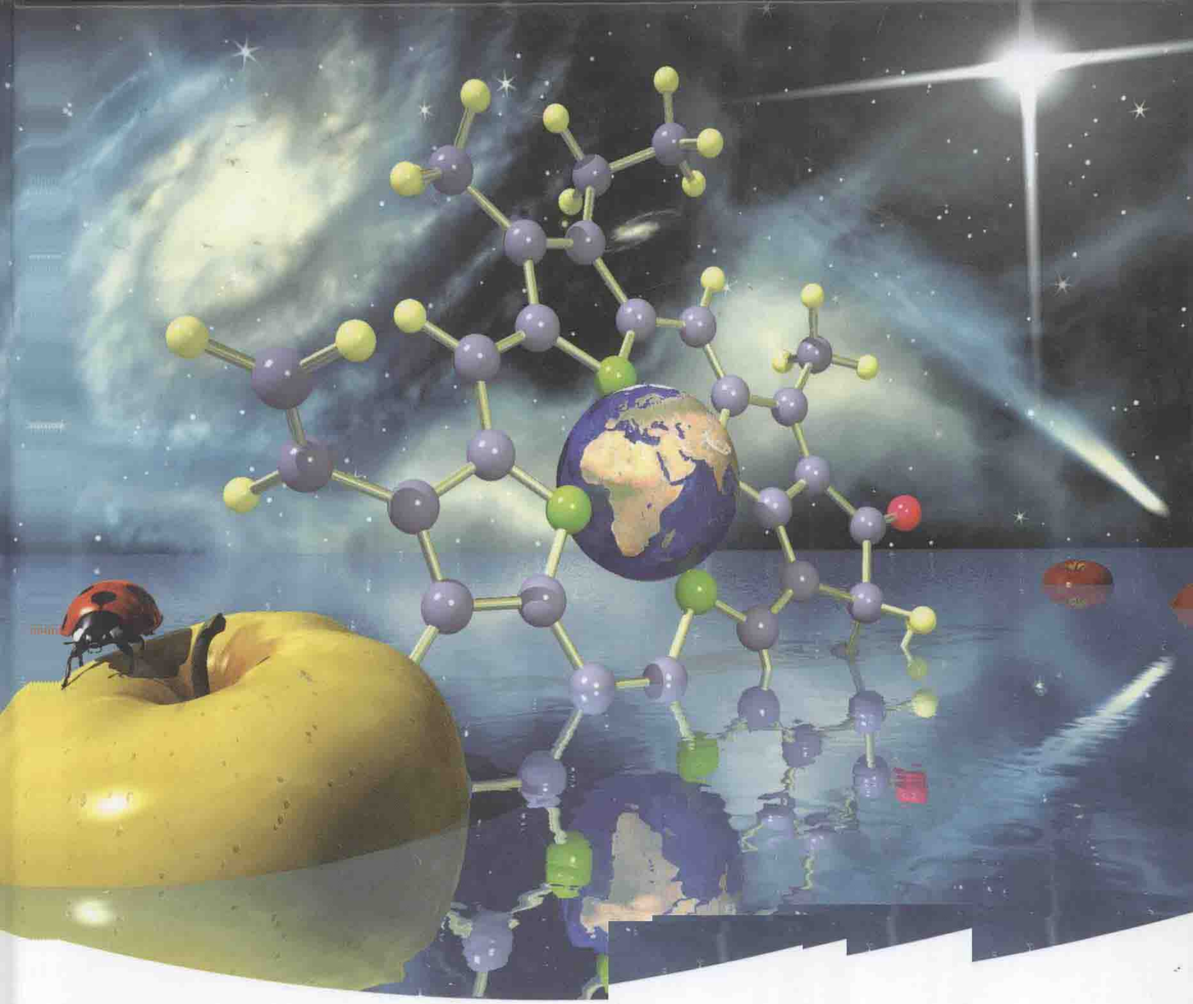

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# Preface

Bioinorganic photochemistry is a new branch of modern science dealing with the interaction of light with inorganic matter, which has a huge impact in all forms of life on the Earth from its origin up to the present: it is responsible for the origin and maturation of biosphere, its environment, and sustainable development.

The photobioinorganic interactions may be found not only now and here but also in the Universe far from Earth and in times dated more than 4 billion years ago, when the first hints of life probably emerged on Earth.

