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Bioinorganic Photochemistry

 WILEY

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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]aneN 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- <i>f</i>]-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- <i>f</i>]-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[<i>h,i</i>]dipyrido[3,2- <i>a</i> :2',3'- <i>c</i>]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- <i>a</i> :2',3'- <i>c</i>]phenazine
dpq	dipyrido[3,2- <i>d</i> :2',3'- <i>f</i>]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-1-naphthyl)imidazo[4,5- <i>f</i>]-1,10-phenanthroline
hnoip	2-(2-hydroxy-5-nitrophenyl)imidazo[4, 5- <i>f</i>]-1,10-phenanthroline
HOMO	highest occupied molecular orbital
hpip	2-(2-hydroxyphenyl)imidazo[4,5- <i>f</i>]-1,10-phenanthroline
HS	humic substance
IC	internal conversion
IFET	interfacial electron transfer
IL (or ILCT)	intra-ligand charge transfer
ip	imidazo[4,5- <i>f</i>]-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-tetraazabenzob[<i>b</i>]triphenylene
mgp	<i>N</i> -(1,10-phenanthroline-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- <i>f</i>]acenaphthylene
pdtb	3-(pyridine-2-yl)-5,6-diphenyl-as-triazine
pdtp	3-(pyridine-2-yl)-as-triazino[5,6- <i>f</i>]phenanthroline
PET	photoinduced electron transfer
Ph	phenyl or phosphorescence
phehat	1,4,5,8,9,10,17,18-octaazaphenanthro[9,10- <i>b</i>]triphenylene
phen	1,10-phenanthroline
Pheo	pheophytin
phi	phenanthrene-9,10-diylidenediamine
phzi	benzo[<i>a</i>]phenazine-5,6-diylidenediamine
pip	2-phenylimidazo[4,5- <i>c</i>]1,10-phenanthroline
PMCT	particle-to-metal charge transfer

POM	polyoxometallate
pq-Nmet	2-{2-[(7-chloroquinolin-4-yl)methylamino]ethylsulfanyl}- <i>N</i> -[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- <i>a</i> :2',3'- <i>c</i>]phenazine
qdppz	naphtho[2,3- <i>a</i>]dipyrido[3,2- <i>h</i> :29,39- <i>f</i>]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- <i>f</i>]quinoxaline
TAP	1,4,5,8-tetraazaphenanthrene
TEOA	2,2',2''-nitritotriethanol; 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

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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 ($<240\text{ nm}$) 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