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C0030 **PHOTOSENSITIZATION AND PHOTOCATALYSIS IN
BIOINORGANIC, BIO-ORGANOMETALLIC AND
BIOMIMETIC SYSTEMS**

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ABSTRACT

Inorganic photochemistry has experienced an enormous progress within the past decades. Many branches of current frontier science including sustainable chemistry, solar fuel production, or modern therapeutic strategies critically depend on light-responsive metal complexes. More recently, the various aspects of bioinorganic and bioorganometallic photochemistry have been systematically explored. In the present review, an attempt is made to provide some unifying concepts and rational design guidelines for the development of novel biomimetic and bioinspired systems controlled and driven by photons. Spectral sensitization of such photoprocesses remains a central challenge for utilizing sunlight as the energy source for enzyme mimetics, artificial photosynthesis, and chemical photocatalysis. Several

applications of metal-based drugs in molecular photomedicine also require light sensitivity in clearly defined spectral regions. Therefore, a brief overview on bioinorganic chromophores and their synthetic counterparts is provided. We also focus on the integration of abundant natural resources and the search for novel photocatalysts based on nonprecious metals and environmentally benign materials.

Keywords: Bioinorganic chromophores; Solar photochemistry; Biomimetic catalysis; Artificial photosynthesis; Photoactivated drugs.

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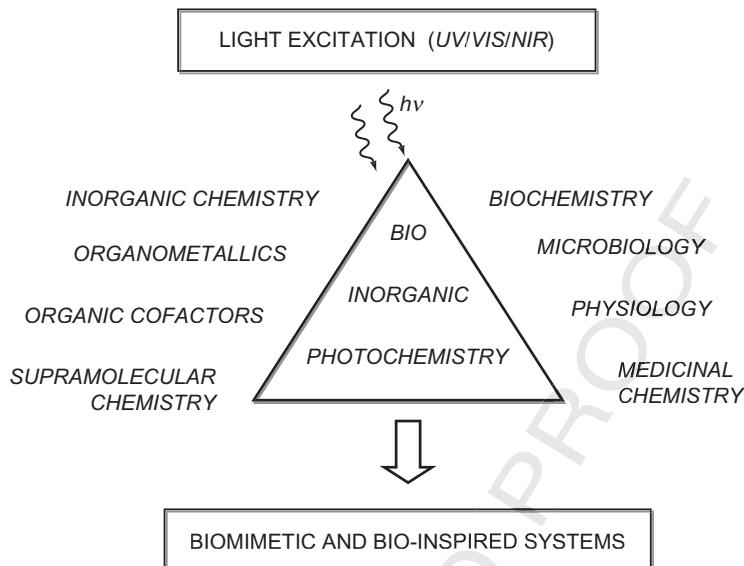
I. Introduction

p0005 The science of inorganic photochemistry has matured over the past 40 years (1). It covers in depth all kinds of chemical effects of photons on inorganic matter. Therefore, it is not surprising that the progress achieved in studying the properties of excited state materials and the photophysics and photochemistry of coordination compounds has significantly driven the frontiers of many other branches of research. Major topics now well established in the field include the detailed characterization of photoexcited metal complexes, photoinduced electron and energy transfer processes, solar energy conversion, homogeneous and heterogeneous photocatalysis, supramolecular photochemistry, semiconductor sensitization, photochromism, luminescent probes, sensors, and the development of light-emitting devices such as OLEDs (2).

p0010 More recently, the various aspects of light-responsive and photoreactive inorganic compounds in biological and bioinspired systems have been addressed (3–6). In the present contribution, some fundamental principles and first advances of the rapidly evolving fields of *bioinorganic photochemistry* and *biomimetic photocatalysis* will be discussed.¹ No attempt will be made to provide a comprehensive coverage of the relevant literature, which is widespread across a bunch of different disciplines (Fig. 1). Our intention is rather to visualize current research horizons and to stimulate further endeavors into this exciting

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¹The term *photocatalyst* is used to characterize a substance able to induce catalytic chemical transformations of reaction partners upon the absorption of light (7).



f0005 FIG. 1. Origins and impacts of bioinorganic photochemistry.

new branch of inorganic photochemistry and photocatalysis, which started about a decade ago (3,8).

s0010 II. Inorganic Photochemistry Inspired by Nature

p0015 Studying the inorganic chemistry of life already has a long history (9). What we now call biological inorganic (bioinorganic and bioorganometallic) chemistry (10,11) is a cross-disciplinary research topic primarily concerned with the role of metals in biology and life sciences. It turned out that approximately one-quarter of the known chemical elements has a crucial function for living organisms and that metal ions are of fundamental importance for all biological systems. A large share of the structurally characterized biological macromolecules contains inorganic cofactors. For instance, the majority of all known enzymes are metalloproteins with one or more transition metal ions such as V, (Cr), Mn, Fe, Co, Ni, Cu, Zn, Mo, or W in their respective active site. Coordination chemistry undoubtedly plays a critical part in stabilizing protein structures (12). The various other functions of metalloproteins in biological systems are illustrated in Table I.

p0020 Metalloenzyme catalysts participate as key compounds in some of the most important biochemical processes of life on earth

TABLE I

t0005 CLASSIFICATION OF METAL SITES IN BIOLOGY.^a

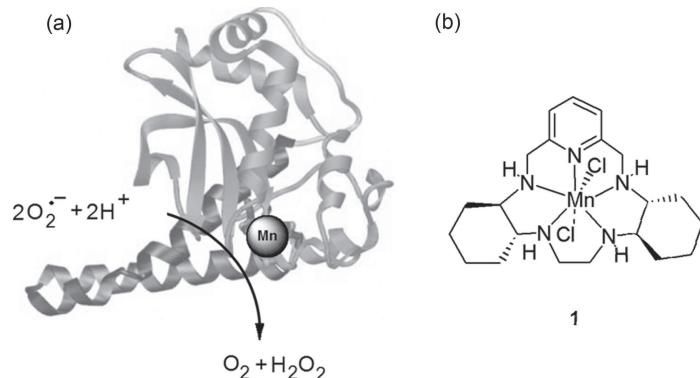
Basic role	Typical functions and metal ions involved
Structural	Stabilization of protein configuration (Ca, Mg, Fe, Zn)
Redox	Transfer of electrons or atoms (V, Mn, Fe, Co, Ni, Cu, Mo, W)
Catalytic	Turnover of substrates (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, W)
Photochemical	Light-harvesting and solar energy conversion (Ca, Mg, Mn, Zn)
Binding	Small molecule coordination, transport, and release (Fe, Ni, Cu)
Storage	Uptake and storage of metal ions, storage of dioxygen (Fe)
Regulation	Switch of protein function (Fe)

^aAdapted from Refs. (13) and (14).

including nitrogen fixation, respiration, and oxygenic photosynthesis (15). To imitate such natural chemical processes and to develop new compounds which are able to mimic biological materials in their structures or functions are the primary goals of biomimetic chemistry (16). Especially, the construction of robust chemical systems acting as artificial enzyme models (*synzymes*, *chemzymes*) has always been attracting considerable interest in the field (17,18), as these synthetic counterparts could replace the role of natural enzymes in various applications such as catalytic substrate conversion, bioanalytics, or medicinal chemistry. A representative example is the development of N₅-macrocyclic transition metal complexes, which are able to act as functional mimics of superoxide dismutase (SOD) enzymes (19). The complex **1** shown in Fig. 2 efficiently catalyzes the conversion of O₂^{•-} into peroxide and dioxygen with a rate nearly approaching that of the native manganese redox enzyme MnSOD (20).

p0025 It is important to note, however, that synthetic bioinorganic model compounds, which can compete with the reactivity of their natural counter parts, are still extremely rare. This is probably due to the fact that despite huge efforts devoted to this topic, a real breakthrough in simulating the crucial role of the protein matrix which surrounds the native reaction centers has not yet been accomplished.

p0030 To mimic the extremely efficient and selective chemistry of biocatalysts in the absence of their dynamic protein environment, novel routes have to be explored (5,6). In this context, we have started to impose light-induced electronic, energetic, and structural changes on the substrate binding sites of biomimetic and bioinspired coordination compounds (*artificial photoenzymes*,



f0010 FIG. 2. (a) Structure and function of *H. sapiens* manganese superoxide dismutase (PDB-code: 1ABM) and (b) synthetic low molecular weight substitute of MnSOD optimized for therapeutical purposes (20).

p0035 *photochemical model enzymes*). Already, the first attempts in this direction have proven to be very promising (3). As will be shown later in more detail, most of the other functions of metal sites in biological systems summarized in Table I can also be reproduced with bioinspired photochemical model systems.

Efficient light absorption and the population of photoreactive excited states are the minimum requirements for this novel approach. The quantum nature of photons furthermore offers a straightforward strategy to incorporate other interesting properties such as selectivity, switching, and regulation of light-responsive processes. Some basic characteristics of the functional components present in the corresponding bioinorganic and biomimetic systems will be discussed in the following sections.

s0015 A. LIGHT ABSORPTION AND SENSITIZATION

p0040 The most fundamental principle of photochemistry, which actually was discovered by exposing inorganic compounds to sunlight (21), states that light must be absorbed by a chemical substance for a photochemical reaction to occur. We will therefore start our discussion with a brief overview on some of the natural chromophores which are known to be involved in photosensory processes or could be useful for the construction of artificial photoreactive systems.

s0020 *A.1. Photoresponsive biomolecules*

p0045 Intensely colored visible-light absorbing molecules are an essential part of our living environment. A quite small number of chromophore types and photoactive pigments seem to be sufficient to deal with the basic photobiological responses and light-dependent functions that have evolved in natural systems. Prominent representatives of organic chromophore molecules in this context are the flavins, pterin derivatives such as MTHF **2**, porphyrins and related tetrapyrrole pigments **3**, carotenoids **4**, or conjugated oxidation products of amino acids such as the chromophores of the green fluorescent proteins **5** (22–24).

p0050 There are also many building blocks and redox cofactors present in biological systems including purines, quinones, coenzymes such as NADH, and other organic chromophores displaying characteristic absorption bands (25). Most of these compounds are able to interact with metal ions or may serve as ligands in biocoordination chemistry (10). Under natural conditions, these chromophores are usually thought not to be directly exposed to electromagnetic radiation. They are therefore considered as irrelevant for photobiological primary processes. Nevertheless, the corresponding compounds frequently turn out to be light sensitive under both *in vitro* and *in vivo* conditions. This feature can be directly exploited to influence biological functions or to construct artificial photoresponsive systems.

p0055 Illustrative examples for such a possibility are found with the cytochromes. The name of these proteins comes from the Greek words meaning “colored substances in the cell.” Cytochromes are intensely red-colored redox enzymes containing a heme prosthetic group as their dominant chromophore. Hemes are iron complexes of protoporphyrin IX derivatives (10,26). One of the most frequently studied metalloproteins of this family is cytochrome *c* (27). The ribbon structure of a cytochrome *c* enzyme together with the protein-bound heme *c* cofactor **6** is shown in Fig. 4.

p0060 Cytochrome *c* has a number of vital functions inside the cell. As part of the mitochondrial electron transport chain in respiration, it shuttles redox equivalents to cytochrome *c* oxidase (28), which can be considered as a kind of natural fuel cell for energy conversion. Mitochondrial dysfunction accompanied with changes in cytochrome *c* oxidase activity, however, seems to be intimately related to aging, neurodegeneration, and disease (29). Effects that can manipulate the functions of such redox enzymes are therefore of great importance for many research fields.