Small inorganic molecules under the influence of light are able to convert and assemble to form a variety of organic compounds, which not only are a life supplement but also may be treated as responsible for primordial life forms. Photochemistry of the inorganic species made its contribution to the creation of the world and played a fundamental role in the evolution of life. Both primordial and present life are protected from the destructive action of the high-energy part of solar radiation by the stratospheric photochemical processes involving oxygen and ozone.

The maintenance of life on Earth is possible only as a result of photosynthesis, which takes place in green plants and did in the past, when it was followed by decomposition and formation of deposits of coal, oil, and natural gas, currently used as fossil fuels. One of the future developments of bioinorganic photochemistry appears to be a pathway to enable the creation of new sources of energy that are both cheap and environmentally friendly.

A lot of photoreactions occurring in the atmosphere, hydrosphere, and soils ensure the health, comfort, and welfare of human beings, creatures, and the environment. These processes are mostly driven by coordination compounds of transition metals, which play the role of (photo)catalysts or (photo)sensitizers. There is also increased understanding of the role of supramolecular inorganic systems in their interaction with light and the great variety of processes that may ensue.

Development of artificial light sources, and especially the introduction of lasers, brought about an enormous increase in research on light–biomatter interactions. Thus the application of inorganic photochemistry and photophysics generates challenging new areas in bioscience and biotechnology.

Recently, nanotechnology and nanomaterials have been revolutionizing important areas in biomedical photonics, especially diagnostics and therapy at the molecular and cellular levels. Once again, inorganic species offer unique possibilities for practical applications.

Despite the rapidly growing knowledge in bioinorganic photochemistry, there is no single book devoted to this new interdisciplinary branch of science. The information of some specific problems from bioinorganic photochemistry is spread throughout various books devoted to bioinorganic chemistry, inorganic photochemistry, photobiology, environmental photochemistry, or bioanalytical and biomedical applications. Therefore the goal of this book is to provide a comprehensive overview of bioinorganic photochemistry taken as a new interdisciplinary branch of science. We hope that the book that arose from the review paper published in Chemical Reviews (2005;105:2657–94) will serve as a guide for newcomers in the field, as well as the first source of information for more involved readers. After introductory remarks on bioinorganic photochemistry as a new area of interdisciplinary science, the second part contains essential information from the field of photochemistry and especially inorganic photochemistry. The next part of the book is devoted to bioinorganic solar photochemistry, from the origin and maturation of the biosphere to the sustainable development of its environment. Parts IV and V focus on artificial light interactions with biomatter both in the context of application (medical, biomedical, environmental) and as models of important biochemical and biophysical phenomena.

*Grażyna Stochel, Małgorzata Brindell, Wojciech Macyk, Zofia Stasicka, Konrad Szaciłowski*

# Abbreviations

| | |
|---|---|
| [12]ane$N_4$ | 1,4,7,10-tetraazacyclotetradecane |
| 8-oxo-G | 7,8-dihydro-8-oxoguanine |
| A | adenine |
| ACT | antimicrobial chemotherapy |
| ADP | adenosine-5′-diphosphate |
| AETE | absorption/energy-transfer/emission |
| AM | air mass |
| AOP | advanced oxidation process |
| AOT | advanced oxidation technique |
| APDT | antimicrobial photodynamic therapy |
| ATP | adenosine-5′-triphosphate |
| BChl | bacteriochlorophyll |
| bet | back electron transfer |
| bphb | 4-[4-(2,2′-bipyridin-4-yl)phenyl]-2,2′-bipyridine |
| bpip | 2-(4′-benzyloxy-phenyl)imidazo[4,5-*f*]-1,10-phenanthroline |
| bpy | 2,2′-bipyridine |
| bpy′ | 4-(4′-methyl-2,2′-bipyridin-4-yl)butanamide |
| bpz | 2,2′-bipyrazine |
| Car | carotenoid |
| CB | conduction band |
| CFT | crystal field theory |
| Chl | chlorophyll |
| chrysi | chrysene-5,6-diylidenediamine |
| cnoip | 2-(2-chloro-5-nitrophenyl)imidazo[4,5-*f*]-1,10-phenanthroline |
| COX | cytochrome oxidase |
| Cp | cyclopentadienyl |
| CT | charge transfer |
| CTTS | charge transfer-to-solvent |
| cyclam | 1,4,8,11-tetraazacyclotetradecane |
| cyt | cytochrome |
| ddz | dibenzo[*h,j*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine |

