction to their science, and this happened at the beginning.

"*The deep reasons leading to Ciamician decision to break off the preceding research and dedicate all his energy to photochemistry stem from his work on the organic chemistry of vegetal substances, from his belief that the utilization of solar energy must be investigated also in laboratory as an ideal method of preparative chemistry.*

**Our synthetic pathways are very different from those encountered in nature and it is this difference in the means that renders more striking the contrast. Plants are synthetic laboratories in which the most intricate chemical reactions take place at ordinary temperatures with the help of light and of certain substances we call enzymes or soluble ferments and more generally catalysts.** (Ciamician, 1902)

*According to Ciamician, this difference led to new awareness and a new task of organic chemistry: identifying and reproducing natural synthetic pathways.*

*This is more than academic interest, it also makes good economic sense since our synthetic pathways are not simply different, they are inferior.*"[33]

According to Arthur Adamson: then and now.

*Then*, in our studies there has been the coordination compound, so much the better of high symmetry, but it looked very complex to us.

Really the historical complexity of coordination compounds is a comfortable symmetrical simplification.

*Now*, in front of us the reality: biosystems, surfaces, interfaces, composites, supermolecules, organized systems and disorganized systems (chemistry and physics of radicals, transients, fragments, metallo-fragments, etc.): that is to say difficulties but challenges.

Now, in my opinion, from nature we must pick up the complicated character of the architecture and chiefly the micropolyphasic essence [34].

## 10. REFERENCES.

1 N. Serpone, E. Pelizzetti (eds), Photocatalysis, Wiley, New York, 1989.

2 J.E. Sheats, C.E. Carraher,Jr., C.V. Pittman,Jr., M. Zeldin, B. Currell (eds), Inorganic and Metal-containig Polymeric Materials, Plenum Press, New York, 1989.

3 G.L. Geoffroy, M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.

4 H. Sato, Applied Organomet. Chem., 3 (1989) 363.

5 I.P. Herman, Chem. Rev., 89 (1989) 1323.

6 J.F. Rabek, Mechanism of Photophysical Processes and Photochemical reactions in Polymers, Wiley, Chichester, 1987.

7 I.R. Bellobono, J. Photochem. Photobiol., A: Chem., 65 (1992) 431.

8 C.E. Hoyle, J.F. Kinstle (eds), Radiation Curing of Polymeric Materials, A.C.S., Washington, 1990.

9 J.F. Rabek, Photostabilization of Polymers, Elsevier, London, 1990.

10 G.Scott (ed), Mechanisms of Polymer Degradation and Stabilization, Elsevier, London, 1990.

11 J.P. Fouassier, J.F. Rabek (eds), Lasers in Polymer Science and Technology: Applications, III, CRC Press, Boca Raton, 1990.

12 D. Mansuy, Pure Applied Chem., 62 (1991) 741.

13 K.S. Suslick, R.A. Watson, New. J. Chem., 16 (1992) 633.

14 C.L. Hill (ed), Activation and Functionalization of Alkanes, Wiley, New York, 1989.

15 V. Balzani, F. Scandola, Supramolecular Photochemistry, Ellis Horwood, New York, 1991.

16 V. Balzani, L. Moggi, F. Scandola in Supramolecular Photochemistry, V. Balzani (ed), Reidel, Dordrecht, 1987.

17 V. Ramamurthy (ed), Photochemistry in Organized and Constrained Media, VCH, New York, 1991.

18 R. Amadelli, M. Bregola, E. Polo, V. Carassiti, A. Maldotti, J. Chem. Soc., Chem. Commun., (1992) 1355.

19 R. Amadelli, R. Argazzi, C.A. Bignozzi, F. Scandola, J.A.C.S., 112 (1990) 7099.

20 H. Miyoshi, H. Yonehama, J. Chem. Soc. Farad. Trans., 85 (1989) 1873.

21 H. Miyata, Y. Sugahara, K. Kuroda, C. Kato, J. Chem. Soc. Farad. Trans., 83 (1987) 1851.

22 D. Meissner, R. Memming, B. Kastening, Chem. Phys. Lett., 96 (1983) 34.

23 M. Krishnan, J.R. White, M.A. Fox, A.J. Bard, J.A.C.S., 105 (1983) 7002.

24 J.H. Fendler, Chemtech., (1985) 686.

25 E. Polo, R. Amadelli, V. Carassiti, A. Maldotti, Inorg. Chim. Acta, 192 (1992) 1.

26 H. Nishida, M. Ohyanagi, O. Okada, E. Tsuchida, Macromolecules, 21 (1988) 2910.

27 T. Shimidzu, Chim. e Ind., 12 (1991) 960.

28 C.C. Wamser et al., J.A.C.S., 111 (1989) 8485

29 R. Amadelli, A. Maldotti, to be publish.

30 B.J. Finlayson-Pitts, J.N. Pitts,Jr., Atmospheric Chemistry, Wiley, New York, 1986.

31 R. Atkinson, Chem. Rev., 86 (1985) 69.

32 R.P. Wayne, Principles and Applications of Photochemistry. Oxford Univ. Press, Oxford, 1988.

33 V. Carassiti, History of Photochemistry at the University of Bologna, EPA Newsletter, 33 (1988) 11.

34 T. Bein (ed), Supramolecular Architecture, ACS, Washington, 1992.