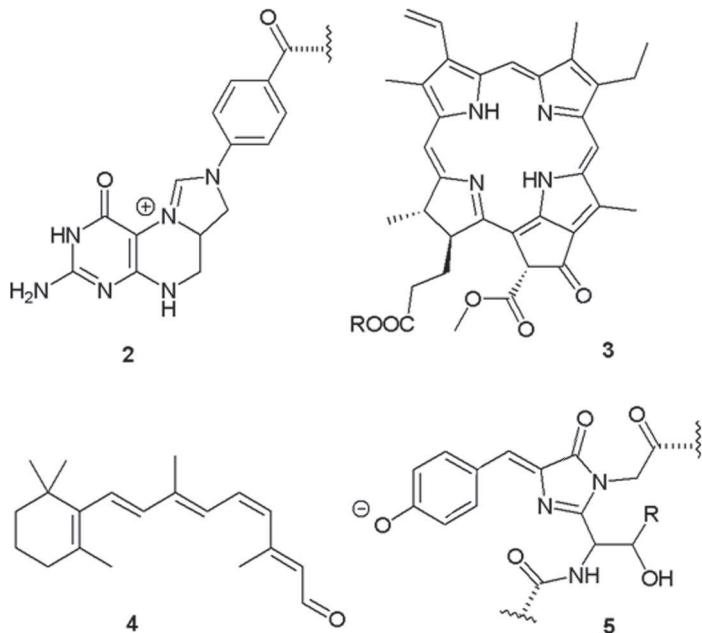
p0065 Photons are able to cause such effects. Light sensitivity of cytochrome containing systems has been known for a long time. For example, when bacteria of the type *Rhodomicrobium* (red microbe) were exposed to near infrared (NIR) radiation, their cytochrome system was oxidized from the ferrous to the ferric state (30). It is important to note that an archaic type of anoxygenic photosynthesis based on the oxidation of Fe(II) species has in the mean time been discovered (31), and that *Rhodomicrobium* strains are now known to belong to such types of photoferrotrophic microorganisms (32).

p0070 More recently, a novel mitochondrial signaling pathway activated by red light in the visible-to-NIR spectral region has been discovered (33), which is thought to depend on a direct light absorption by the metal-binding sites of the cytochrome c oxidase machinery. These findings may help to understand the beneficial effects of red light therapy for accelerated wound healing and other medical applications (34). Although the detailed mechanisms causing such effects are not fully clear, it seems that the cells directly involved in wound repair are affected upon irradiation. An overall acceleration of the electron transfer processes in the respiratory chain could provide more ATP, which is necessary for the wound-healing process. However, also some other types of bioinorganic photoreactions may be of crucial relevance in this context and have to be discussed (6). For example, the nitric oxide generated in injured tissue is well known to inhibit the catalytic center of cytochrome c oxidase (35), and photoinduced NO release can recover its function (36).

p0075 Another very interesting example of a photochemical reaction directly involving the two chromophores **5** and **6** (Figs. 3 and 4) has recently been described (37,38). The spectral changes of the corresponding photoredox process are shown in Fig. 5.

p0080 Oxidative quenching of the photoexcited EGFP protein is not only possible with cytochrome c but also achieved with a variety of other electron acceptors, including biologically relevant ones such as NAD⁺ or flavins (37). Further, the photoinduced electron transfer (PET) seems to favor a net two-electron process. It has been observed both in solution and inside living organisms without any special treatment. These findings give rise to speculations that a possible biological function of green fluorescent proteins might be that of a light-activated electron donor similar to the role of chlorophyll donating electrons to an acceptor in photosynthesis.

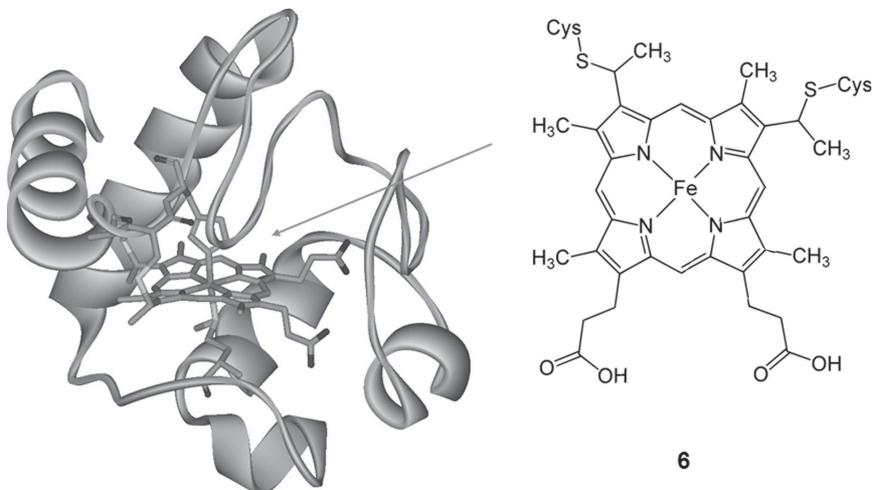
p0085 In this context, it is interesting to note that it has been pointed out that enzyme catalysis driven by light represents photosynthesis in its simplest biological form, and that photoenzymes



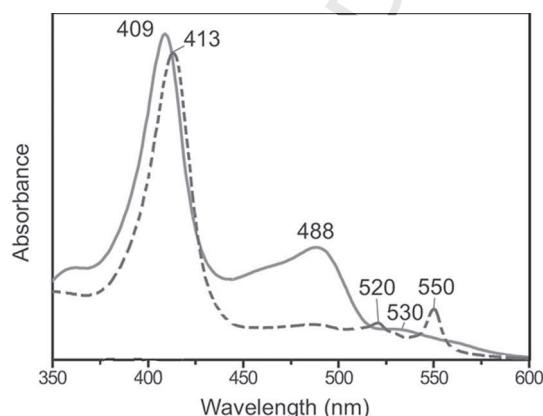
f0015 FIG. 3. Examples of natural photoantenna chromophores: (2) 5,10-methenyltetrahydrofolate (MTHF), a blue light photoreceptor pigment present in photolyase and some cryptochromes; (3) Pheophytin *a*, the primary electron acceptor in cyanobacterial oxygenic photosynthesis. (4) 11-*cis*-retinal, which is involved as sensory photoreceptor component in the opsin-based visual process of animals; and (5) the *p*-hydroxy-benzylidene-imidazolinone chromophore (HBDI) of the green fluorescent protein from bioluminescent marine species.

probably played an important role in the early biotic environment on earth (39). Today, the only metalloenzyme directly involved in photochemical processes under natural conditions is the visible light-driven water-plastoquinone oxidoreductase, better known as photosystem II (PS II) of oxygenic photosynthetic organisms (40). However, the functional properties of many other metal sites in bioinorganic systems are also known to be modified by irradiation. Some of these examples are given below (Table II).

p0090 The reasons for light sensitivity in these enzymes are not always well understood, and several other examples will probably be discovered when the nature of the light-absorbing species is clarified. It therefore seems appropriate to provide a brief overview on the basic types of inorganic chromophores occurring in biological metal sites.



f0020 FIG. 4. Structures of cyt c (PDB-code: 3CYT) and *c*-type heme (**6**).



f0025 FIG. 5. Electronic spectra of a mixture of ferric cytochrome *c* and enhanced green fluorescent protein EGFP before (—) and after (---) 490 nm photolysis indicating the formation of the ferrous form of heme *c* (**6**) with maxima at 413, 520, and 550 nm. Adapted from Ref. (37).

s0025 A.2. *Bioinorganic chromophores*

p0095 Excitation of proteins, nucleic acids, or organic cofactors acting as ligands in biological systems frequently involves individual functional groups or isolated conjugated π -systems. When a metal is coordinated to such moieties, the resulting molecular orbitals are usually classified as predominately located at the

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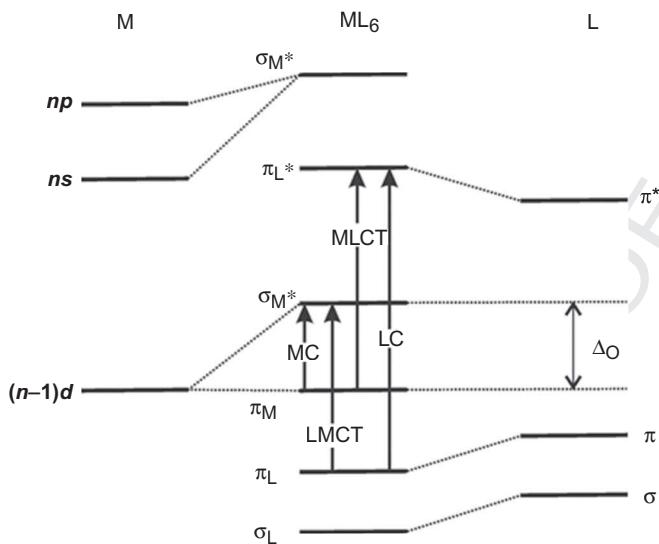
TABLE II

t0010 EXAMPLES OF METALLOPROTEINS INFLUENCED BY LIGHT ABSORPTION

Protein	Metals involved	Effects observed	Reference
Catalase	Fe	Inactivation	(41)
Horseradish peroxidase	Fe	Inactivation	(42)
[Fe]-Hydrogenase	Fe (?)	Inactivation	(43)
Methionine synthase	Co	Inactivation	(44)
Ferredoxin nitrate reductase	Mo	Inactivation	(45)
Cytochrome P450	Fe	Activation	(46)
Cytochrome <i>c</i> oxidase	Fe, Cu (?)	Activation	(47)
Nitrile hydratase	Fe	Activation	(48)
Ethanolamine ammonia-lyase	Co	Activation (?)	(49)
CH ₃ SCoM reductase	Ni (?)	Activation	(50)
Tyrosinase	Cu (?)	Activation	(51)
Fd-thioredoxin reductase	Fe	Regulation	(52)
Ascorbate oxidase	Cu	Regulation	(53)
Xanthine oxidase	Mo, Fe (?)	Regulation	(54)
Methylamine dehydrogenase	Cu (?)	Switch of function	(55)

metal (M) or at the ligands (L). In such a case, three fundamental types of electronic transitions can be distinguished. Transitions localized at the metals (metal-centered, MC), ligands (ligand-centered, LC or intraligand, IL), or charge transfer (CT) transitions with a spatial redistribution of electron density occurring between reducing (donor) and oxidizing (acceptor) subunits of the system (56,57).

p0100 A schematic representation of the typical classes of electronic transitions (MC, LC, CT) observed in metal complexes is shown in Fig. 6. In bioinorganic chromophores, the MC transitions usually involve metal ions with a partially filled d-electron shell, which are then characterized by the presence of low-energy ligand field ($d \rightarrow d$) electronic transitions or excitations involving metal–metal σ -bonds. The corresponding absorptions are sometimes covered by other bands and therefore hard to detect. It has been pointed out that whenever metallobiomolecules are described as being highly colored and having unique spectral features, this may indicate the presence of intense low-energy CT transitions (57). The typical absorption characteristics and the conspicuous colors related to the presence of such inorganic chromophores in biological samples have frequently been used to classify complete enzyme families, to coin names for certain

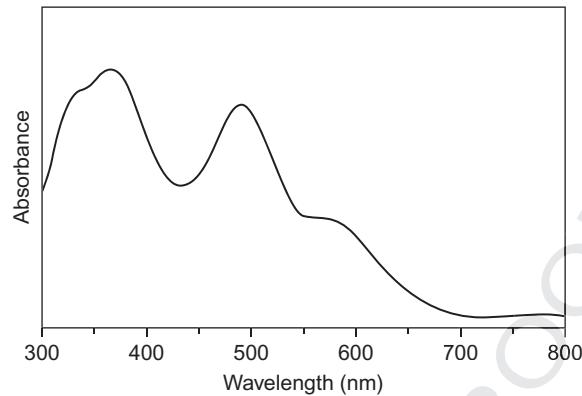


^{f0030} FIG. 6. Molecular orbital diagram for an octahedral transition metal complex ML_6 illustrating different types of electronic transitions based on localized orbital configurations (MC, metal-centered; LC, ligand-centered; MLCT, metal-to-ligand charge transfer; LMCT, ligand-to-metal charge transfer). Adapted from Ref. (1).

compounds, or to identify the involvement of characteristic intermediates or cofactors in biochemical processes. Illustrative examples in this context are metalloproteins with blue copper sites, purple acid phosphatases, or the red iron–sulfur proteins of the rubredoxin type (Fig. 7).