| | |
|---|---|
| dicnq | dicyanodipyrido quinoxaline |
| dip | 4,7-diphenyl-1,10-phenanthroline |
| dmb | 4,4′-dimethyl-2,2′-bipyridine |
| dmso | dimethyl sulfoxide |
| dpb | 2,3-bis(2-pyridyl)benzo[*g*]quinoxaline |
| dpp | 2,3-dipyridin-2-ylpyrazine |
| dppz | dipyrido[3,2-*a*:2′,3′-*c*]phenazine |
| dpq | dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline |
| ed3a | ethylenediaminetriacetate |
| edta | ethylenediaminetetraacetate |
| en | 1,2-diaminoethane |
| ESR | electron spin resonance |
| ET | electron transfer |
| FAD | flavine adenine dinucleotide |
| FRET | Förster resonant energy transfer |
| fttp | tetrakis(4-trifluoromethylphenyl)porphyrin |
| G | guanine |
| $G^{ox}$ | oxidized guanine |
| GMP | guanosine monophosphate |
| GOD | glucose oxidase |
| $h^+$ | hole |
| hat | 1,2-diaminoethane |
| hat | 1,4,5,8,9,12-hexaazatriphenylene |
| Hb | haemoglobin |
| hnaip | 2-(2-hydroxy-l-naphthyl)imidazo[4,5-*f*]-1,10-phenanthroline |
| hnoip | 2-(2-hydroxy-5-nitrophenyl)imidazo[4, 5-*f*]-1,10-phenanthroline |
| HOMO | highest occupied molecular orbital |
| hpip | 2-(2-hydroxyphenyl)imidazo[4,5-*f*]-1,10-phenanthroline |
| HS | humic substance |
| IC | internal conversion |
| IFET | interfacial electron transfer |
| IL (or ILCT) | intra-ligand charge transfer |
| ip | imidazo[4,5-*f*]-1,10-phenanthroline |
| IPCT | ion-pair charge transfer |
| IR | infrared |
| ISC | intersystem crossing |
| IT (or IVCT) | intervalence transfer |
| L | ligand |
| LC | ligand centred |
| LDH | lactate dehydrogenase |
| LED | light emitting diode |
| LF | ligand-field |
| LHC | light-harvesting centre |
| LLCT | ligand-to-ligand charge transfer |
| LMCT | ligand-to-metal charge transfer |
| LSPR | localized surface plasmon resonance |

| | |
|---|---|
| LUMO | lowest unoccupied molecular orbital |
| MBCT | metal-to-band charge transfer |
| MC | metal centred |
| $Me_2$dppz | 11,12-dimethyl-4,5,9,14-tetraazabenzo[*b*]triphenylene |
| mgp | *N*-(1,10-phenanthrolin-4-ylmethyl)guanidine |
| MLCT | metal-to-ligand charge transfer |
| MMCT | metal-to-metal charge transfer |
| MPCT | metal-to-particle charge transfer |
| MRH | nitromerocyanine |
| MRI | magnetic resonance imaging |
| mRNA | messenger ribonucleic acid |
| NADPH | the reduced form of nicotinamide adenine dinucleotide phosphate |
| nc | naphthalocyanine |
| NHE | normal hydrogen electrode |
| NIR | near infrared |
| MTHF | 5,10-methenyltetrahydrofolylpolyglutamate |
| NADPH | the reduced form of nicotinamide adenine dinucleotide phosphate |
| NCPs | nucleosome core particles |
| NOS | nitric oxide synthase |
| NP | nanoparticle |
| OAc | acetate |
| OEC | oxygen-evolving complex |
| oep | octaethylporphyrin |
| OSCT | outer-sphere charge transfer |
| PACT | photodynamic antimicrobial chemotherapy |
| PAN | peroxyacetyl nitrate |
| pc | phthalocyanine |
| PCT | photoinduced charge transfer |
| PD | photodiagnosis |
| PDD | photodynamic diagnosis |
| PDI | photodynamic inactivation |
| PDT | photodynamic therapy |
| pdta | 3-(pyridine-2-yl)-as-triazino[5,6-*f*]acenaphthylene |
| pdtb | 3-(pyridine-2-yl)-5,6-diphenyl-as-triazine |
| pdtp | 3-(pyridine-2-yl)-as-triazino[5,6-*f*]phenanthroline |
| PET | photoinduced electron transfer |
| Ph | phenyl or phosphorescence |
| phehat | 1,4,5,8,9,10,17,18-octaazaphenanthro[9,10-*b*]triphenylene |
| phen | 1,10-phenanthroline |
| Pheo | pheophytin |
| phi | phenanthrene-9,10-diylidenediamine |
| phzi | benzo[*a*]phenazine-5,6-diylidenediamine |
| pip | 2-phenylimidazo[4,5- 2 2*f*]-1,10-phenanthroline |
| PMCT | particle-to-metal charge transfer |