^{p0105} Many of the biological ligands present in metalloproteins (oxide, sulfide, phenolate, thiolate, and peroxide) exhibit low-energy ligand-to-metal charge transfer (LMCT) transitions. Due to the strong donor character of the coordinated groups involved in such systems, this may also reflect the presence of highly covalent ligand–metal bonds, which considerably contribute to the observed reactivity of these active sites in biology. Low-energy metal-to-ligand charge transfer (MLCT) transitions are less frequently assigned in bioinorganic systems. They require the presence of a reducing metal donor site and ligands with sufficiently low-lying acceptor orbitals. This situation is frequently observed in bioorganometallic systems and in the presence of tetrapyrrole macrocycles or redox cofactors.

^{p0110} Besides the CT transitions shown in Fig. 6, several other combinations of donor and acceptor moieties in metalloproteins can



f0035 FIG. 7. Electronic absorption spectrum of the oxidized rubredoxin protein from the dinitrogen fixing bacterium *Clostridium pasteurianum*. Adapted from Ref. (58).

lead to low-energy CT interactions. This includes the observation of mixed-valent compounds with ligand-to-ligand charge transfer (LLCT) transitions between reducing and oxidizing ligands simultaneously present at a metal-binding site, or the possibility of metal-to-metal charge transfer (MMCT) or intervalence charge transfer transitions in polynuclear metal-binding sites and cluster structures with ligand bridged reducing and oxidizing metal centers (56).

p0115 In all these cases, the degree of coupling between the donor and acceptor sites crucially determines the electronic structures and optical properties. Whenever strong covalent bonding occurs, as is the case for bioorganometallic systems, the degree of molecular orbital delocalization may become dominant and the description of electronic transitions with localized orbitals and discrete oxidation states is then no longer appropriate. Nevertheless, this simplified classification has proven to be very useful to discuss different types of excited states in both inorganic photochemistry and bioinorganic spectroscopy (56,57). A representative overview on the diversity of bioinorganic chromophores following this terminology is given in Table III.

p0120 As can be clearly seen from the data provided in Table III, the excitation energies of different bioinorganic chromophores are completely covering the photochemically relevant spectral region from ultraviolet to NIR light. Moreover, the observed intensities of the absorption features directly involving metal-binding sites strongly vary and span many orders of magnitude. To populate a desired excited state manifold more efficiently, it may therefore

TABLE III

t0015

SOME BIOINORGANIC CHROMOPHORES

Metalloprotein	Metal	Absorption ^a	Assignment	Reference
Horseradish peroxidase	Fe	400 (100,000)	LC	(42)
Cytochrome P450	Fe	363 (50,000)	LC/LLCT	(59)
Methylmalonyl CoA mutase	Co	376 (12,800)	LC/LLCT (?)	(60)
Methyl CoM reductase	Ni	420 (22,000)	LC	(61)
Bovine serum amine oxidase	Cu	480 (3500)	LC	(62)
Ribonucleotide reductase	Fe/Mn	408 (3400)	LC	(63,64)
Galactose oxidase	Cu	900 (1000)	LLCT	(65)
Deoxyhemerythrin	Fe	1110 (4)	MC	(66)
Nitrile hydratase	Co	575 (30)	MC	(67)
CuZn superoxide dismutase	Cu	610 (155)	MC	(68)
Cytochrome <i>c</i> oxidase	Cu–Cu	769 (1500)	MMCT/MC	(69)
Photosystem II	Mn, Mn	820 (?)	MMCT/MC	(70)
Clavaminate synthase	Fe	500 (375)	MLCT	(71)
Taurine α -KG dioxygenase	Fe	530 (140)	MLCT	(72)
Methyl CoM reductase	Ni	754 (2500)	MLCT	(61,73)
Vanadium chloroperoxidase	V	315 (3000)	LMCT (?)	(74)
Mn superoxide dismutase	Mn	480 (800)	LMCT	(75)
Acid phosphatase	Mn	515 (2460)	LMCT	(76)
Formate dehydrogenase	Fe	400(16,000)	LMCT	(77)
Rubredoxin	Fe	490 (8700)	LMCT	(78)
Phenylalanine hydroxylase	Fe	700 (1140)	LMCT	(79)
Thiocyanate hydrolase	Co	340 (?)	LMCT (?)	(80)
Azurin	Cu	630 (5000)	LMCT	(81)
Ascorbate oxidase	Cu	610 (9600)	LMCT	(82)
DMSO reductase	Mo	720 (2000)	LMCT	(83)
DMSO reductase	W	560 (1800)	LMCT	(84)

^aWavelength (nm) ($\epsilon M^{-1} cm^{-1}$); approximate values extracted from the published data.

become necessary to sensitize the systems by introducing additional excited state levels.

s0030 A.3. Spectral sensitization

p0125 The process of photosensitization occurs, whenever the absorption of radiation by one molecular entity causes photophysical or photochemical alterations in another molecular entity or

material. This may involve either energy transfer or electron transfer (1). In a strict mechanistic sense, however, the sensitizer must not be consumed in the process. Scientific work on this topic dates back to the pioneering days of photography, when the sensitivity of silver halides was for the first time extended to longer wavelengths by using various organic dyes and pigments (85). Later, the dye sensitization of solids and semiconductors was systematically explored (86), which finally led to the development of modern solar cell materials (87).

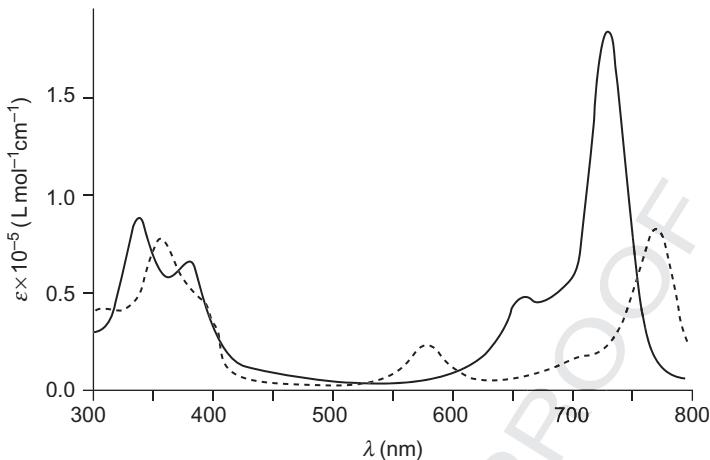
p0130 Biological effects of sunlight and synthetic organic dyes on enzymes, microbes, and higher organisms have been discovered in the end of the nineteenth century and soon were exploited for medical applications (88). Today, the optimization of sensitizers for photodynamic therapy is still a very active branch of research in bioinorganic photochemistry and molecular photomedicine (6,89).

p0135 The majority of organic compounds and biological metabolites are colorless but may be severely damaged under UV-light exposure. Therefore, spectral sensitization is a crucial prerequisite for the efficient accumulation of permanent photoproducts in all kinds of synthetic processes driven by light. The big advantage of photosensitized processes avoiding undesired side reactions caused by secondary photolysis now gradually becomes recognized as extremely useful for photocatalytic organic synthesis driven by visible light (90).

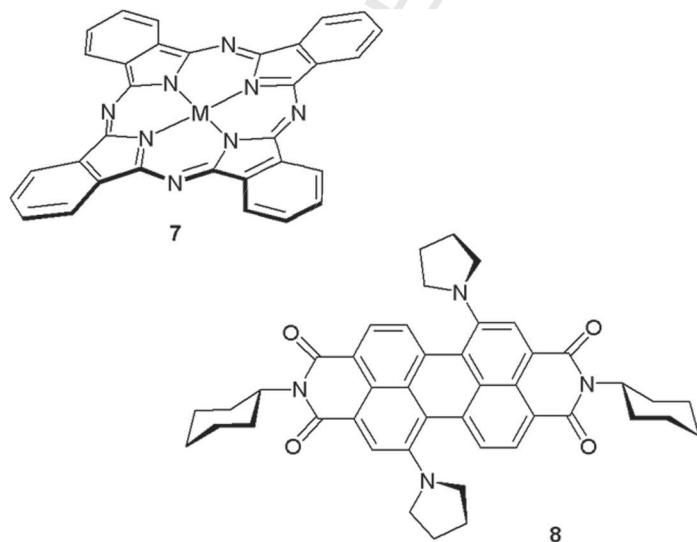
p0140 Here, we will mainly focus on two other important aspects of photosensitization: the fundamental role of deeply colored compounds as light-harvesting antenna chromophores for solar energy conversion and the possibility of reaching spectroscopically hidden, but photochemically active excited state levels by means of spectral sensitization.

p0145 Porphyrins and related tetrapyrrole pigments represent the most important class of sensitizers in both natural and artificial photosynthesis (8,87,91). These compounds are ideally suited for collecting light in the far-red and NIR spectral region, which represents a natural limit for directly driving energetically uphill bond-formation processes suitable for the photochemical storage of solar energy. To reproduce the spectroscopic and light-harvesting features of the chlorophylls is therefore an important goal of biomimetic and bioinspired chemistry (5,92,93). A comparison of natural and synthetic photosensitizers with quite similar absorption characteristics is given in Fig. 8.

p0150 Besides metallophthalocyanines **7** as photosensitizers (91,93), some intensely colored perylene diimine derivatives such as **8** have also been proposed as functional chlorophyll analogues



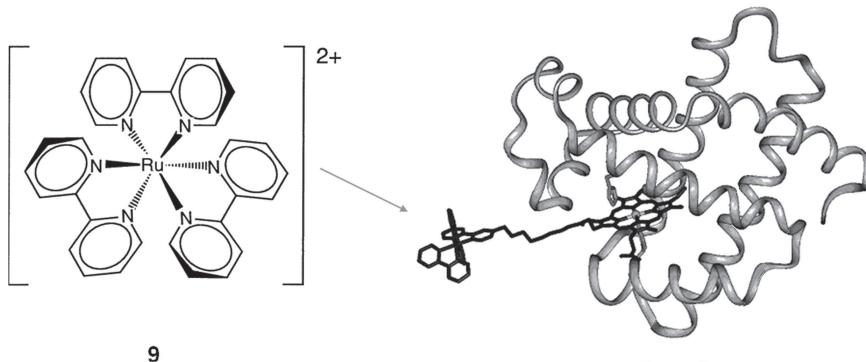
f0040 FIG. 8. Electronic spectrum of bacteriochlorophyll *a* (---) extracted from antenna complexes of purple bacteria compared to the spectrum of a synthetic phthalocyanine metal complex (—). Reproduced with permission from Ref. (5). Copyright Wiley-VCH.



f0045 FIG. 9. Structures of robust biomimetic photosensitizers with chlorophyll-like excited state properties (93,94).

(94). Chlorophyll *a* with a Q_y -band at $\lambda_{\max}=665$ nm (95) is the magnesium complex of the dihydroporphyrin derivative **3** already shown in Fig. 3. The chemically quite different structures of compounds **7** and **8** are given in Fig. 9.

- p0155 In the context of artificial photosynthesis and solar fuel production, the long-wavelength spectral sensitization of photo-reactions into the far-red and NIR region is of prime interest. Without suitable chromophores, a reasonably high efficiency of an abiotic solar energy storage process, which is always characterized by a specific optimum threshold wavelength (5,96,97), will not be reached.
- p0160 As already mentioned above, spectral sensitization may also become indispensable when the light absorption properties of a potentially photoreactive compound do not permit direct excitation in the desired wavelength region. By application of sensitizers with adjusted excited state properties, it is, for example, possible to induce photochemical reactions of otherwise colorless compounds with visible light. Another important application in photochemistry is the sensitized population of excited state levels, which are not easily reached by direct absorption of light due to the limitations of quantum chemical selection rules. This phenomenon has been extensively exploited in mechanistic and synthetic organic photochemistry, where enhanced yields of triplet state population could be achieved in various dye-photosensitized processes (98).
- p0165 In the pioneering years of inorganic photochemistry, the basic inter- and intramolecular sensitization processes were introduced by Vogler and Adamson (99), which soon was followed by organometallic examples (100). In this decade, also the blue-light absorbing tris(2,2'-bipyridyl)ruthenium(II) cation $[\text{Ru}(\text{bpy})_3]^{2+}$, **9** was promoted as an interesting new sensitizer for energy and electron transfer processes (101,102). In a plethora of slightly modified forms, $[\text{Ru}(\text{bpy})_3]^{2+}$ became an extremely popular prototype of an inorganic photosensitizer (103). This also opened fascinating new routes in bioinorganic photochemistry such as probing and modulating the active site properties of metalloenzymes with blue light (104). Derivatives of $[\text{Ru}(\text{bpy})_3]^{2+}$ continue to be extensively studied in the context of photocatalysis, biomimetics, solar energy conversion, and artificial photosynthesis (105–109). The structure of the parent ruthenium polypyridine complex **9** together with a representative application of this structural motif in bioinorganic photocatalysis is depicted below (Fig. 10).
- p0170 While the MLCT excited state properties of sensitizers such as **9** are easily studied and spectroscopically characterized, these compounds are not yet the best choice for certain applications. This includes all kinds of photosystems requiring to collect a much larger share of the solar spectrum such as artificial photosynthetic architectures or solar cells. Even more severely, in PET



f0050 FIG. 10. The photosensitizer $\text{Ru}(\text{bpy})_3^{2+}$ (**9**, left side) covalently wired to the heme prosthetic group of horse heart apomyoglobin. This hybrid system allows to create and characterize radical intermediates in the enzyme active site triggered by light (110).

processes, sensitizers such as $[\text{Ru}(\text{bpy})_3]^{2+}$ are acting as a one-electron reagents, while many photocatalytically attractive processes for the synthesis of permanent reaction products require the exchange of more than one electron to avoid destructive side reactions and thermodynamically unfavorable free radical chemistry (5,8). Serious efforts are therefore necessary to efficiently couple the photoinduced primary processes to other catalytically competent moieties. As an alternative, a new generation of light-harvesting photocatalysts termed *multielectron transfer (MET) photosensitizers* has been introduced (8,111). These compounds are able to directly promote net two-electron processes following the absorption of only one photon.

p0175 Besides color, sensitization, and light-harvesting efficiency, the actual reactivity of the excited states populated is therefore a crucial property. Some aspects of relevance for bioinorganic and biomimetic systems will be discussed in the following chapters.

s0035 B. PHOTOCHEMICAL REACTIVITY

p0180 Absorption of light always leads to an activation of the irradiated compound, as excited state energy levels are situated considerably higher than those of the corresponding ground state species. Thus, it is not surprising that many reactions, which are thermodynamically or kinetically inaccessible in the ground state, can occur with high efficiency from electronically excited states. This general feature makes photochemical activation

under ambient conditions an ideal strategy for the functional modeling of difficult or energetically demanding chemical transformations that are otherwise restricted to biocatalysis and natural photosynthesis. In Table IV, some complementary functions of biological systems and basic types of photochemical reactions are compared.

p0185 The design principles for the rational construction of light-driven counterparts of bioinorganic, bioorganometallic, and biocatalytic systems have recently been reviewed in more detail (5). Here, we will limit our discussion on the most important aspects and advantages of photoreactive components in bioinspired energy conversion and catalysis.

s0040 *B.1. Electrons*

p0190 Light absorption modifies the driving force for electron transfer processes in all kinds of materials. As photoactivated species are always better oxidants *and* reductants than their ground state equivalents, an enhanced redox reactivity is usually observed in the excited state. Photoreactions are therefore ideally suited to trigger, study, and mimic bioinorganic electron transfer.

p0195 The typical one-electron redox reactions resulting from PET processes can be applied to control the generation of reactive intermediates similar to the way radical enzymes are performing (112). To achieve an accumulation of permanent reaction products, as is the case with most oxidoreductase enzymes and photosynthetic systems, it is very important to provide suitable (photo)-catalytic MET pathways. The crucial advantage of

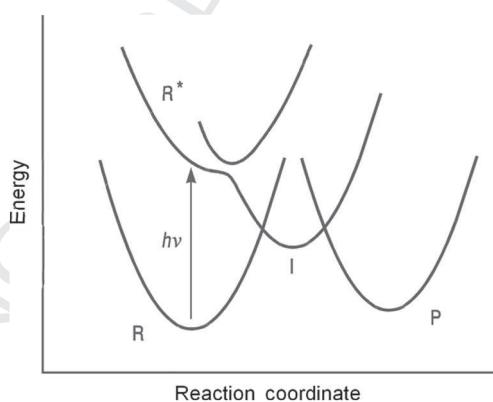
TABLE IV

t0020 EXCITED STATE PROCESSES AND THEIR FUNCTIONAL COUNTERPARTS

Light-dependent reaction types	Biosystems with related functions
Bond distortion, spin crossover	Enzyme-substrate complexes
Sensitization, energy transfer	Light-harvesting antenna systems
Photoinduced electron transfer	Photosynthetic reaction centers
Hydrogen atom abstraction	Radical enzymes
Photooxidation, photoreduction	Oxidoreductase enzymes
Photoaddition, photosubstitution	Transferases, kinases
Photodissociation, photo-cleavage	Hydrolases, lyases, nucleases
Photoisomerizations	Isomerases, mutases
Photodimerization, photo-polymerization	Ligases, polymerases
Phototriggered release of compounds	Hormones, neurotransmitters
Photodeposition of materials	Biomineralization and storage proteins

collecting and coupling redox equivalents is to avoid free-radical side reactions, as these processes tend to decrease both the long-term stability and the overall efficiency of the system. Especially, the light-induced substrate transformations in natural and artificial photosynthesis strongly depend on the feasibility of MET catalysis. For example, the fixation of CO₂ to form carbohydrates in a photocatalyzed four-electron process allows a long-wavelength spectral sensitization down to a photon energy of 1.3 eV, corresponding to an NIR threshold absorption wavelength of about 950 nm. In contrast, a minimum energy of 3.6 eV (340 nm, UV-light) is necessary to drive the reaction in highly unfavorable one-electron steps, and two-thirds of the solar energy suitable for carbon dioxide reduction are wasted (8). Also many energetically downhill reactions in bioinorganic and bioinspired catalysis require optimized MET reagents to be sufficiently accelerated and to guarantee a large total number of possible redox cycles.

p0200 The qualitative reaction profile given in Fig. 11 shows how a light-induced single-electron transfer process can be coupled to suitable follow-up steps to facilitate the formation of permanent two-electron photoredox products. Larger bond and shape reorganizations of excited state molecules, which typically involve the population of CT states or the formation of Jahn–Teller distorted species, are very helpful to achieve such a favorable situation of the potential energy surfaces (5,8).



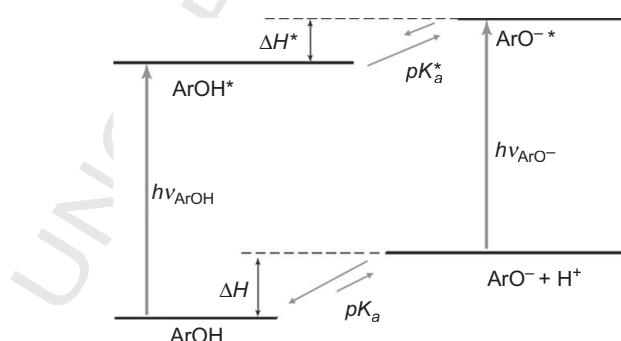
f0055 FIG. 11. Schematic illustration of a net two-electron transfer photoredox process. Excitation of reactants (R) forms a metastable one-electron intermediate (I), which finally can yield an energy-rich permanent product (P) after a second electron transfer step. Adapted from Ref. (8).

Ideally, the thermal back reaction of the products formed should have a sufficiently high activation barrier to enable a continuous accumulation of the desired product molecules during many photocatalytic cycles. According to the Hammond postulate (113,114), which claims that exothermic reactions have an early barrier, the structural features of the one-electron transfer intermediates formed photochemically should already be as close as possible to the transition state of the follow-up electron transfer step. This requirement gives an important guideline for choosing the type of excited state to be built into such systems.

s0045 *B.2. Protons*

p0205 The most common type of biocatalytic reactions is proton transfer (115). Nearly, every enzymatic reaction involves one or more proton-coupled steps. Transition-state proton bridging and intramolecular proton transfer (general acid–base catalysis) are an important strategy to accelerate substrate conversion processes. Moreover, proton transfer also plays a fundamental role in bioenergetics (116).

p0210 There are also many well-documented cases of excited state proton transfer reactions. It has been known for a long time that the acid–base properties of organic molecules such as phenols are drastically modified upon light absorption. About 60 years ago, Förster suggested a simple method for estimating the excited state pK^* values of photoactivated species from thermodynamic and spectroscopic data (117), which became very popular (Fig. 12).