| | |
|---|---|
| POM | polyoxometallate |
| poq-Nmet | 2-{2-[(7-chloroquinolin-4-yl)methylamino]ethylsulfanyl}-*N*-[1,10]-phenantrolin-5-yl-acetamide |
| ppip | 2-(4′-phenoxy-phenyl)-imidazo-1,10-phenantroline |
| PQ | plastoquinone |
| PSI | photosystem I |
| PSII | photosystem II |
| PTT | photothermal therapy |
| pydppz | 3-(pyrid-2′-yl)dipyrido[3,2-*a*:2′,3′-*c*]phenazine |
| qdppz | naptho[2,3-*a*]dipyrido[3,2-*h*:29,39-*f*]phenazine-5,18-dione |
| QD | quantum dot |
| qpy | 2,2′:4′,4″:2″,2‴-quaterpyridine |
| RC | reaction centre |
| RNOS | reactive NO species |
| ROS | reactive oxygen species |
| SCF | supercritical fluid |
| SEM | semiconductor |
| Sens | sensitizer |
| SOD | superoxide dismutase |
| SP | nitrosporopyran |
| SPE | single-photon excitation |
| SSCT | second-sphere charge transfer |
| T | thymine |
| tap | pyrazino[2,3-*f*]quinoxaline |
| TAP | 1,4,5,8-tetraazaphenanthrene |
| TEOA | 2,2′,2″-nitrilotriethanol; triethanolamine |
| tex | texaphyrin |
| TON | turnover number |
| tmtp | tetra(4-methylphenyl)porphyrin |
| TPE | two-photon excitation |
| tpp | tetraphenylporphyrin |
| tpy (terpy) | 2,2′:6′,2″-terpyridine |
| tren | triethylenetetramine |
| TS | transition state |
| U | uracil |
| UV | ultraviolet light |
| VB | valence band |
| VR | vibrational relaxation |
| XOD | xanthine oxidase |

# Contents

# 1

# Philosophy of Bioinorganic Photochemistry

*The most important thing in science is not so much to obtain new facts as to discover new ways of thinking about them.*
Sir William Bragg

Bioinorganic photochemistry is a rapidly growing and evolving new interdisciplinary research area integrating inorganic photochemistry with biological, medical, and environmental sciences (Figure 1.1) [1]. The role of light and inorganic species in natural systems and the possibility of their application in artificial systems of medical or environmental importance are in the limelight of bioinorganic photochemistry. From the earliest times humans have been aware of the influence that solar radiation exerts on matter and life; however, it is mainly during the last century that a systematic understanding of this phenomena has been developed [2–9]. Photochemistry of the inorganic species had its contribution in the creation of the world and has played a fundamental role in the evolution of life. Photosynthesis and many photoreactions proceeding in the atmosphere, hydrosphere and soil, involving inorganic species, ensure life on Earth. Bioinorganic solar photochemistry deals with the interaction of sunlight with inorganic matter, which has a huge impact on all forms of life on the Earth from its origin until now.

Sunlight supplies energy to the whole terrestrial environment: atmosphere, hydrosphere, lithosphere and biosphere. The spectral range of sunlight reaching our planet has varied with time. Atmospheric oxygen appeared owing to photosynthesis around 2.7 billion years ago. Atomic oxygen produced by short-wavelength ultraviolet (UV) irradiation (<240 nm) reacted then with molecular dioxygen to form an ozone layer shielding the Earth's surface from the most harmful UV. Four hundred million years ago the concentration of ozone reached 10% of the present level and allowed living systems to evolve from aquatic to terrestrial life. Today this ozone layer, with a maximum concentration in the stratosphere at 25 km above sea level, absorbs solar UV at wavelengths shorter than 290 nm. The radiation energy effective