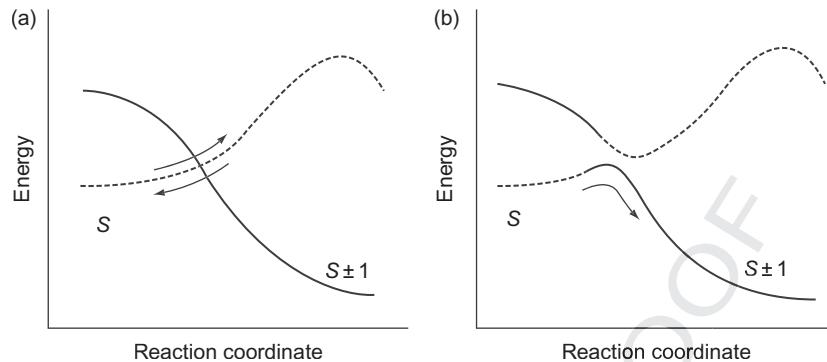
f0060 FIG. 12. Förster-cycle for the acid–base equilibria between a phenol derivative (ArOH) and the corresponding phenolate anion (ArO⁻) in the ground state S₀ and the first excited singlet state S₁.

p0215 The first example of such a reversible proton translocation cycle occurring within a protein core (118) was described for the GFP chromophore **5** already mentioned in the previous sections (Fig. 3). In the presence of light, excited state proton transfer should also be relevant for many other biological systems carrying phenols such as tyrosine residues or other deprotonable moieties in their active sites. In inorganic photochemistry, the acid–base properties of the coordinated ligands can also be drastically modified upon excitation. Although some attempts to generalize the Förster concept for coordination compounds have been made (119), the possible benefit of utilizing such effects is still underestimated. Nevertheless, it is already quite clear that metal complexes with potential proton translocation sites on the ligand periphery also exhibit immense changes in their nucleophilic character and their acid–base properties upon light absorption (120). The chemical bonds most frequently involved in the context of excited state proton transfer reactions include OH, NH, and CH. Typical photoinduced changes in acidity or basicity are characterized by p*K*-value variations of 4–6 units, which is in the range of the transition-state effects observed in hydrolytic enzyme catalysis (5). These effects could therefore become a very useful functional tool for many applications in biomimetic and bioinspired photocatalysis.

s0050 *B.3. Spin*

p0220 When chemical bonds are formed or broken, the valence electrons of the participating species are redistributed. In some cases, the necessary changes in electron angular momentum (spin) in the course of a chemical reaction may represent the decisive rate-limiting factor (Fig. 13). For example, the majority of stable organic substances are diamagnetic with a singlet ground state. Spontaneous reaction with dioxygen, which has a triplet ground state, is therefore constrained due to spin-barrier effects. These limitations are immediately circumvented, when O₂ is converted into singlet oxygen by photosensitization or by other means.

p0225 Rate acceleration is the most fundamental aspect of catalysis. To elucidate the electronic mechanisms of spin–acceleration phenomena therefore represents an important topic in both bio-inorganic and biomimetic dioxygen activation (5,122). Many other types of substrate transformations catalyzed by metal complexes or redox enzymes also involve key steps with a change in spin along their reaction coordinates. The abundance of such phenomena seems to be much wider than initially thought. This



f0065 FIG. 13. Energy curves along the reaction coordinate of a spin-forbidden two-state process (a). In such a situation, spin crossover can accelerate product formation by opening up a novel low-energy reaction pathway (b). Adapted from Ref. (121).

includes all kinds of radical reactions and electron transfer processes, which can be catalyzed by metal ions (123). Some spin-forbidden proton transfer reactions have also been characterized (124).

p0230 Paramagnetic metal complexes or radical species present in the coordination sphere of active sites can open up initially closed reaction channels when their own spin is combined with those of the reactants. In photosynthetic reaction centers, the fate of the radical-ion pairs generated by photoinduced charge separation is, for example, defined by the exchange interactions with a close-by iron site. Also, the course of bond cleavage processes, hydrogenations, and isomerizations can be influenced by the presence of paramagnetic compounds. All the basic aspects of this ubiquitous phenomenon termed *spin-catalysis* (125–127) can also be exploited for bioinspired photocatalytic systems, where spin crossover and intersystem crossing (ISC) processes can be triggered by light, and the degree of spin-orbit coupling can be employed to partially control such effects (5).

s0055 C. SELECTIVITY AND REGULATION

p0235 The interaction between light and matter, unlike thermal activation of compounds in the form of heat, is always a very selective process. Photochemical activation may induce the twisting, stretching, or destabilization of certain bonds located in a specific region of an individual molecule, while other subunits remain

almost unaffected. This resembles the strategies evolved in biocatalytic systems, where activation, regioselectivity, and branching between alternative substrate transformation pathways are carefully controlled by the formation of enzyme–substrate complexes.

p0240 The convenient triggering of selective reactions by light and the regulatory effects of light intensity variations are crucial benefits of the photochemical approach toward biomimetic model compounds. These two important aspects of biological systems, which are otherwise hardly achieved in synthetic molecular devices, will be briefly discussed in the following sections.

s0060 *C.1. Controlling reaction pathways*

p0245 In photochemical reactions, the population of excited states of different orbital origins can result in quite different reactivity patterns. Therefore, reaction products may occur, which are not accessible at all in thermochemical pathways. Especially in organometallic and coordination compounds, the primary photoproducts obtained are not always resulting from the lowest-lying excited state levels. Wavelength-selective excitation may then be exploited to channel the product formation process and to control a possible branching between different reactivity patterns.

p0250 As already mentioned in the previous section, also the fundamental laws of spin conservation may completely close or at least slow down certain reaction channels. ISC and spin inversion thus can strongly influence the balance between competing processes with a different regio- and stereoselectivity (5). While such effects are very common in metalloenzyme redox catalysis, their rational exploitation in bioinorganic photochemistry and photocatalysis is still in its infancy (3,6).

p0255 Successful fine-tuning of the branching reactivity patterns observed in metal complexes and organometallics requires a profound set of experimental and spectroscopic data. Especially in complicated systems with various close-lying electronic excited states of different orbital parentage, an in-depth interpretation of the experimental results can only be supported and further refined by highly sophisticated quantum chemical calculations (128,129). A well-documented example of such a situation with a competitive spin-multiplicity- and wavelength-dependent photoreactivity is the selective bond cleavage of $[\text{HMn}(\text{CO})_5]$ and related organometallic manganese hydride complexes (Fig. 14).

p0260 The carbonyl-hydrido complex $[\text{Mn}(\text{H})(\text{CO})_3(\text{DAB})]$ displays nine low-lying singlet and triplet excited states, which all are

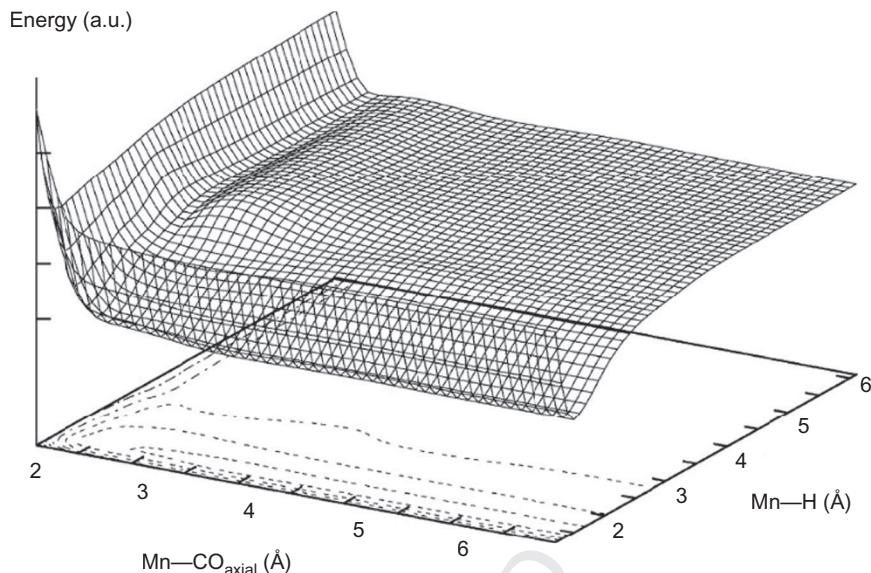


FIG. 14. Calculated potential energy surface of the $^1\text{MLCT}$ state of $\text{Mn}(\text{H})(\text{CO})_3(\text{DAB})$ as a function of the MnH and MnCO bond lengths (DAB, 1,4-diaza-1,3-butadiene). Adapted from Ref. (128).

potentially photoreactive. It could be shown (128) that only two of those, the singlet metal-to-ligand $^1\text{MLCT}$ ($d_{\text{Mn}} \rightarrow \pi^*_{\text{DAB}}$) state and the triplet sigma-bond-to-ligand $^3\text{SBLCT}$ ($\sigma_{\text{MnH}} \rightarrow \pi^*_{\text{DAB}}$) state, define the photochemistry of the compound. While the lower-lying triplet SBLCT (or mixed MLCT/LLCT) state should induce a homolytic cleavage of the metal-hydride bond, visible light excitation and population of the singlet MLCT state allow an ultrafast direct dissociative process of the axial CO ligand (Fig. 14), which is completed within 400–500 fs.

C.2. Controlling catalytic activity

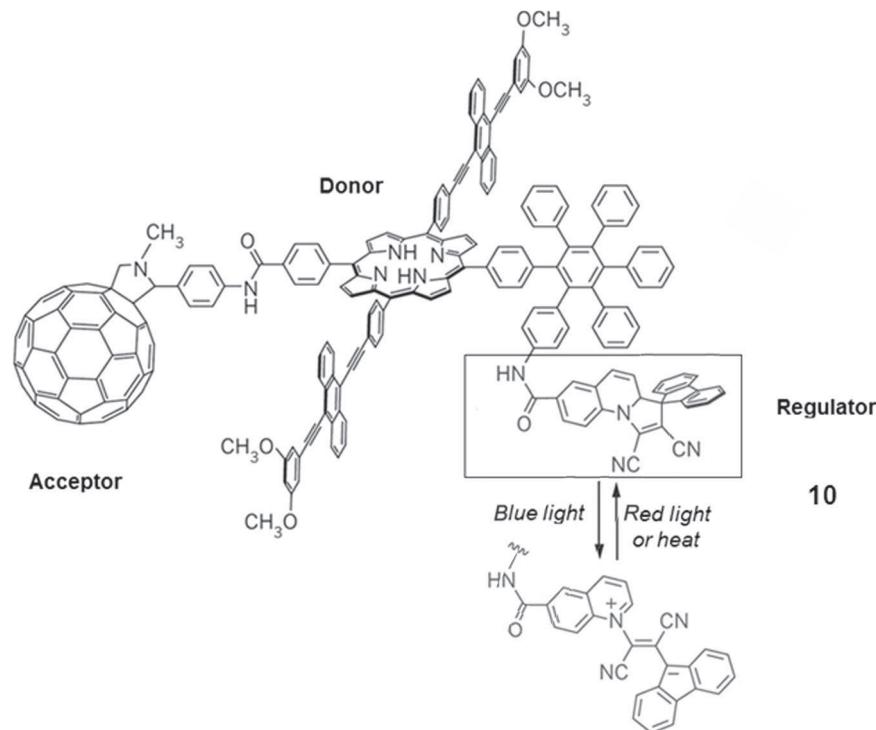
The metabolic functions of living organisms are maintained by a complex interplay of regulatory networks. Enzymatic activity and gene expression are permanently adapted for an optimum performance and may be completely switched on and off in a reversible manner. Typical mechanisms involved in biological systems include the stimulation and inhibition by control proteins or metabolite molecules, allosteric interactions, proteolytic activation, redox transformations, and reversible covalent bond modifications such as phosphorylation and dephosphorylation (5).

p0270 In a similar way, photochemical remote control of chemical and biological processes can serve to mimic or influence important aspects of these natural regulatory systems. The most simple version of deactivation and activation of any photochemical process can be achieved by switching between dark- and light-adapted conditions, which is comparable to the presence or absence of an inhibitor. Photosubstitution reactions of metal complexes and light-induced fragmentation processes can be employed to trigger the signal transduction function of small gaseous molecules and other neurotransmitter substances. Another common strategy is the photochemical cleavage of a light-sensitive protection group to trigger the release of otherwise hidden (so-called caged) bioactive or biomimetic compounds (130,131). The big disadvantage of most of these simple strategies is that the desired function is only available for one time in an irreversible light-responsive process.

p0275 In many types of photocatalytic reactions, however, the variation of incident light intensity is directly related to the actual photostationary concentration of the active species involved (5). This feature can then be easily applied for a certain degree of continuous up- and downregulation of an already running biomimetic processes under ambient conditions. An even higher level of control can be reached, whenever a wavelength-selective response of the system is built in. Some photochromic compounds, for instance, (132) enable a reversible switching of catalytic activity and other types of light-dependent processes. This is a very powerful tool for the construction of biomimetic and bioinspired enzyme models.

p0280 In the field of artificial photosynthetic devices, regulatory strategies could also be advantageous. An interesting recent example for such an approach is given in Fig. 15.

p0285 The multichromophoric system shown above consists of a covalently linked porphyrin–fullerene donor–acceptor core designed for photoinduced charge separation (133). In the periphery, additional aromatic antenna subunits and a photochromic switch are situated. Under intense white-light conditions, the spiro-dihydroindolizine-based regulator subunit **10** opens up to form a larger photostationary concentration of its deeply colored betaine form, which in competition to the donor–acceptor moiety also absorbs in the visible spectral region and efficiently quenches the donor excited state. In a certain sense, this self-regulating molecule mimics the way green plant photosynthesis responds to potentially damaging light levels by controlling the fraction of excitation energy that can drive PET processes.



f0075 FIG. 15. Example of a covalently linked donor–acceptor system featuring a photochromic control moiety (11) for the downregulation of photoinduced electron transfer under intense light conditions. Adapted from Ref. (133).

s0070

III. Design Strategies and Building Blocks

p0290

In the second part of this contribution, we will demonstrate how the basic principles discussed above can be utilized as a starting point for creating artificial biomimetic and bioinspired catalytic and photosynthetic devices. At present, only very few examples of synthetic molecular systems, which are able to replace all important functional aspects of their native counterparts under mild and ambient conditions, have been described in the literature (6), including some important results of our own work. In the last sections of this review, several selected case studies from the author's research efforts in this direction will therefore be presented.

p0295

Here, we will also try to promote our own personal view on the possible roadmap to be followed for a rational development of such light-controlled photocatalytic systems (3,5,8). The first

important step is to analyze the structural and mechanistic details of the natural process to be copied as far as possible. Then, instead of trying to create a synthetic blueprint of all the molecular components involved, the next step should be to define the most fundamental functional requirements for a certain process and to find out, which photoreactive components could possibly fulfill the same kind of function in a more easily accessible way. It is important to note that such a bioinspired design strategy is not at all limited to the bioavailability of certain chemical elements or to the arsenal of biological ligands, which had defined the evolution of the natural systems.

p0300 Once a working model for a functional analogue has been identified and tested, available theoretical concepts can serve as a helpful guideline for optimizing the performance of the biomimetic compounds. This may include more detailed insights in MET reactivity, proton-coupled steps, conical intersections, stereoselectivity, and selection rule constraints including spin catalysis effects. At this stage of the development, the efficiency and selectivity of important mechanistic key steps of biological systems can already be directly compared with the photochemical reactions chosen to copy the same function. Long-term stability criteria, undesired side reactions, and the possibility of light-dependent regulation should be included in the considerations to optimize the synthetic compounds.

p0305 Finally, the best building blocks identified can be coupled in a modular way to complete photocatalytic reaction cycles, which then should be able to mimic a certain biological process. If these bioinspired photocatalytic systems are performing under identical conditions as their native counterparts, a direct comparison of quantitative criteria such as turnover frequencies and the total number of catalytic cycles is possible and should always be the final goal to demonstrate the potential usefulness of the biomimetic process.

s0075 A. IDENTIFYING FUNCTIONAL ANALOGIES

p0310 Nature sometimes solves identical problems at the first glance AU4 with quite different solutions. An important example of such a convergent evolution at the molecular level is the functional parallels between iron and copper centers in bioinorganic chemistry. The dioxygen-carrier proteins of different organisms may, for instance, be based on mononuclear iron tetrapyrrole complexes or in contrast may involve dinuclear copper sites (10). Synthetic chemistry can even go a step further and try to

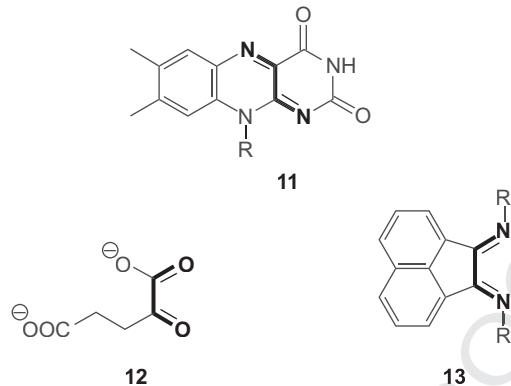
mimic basic biological functions with abiotic building blocks. It is therefore very important to identify and compare different types of molecular entities with an intrinsic functional relationship. Some instructive examples of such a possibility, which may become very useful for biomimetic photochemistry, are given below.

s0080 *A.1. Two-electron redox relays*

p0315 In many biocatalytic systems, the conversion of substrate molecules is accompanied by the transfer of two electrons and two protons. Several different types of organic ligands are able to assist such a catalytic exchange of multiple redox equivalents. They are either directly acting as electron and proton transfer cofactors or may be coordinated to a redox-active metal site. Typical examples in biological systems are quinone and hydrochinone couples which shuttle redox equivalents between different proteins or porphyrin and hydroporphyrin ligands acting as catalytic subunits in oxidoreductases.

p0320 Frequently, such systems undergo reversible structural distortions to better control the redox equilibria and to slow down undesired back reactions. Sometimes, even an irreversible reaction involving cofactor fragmentation is applied to completely shift the redox equilibrium into the desired direction. An important example in this context is the biocatalytic reactivity of α -keto acid-dependent iron enzymes (134), where the two-electron oxidation of ferrous active sites to form iron(IV) oxo species is assisted by a decarboxylation process of the coordinated carbonic acid in the presence of dioxygen. Interestingly, quite similar strategies to utilize the efficiency of irreversible processes and thus to better couple two consecutive one-electron radical reactions are well established in the field of inorganic photochemistry. The classical ferrioxalate system for chemical actinometry based on the irreversible LMCT-induced decomposition of iron-coordinated oxalato ligands (135) and the more recent development of sacrificial two-electron sensitizers for improving the sensitivity of silver halide photography should be mentioned in this context (136).

p0325 The employment of robust aromatic ligand architectures able to introduce the same kind of reactivity in a reversible manner is of course much more desirable. For this purpose, biological redox cofactors such as quinones, porphyrins, flavins, and their functional analogues in biomimetic chemistry contain a built-in butadiene-type moiety as part of their π -electron system, which can be considered as a minimum functional motif for assisting

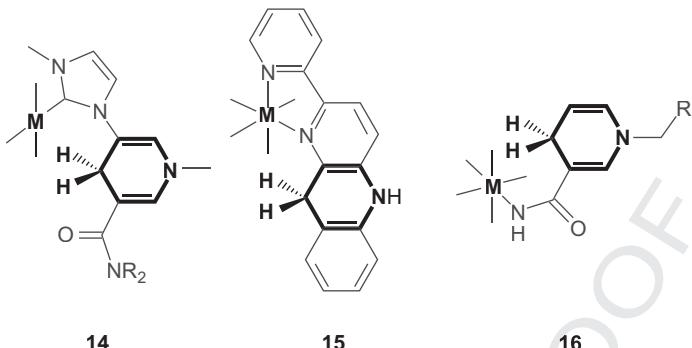


f0080 FIG. 16. Structures of different types of ligands acting as two-electron redox relays in natural and artificial systems: Flavins such as (11) are the essential constituents of flavodoxines and flavoproteins (137). The α -ketoglutarate anion (α -KG, 12) is a typical example of a sacrificial redox mediator which decomposes during catalysis (72). Synthetic chelates such as bis-arylimino-acenaphthene (BIAN, 13) have been proposed for the development of bio-inspired multielectron transfer photosensitizers (138).

the reversible uptake of two electrons and two protons. This property can also be exploited in photochemical model systems involving such types of ligands either directly or in the first or second coordination sphere of redox active metal centers. Some examples of natural and synthetic ligands that can undergo reversible or irreversible two-electron transformations are presented below (Fig. 16).

s0085 A.2. *Hydride transfer shuttles*

p0330 Several enzymes such as reductases and dehydrogenases utilize nicotineamide derivatives as reversible carriers of redox equivalents. The reduced dihydronicotinamide moiety NAD(P)H acts by donating a hydride equivalent to other molecules. In the corresponding two-electron oxidized NAD(P)⁺ form, the cofactor formally accepts a hydride ion from the substrate. Functional models of such reversible hydride transfer processes are of considerable interest for biomimetic chemistry, and the strategies to regenerate nicotineamide-type cofactors are crucial for the performance of many organic transformations involving biocatalytic key steps (139,140).



f0085 FIG. 17. Some examples of organic ligands acting as nicotinamide cofactor mimetics (141–143) with redox-active metals **M** bound to *N*-heterocyclic carbene (**14**), 1,2-diimine (**15**), and amide groups (**16**).

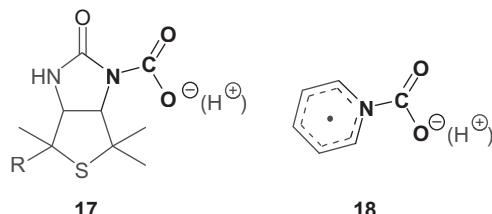
p0335 Efficient photochemical systems based on small molecular synthetic compounds with a ligand-based hydride transfer functionality in close proximity to a metal coordination site are still quite rare. In Fig. 17, some possible ligand architectures described in the recent literature are shown.

s0090 A.3. *Carbon dioxide docking sites*

p0340 Small carbon-containing molecules such as atmospheric CO₂ are considered to be important renewable feedstocks (144, 145). In the context of mankind's increasing demand for carbon-based materials, food, and liquid fuels, the photocatalytic reduction of carbon dioxide under solar light irradiation is an attractive option. Such types of artificial photosynthetic processes could greatly enlarge the possibilities of abiotic CO₂ recycling.

p0345 To activate carbon dioxide for chemical reactions, it is advantageous to fix and destabilize this rather inert molecule. An important strategy to control and influence the reactivity of CO₂ is its coordination to amines, metal-bound imido moieties, or metal centers (144), which leads to a decrease of the CO bond order, while the molecule in most cases becomes considerably bent. In biochemical pathways, the CO₂ adduct of the coenzyme biotin (17) is involved in various carboxylation and transcarboxylation reactions (146). Similar structural motifs could become important functional building blocks for bioinspired photoreactions involving carbon dioxide activation steps (Fig. 18).

p0350 Bocarsly recently described the detailed mechanism of a very interesting photoelectrochemical process with a pyridinium-



f0090 FIG. 18. Ligand architectures for coordinative carbon dioxide activation: structure of the biotin-CO₂ coenzyme (**17**) involved in many biological carboxylations (146). Proposed pyridinium-CO₂ adduct (**18**) accelerating electrocatalytic carbon dioxide reduction processes (147).

catalyzed multielectron reduction of carbon dioxide in aqueous solution (147). An inner-sphere electron transfer mechanism proceeding through coordinative interactions between pyridinium radicals and CO₂-derived species bound to the nitrogen atom of the aromatic heterocycle (**18**) is suggested. A systematic ligand design aiming at an inclusion of this kind of catalytically competent building block might become very advantageous for biomimetic photocatalysis and artificial photosynthetic carbon dioxide conversion.

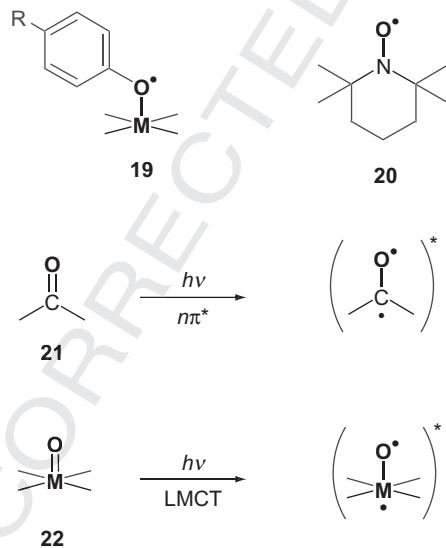
s0095 **A.4. Oxyl radical functionality**

p0355 A widespread structural motif in many biocatalytic oxidations is the presence of electrophilic oxygen species and reactive oxyl radical species in close proximity to preorganized substrate molecules. The most prominent example is the attachment of a Lewis acid-activated water molecule in the second coordination sphere of a high-valent manganese oxygen center, which is supposed to be involved in catalyzing the crucial first OO bond formation step in natural oxygenic photosynthesis (5,148,149). Some monooxygenase enzymes including the versatile hemoprotein catalysts of the cytochrome P450 family (3,150) and the iron- or copper-based enzymes involved in the partial oxidation of methane to methanol are probably operating in a quite similar way (151,152). Also many other kinds of oxidoreductases rely on the intermediate generation of oxyl radicals to accelerate substrate conversion and to overcome rate limiting steps such as hydrogen abstraction in a controlled and efficient manner.

p0360 In earlier work (3), we have already pointed out the striking similarities of such electrophilic oxygen sites and biocatalytic oxyl radical reagents with the electronic structures and

reactivity patterns of certain excited state species. These analogies can be readily exploited for triggering the corresponding substrate transformations in biomimetic photocatalysis. A selection of different building blocks, which, however, can display a very similar chemical reactivity, is given in Fig. 19.

p0365 The functional equivalence between the CT excited states of certain metalloporphyrin photosensitizers carrying a high-valent metal-oxo moiety and the porphyrin radical intermediate supposed to be critically involved in cytochrome P450 oxidations has already been recognized several years ago (155). Indeed, the biological system and the biomimetic photocatalysts display very similar reactivity patterns. In their electronic ground state, the light-driven enzyme models could be readily characterized and studied (3,155). In contrast, despite decades of continuous efforts, a detailed spectroscopic characterization of the Fe(IV)-oxo-porphyrin cation radical thought to be the key intermediate in P450 catalysis has been absent for a long time (153,156).



f0095 FIG. 19. Different ways to introduce oxyl radical reactivity: nature employs metal bound tyrosyl radicals (**19**) or high-valent metal oxo fragments in many active sites (65,153). Nitroxyl radicals such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, **20**) are reactive species used in organocatalysis (154). The excited states of carbonyl functional groups (**21**) and metal oxo-fragments (**22**) display a radical pair character, which may become very attractive for biomimetic photoredox processes upon spectral sensitization (3,5).

p0370 From a mechanistic point of view, the cytochrome P450 enzymes are monooxygenases (150) and therefore they release one molecule of water in every catalytic turnover. As the oxygen atom of the formed H₂O molecule is originating from O₂ reduction, it has been tempting to exploit the fundamental principles of microscopic reversibility and detailed balancing (157,158), and to photochemically drive the catalytic reaction pathways in a reverse direction, thus resulting in a novel type of bioinspired water oxidation process. In fact, it could be shown that the biomimetic MET photocatalysts described above are able to induce an OO bond formation at the metal-oxo site with water as the donor substrate (111). In this context, it is important to keep in mind that a quite similar mechanism at a single metal-oxo site has been proposed for the first step in photosynthetic water oxidation (5,148), which among other possible pathways becomes more and more plausible with the advent of the crystal structure of oxygen-evolving PS II at an atomic resolution (149).

s0100 **B. EMERGING THEORETICAL FRAMEWORKS**

p0375 Once the required functional features for a certain substrate transformation have been defined, individual building blocks such as the structural motifs presented in the previous section have to be combined in a synergistic manner to create an operating photocatalytic system. The choice of suitable metal centers according to their relative atomic energy levels (159), and the fine-adjustment of the different components organized in the coordination sphere of the active site is a very crucial stage of development in biomimetic photochemistry. As already discussed before, a rough guideline for potentially useful combinations of the desired fragments can be derived from electrochemical and spectroscopic data, which may serve to predict the predominant orbital parentage and to estimate the relative energetic ordering of the lowest excited states (Fig. 6). When the first experiments at this stage of development have led to promising results, further optimization of such systems can be guided by an arsenal of emerging theoretical models and unifying concepts.

p0380 Interestingly, there is a current renaissance of classical bond-theoretical models which are able to illustrate the crucial molecular features of complex systems qualitatively by an interpretation of more or less localized fragment orbitals. Straightforward arguments based, for example, on fundamental aspects of ligand field theory or on the interpretation of valence-bond state

correlation diagrams turn out to be extremely useful for the discussion and prediction of reactivity patterns such as radical coupling mechanisms or bond-formation processes between nucleophilic and electrophilic species (160,161). Such types of easily generalized models are very important for the rational design of biomimetic photocatalytic systems, as they are able to directly connect the elementary reactions occurring between reactants, products, and CT excited states in an intuitive and pictorial way (161), which can help to adjust the critical reaction barriers as described already before (Fig. 11).

p0385 With the continuous development of theoretical and computational photochemistry (162,163), also the available quantitative tools for predicting light-induced reactivity are improving rapidly. It is impossible here to cover the immense progress made in this field comprehensively, and therefore, the reader is encouraged to consult and follow the relevant literature. As a starting point, we can only mention a few topics considered to be of prime interest for bioinorganic photosensitization and photocatalysis.

p0390 A lot of valuable information can now be derived from a detailed computational analysis of excited state potential energy hypersurfaces. This includes the location of areas where either an extended touching of two surfaces occurs or surface crossing regions such as funnels or conical intersections exist (164,165). Studying not only the minima of these crossing points but also a broader energetic region along the so-called extended conical intersection seam (166) allows to shape product distributions resulting from branching photochemical pathways, and it is quite clear now that nature makes extensive use of this possibility by exploiting control and selectivity effects induced by the protein environment.

p0395 The construction of valence-bond state correlation diagrams (167) is also a powerful tool for predicting and shaping critical barriers or describing reactivity patterns in homogeneous catalysis. This conceptual approach can be readily adopted for the field of bioinorganic photocatalysis, as low-lying CT excited states are frequently found to strongly mix with the critical transition states of bioinorganic reactions (161,167).

p0400 Another important trend already mentioned in previous sections is the increasing attention to angular momentum conservation and spin catalysis (Fig. 13). Attempts are now also made to find analogies between established semiempirical scales such as the spectrochemical and nephelauxetic series and local spin-philicity parameters included in calculations using spin-polarized conceptual DFT descriptors (168).

Au5

p0405 The requirement of spin conservation also seems to be controlling the rates of energy transfer processes, which is directly relevant for the field of bioinorganic and biomimetic photosensitization. Recently, it could be shown, for example, that spin effects can result in significant changes in the rate of Dexter transfer by up to two orders of magnitude at room temperature (169). Orbital-specific energy transfer in coordination compounds, occurring preferentially from excited states with a favorable dipole orientation, has also been documented (170). These findings especially should be considered for the optimization of all kinds of biomimetic and artificial photosynthetic systems based on polynuclear metal complexes.

p0410 Many other important theoretical concepts of paramount importance for biomimetic photochemistry are still in their infancy. This includes the strategies to mediate and accelerate proton-coupled single and multiple electron transfer catalysis (171–173), and the fundamental aspects of catalytic hydride transfer and hydrogen tunneling processes (174–176) among several others.

s0105 C. PHOTOCHEMICAL MODELING OF KEY STEPS

p0415 Various basic reaction sequences occurring in biological systems can actually be simulated and completely replaced by biomimetic model systems containing light-responsive metal complexes as their active components. Only a few illustrative examples of this strategy will be given below, which have been selected according to our own research interests.

s0110 C.1. Charge separation

p0420 The primary processes in natural photosynthesis involve the conversion of solar into electrochemical energy (6,8). Light absorption by antenna chromophores is followed by energy transfer to a reaction center, where the initial charge separation takes place. Enormous efforts have therefore been made by many research groups to create artificial photosynthetic reaction center models, which are able to integrate light-harvesting and PET properties in large and complex molecular assemblies (177–179). A main goal in this field had always been the formation and spectroscopic characterization of long-lived charge-separated states. Coupling of such systems to catalytic sites where multielectron redox processes can occur, however, was largely neglected. Nature has solved this crucial problem by

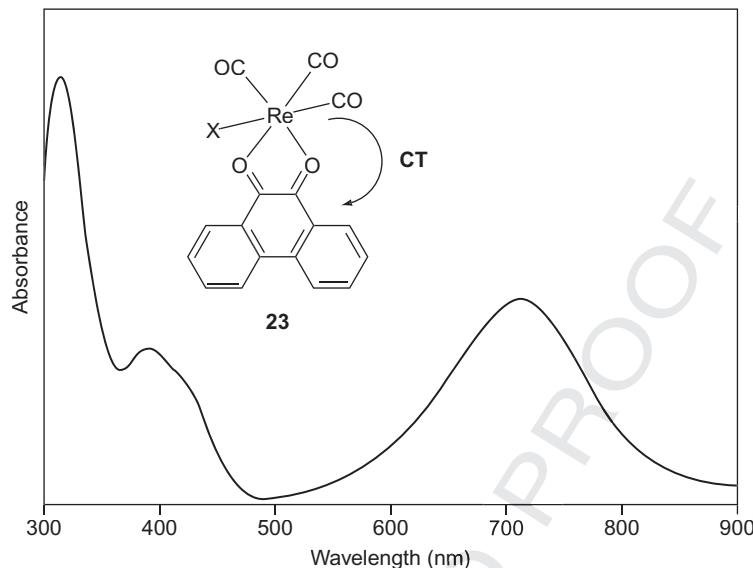
employing quinone cofactors as the primary electron acceptors in photosynthetic reaction centers, which helps to avoid unproductive charge-recombination processes (180).

p0425 From a functional point of view, this important property can be readily built into low molecular weight chromophore assemblies acting as artificial reaction centers (6). In simple coordination compounds, the population of CT states is directly related to the concept of light-induced charge separation in photosynthesis. Whenever such CT states are photoreactive and lead to the formation of the same kind of permanent redox products as observed in photosynthesis, the most essential features of the primary light reactions have been successfully duplicated. In a more strict sense, this is of course only true, if actinic red or NIR-light of comparable wavelength is absorbed by both the natural and artificial photosynthetic systems.

p0430 Biologically relevant electron acceptors such as quinones are able to act as redox-active chelate ligands (181,182). Frequently, a coordination of these cofactors leads to intensely colored metal complexes with low-lying CT excited states. With such types of inorganic chromophores, very simple functional model compounds for mimicking the charge separation cascade in photosynthetic reaction centers can be constructed. As an illustrative example (181), the organometallic rhenium complex **23** carrying a loosely coordinated 9,10-phenanthrene-quinone (PQ) moiety is presented here (Fig. 20). The deeply colored compound $[Re^I(PQ)(CO)_3Cl]$ contains a low-valent diamagnetic metal site which can replace the PET functionality of the primary donor of photosynthetic reaction centers, which usually consists of a special pair of chlorophyll pigments (6). At the same time, this compound carries a preorganized quinone cofactor, which can mimic the functional role of the rigidly orientated primary quinone acceptor Q_A present in the PS II-type reaction centers (180). The very simple biomimetic system **23** displays a broad and intense CT band in the visible and NIR-spectral region, which has been assigned as a MLCT transition (181). Interestingly, the maximum of this band at around 711 nm is almost coinciding with the NIR absorption features of the recently discovered cyanobacterial light-harvesting pigment chlorophyll *f*, which is now believed to represent nature's best choice to match the intrinsic threshold wavelength limits required for oxygenic photosynthesis (95).

s0115 *C.2. Oxygen activation*

p0435 Modeling the active site features and the mechanistic key steps occurring in biological dioxygen activation is one of the most

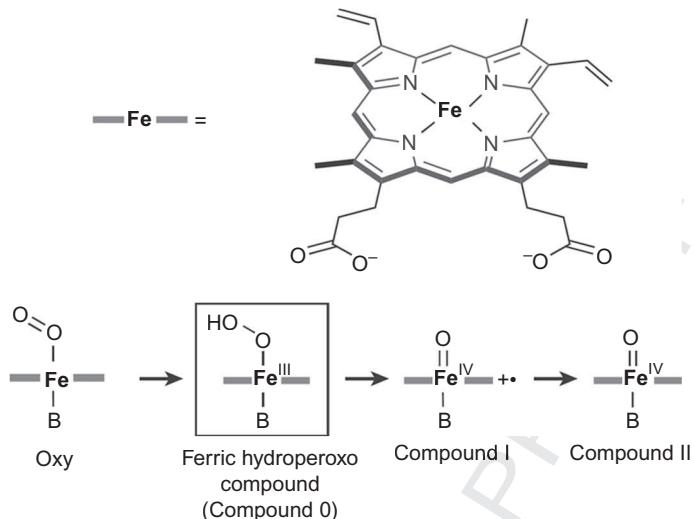


f0100 FIG. 20. Electronic spectrum of a rhenium(I) carbonyl complex (**23**) featuring an optical charge transfer transition at $\lambda_{\text{max}}=711$ nm involving a coordinated quinone acceptor ligand (181).

important topics in biomimetic chemistry (183). Detailed knowledge about O₂ activation at metal sites opens the scene for highly selective bioinspired substrate conversions with novel types of redox catalysts. These properties are highly relevant for many environmentally benign technological processes using dioxygen molecules from ambient air as their only oxidant. The investigation of functional chemical models for critical reaction intermediates involved in bioinorganic redox processes of reactive oxygen species is therefore of prime interest for bioinorganic photochemistry.

p0440 Nature uses many different types of metalloproteins for the binding, transportation, and controlled activation of oxygen (10, 13). An extremely versatile catalyst system is present in the biochemistry of iron-containing heme enzymes (Fig. 21).

p0445 The reaction sequence at the heme active site starts with the binding of unactivated triplet dioxygen forming the so-called oxy–heme complexes. The iron center in O₂-activating heme enzymes is then thought to be converted into a peroxy anion species. It can be protonated to form a ferric hydroperoxy intermediate usually termed compound O (183), which is a crucial reactive species in catalase and peroxidase enzyme catalysis (Fig. 21). These hydroperoxy intermediates of hemoproteins are important



f0105 FIG. 21. Typical intermediates in hemoprotein enzyme active sites. The iron protoporphyrin IX cofactor (heme) forms dioxygen adducts termed oxy-species. In the course of oxygen activation and catalytic redox transformations, the oxy form can be consecutively converted into hydroperoxo- and oxo-type intermediates, which are usually referred to as compound 0, compound I, and compound II. Reproduced with permission from Ref. (183). Copyright Nature Publishing Group.

precursors for more highly oxidized iron–oxygen species which are formed in the course of an OO bond cleavage process starting from compound 0. Among those powerful oxidizing catalyst species are the Fe(IV)-oxo-porphyrin cation radicals referred to as compound I (156), and the closely related compound II species (183), which are also acting as very versatile and strong oxidants (Fig. 21).

p0450 Although the knowledge about metal-mediated dioxygen binding and activation has grown immensely within the past decades, there are not many examples of functional biomimetic systems which are able to transfer O-atoms directly from dioxygen to substrate molecules (184). With only a few exceptions including some copper peroxy complexes (185), most of the reported model compounds and active species are only observable and functional at low temperature, which makes them quite impractical for synthetic oxidative transformations. Several years ago, we have therefore started to search for more robust photochemical model compounds that can be applied in biomimetic dioxygen activation and light-controlled substrate oxidations under ambient conditions (155).

p0455 For certain reasons described elsewhere in more detail (8,93), our first choice fell on the combination of tetrapyrrole photosensitizers including porphyrins or phthalocyanines with redox-active group 14 and group 15 elements such as tin, lead, antimony, or bismuth. Close relationships between the electronic structures of low-valent group 15 metalloporphyrins and the reduced heme groups of cytochrome P450 and chloroperoxidase enzymes had already been recognized before by a comparison of their absorption and magnetic circular dichroism spectra (186). Functional similarities with the hemoproteins were also reflected by the facts that the tin complex of protoporphyrin IX is able to act as an efficient competitive inhibitor of heme oxygenase (187), and that lead compounds are blocking the natural metallation process of protoporphyrin IX catalyzed by heme synthetase (188).

p0460 By studying the catalytic properties of a series of antimony(III) porphyrin complexes in the presence of dioxygen, it could be demonstrated that the reactivity of these compounds toward O₂ activation can be triggered and controlled by light activation (155). A MC sp-excited triplet state of the low-valent main group metal center has been identified to be responsible for this photo-reactivity. The population of the dioxygen activating state can be spectrally sensitized by the coordinated porphyrin antenna chromophores, which allows the controlled generation of oxy- and hydroperoxo-metalloporphyrin species with long-wavelength visible light. It could also be shown that catalytic two-electron photoredox processes involving reactive metallocporphyrin species with a direct functional analogy to the hemoprotein compound 0 and compound I intermediates shown in Fig. 21 are involved in the substrate transformations catalyzed by these visible light-driven metalloenzyme models. These compounds, for example, display cytochrome P450 and chloroperoxidase-type reactivity under visible-light and solar irradiation (3,155,189,190).

p0465 More recently, we have continued to study this interesting kind of bioinspired photocatalysis and expanded our studies toward metallocorrole compounds (Fig. 22), as it is well established that these ring-contracted macrocycles tend to stabilize the formation of high-valent metal complexes (192). This strategy for the first time in tetrapyrrole chemistry opened the possibility to create high-valent lead(IV)- and bismuth(V)-oxo species as potential redox catalysts, which are currently investigated in our group (191,193). The molecular structures of the heme compound 0 and compound 1 analogous species **24** and **25** obtained in the course of biomimetic oxygen activation

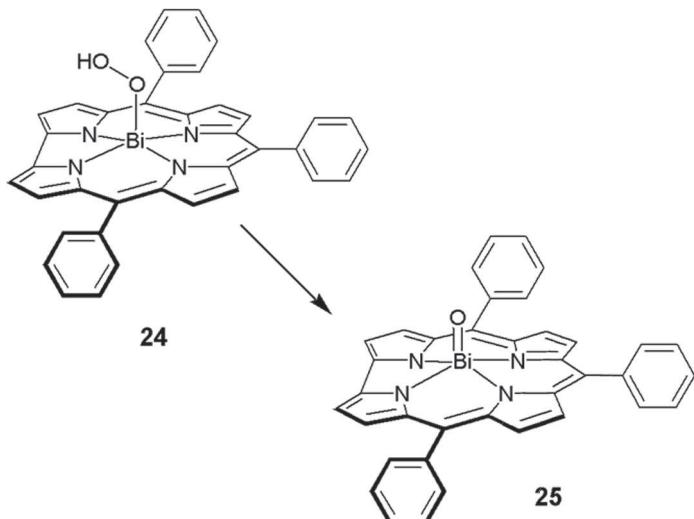


FIG. 22. Structures of hydroperoxo- and oxo-derivatives of bismuth triphenylcorrole photosensitizers (191).

photoreactions of the corresponding bismuth corrole catalysts are shown in Fig. 22 (191). In this context, it is very interesting to recall the CT properties of high-valent metal-oxo moieties (Fig. 19), which could proof to become very versatile tools for catalyzing the OO bond formation step in bioinspired artificial photosynthetic water oxidation schemes (111,193,194).

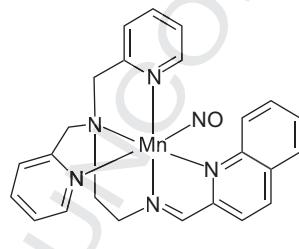
C.3. *Hydrogen atom transfer*

Controlled radical reactivity and H-atom abstraction from substrates are common features of many metalloenzymes (112,195). Photochemical strategies can be successfully applied for modeling the biocatalytic transformations involving protein radicals (3,196). For example, one of the possibilities to achieve CH bond activation of inert compounds under mild and controlled reaction conditions is to create unpaired spin density at an oxygen atom accessible to the substrate, which should also be preorganized in the microenvironment of this active site. In bioinorganic photochemistry, this can be achieved by introducing oxyl-radical type photoreactivity in low-lying excited states as discussed in the previous sections (Fig. 19). The fundamental design criteria for such types of biomimetic systems based on MET photosensitizers carrying terminal oxo-functionalities and radical-stabilizing cofactors have already been described in more detail elsewhere (3,5).

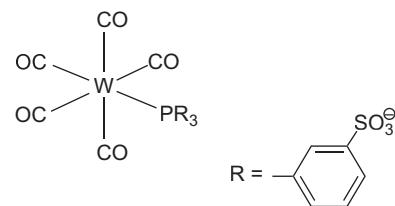
s0125 *C.4. Release of bioactive molecules*

p0475 The selective activation of compounds with potential therapeutic effects and the controlled delivery of bioactive molecules triggered by light are topics of intensely growing interest (6,197–200). Besides the search for light-sensitive prodrugs activated by photochemical cleavage, isomerization or photoredox processes (201–203), especially the release of small molecules such as NO, CO, CS₂, and H₂S, have attracted a lot of interest in the past years (204–208).

p0480 Inorganic photochemistry offers all the necessary tools required for the design and optimization of such systems. The typical reactivity patterns observed for photoexcited transition metal complexes can be readily exploited for the controlled delivery of therapeutically relevant compounds from physiologically inert precursor species. Such a process was for the first time described in the nineteenth century, when Haldane discovered by serendipity that the dioxygen binding activity of inactivated carboxy-hemoglobin (COHb) was regenerated by the rapid dissociation of CO upon exposure to sunlight (209). Today, the basic features of inducing this kind of reactivity are very well settled (210,211), and current research efforts can focus on the optimization of the required molecular properties such as bioavailability, solubility, drug-targeting strategies, and photoreactivity in the therapeutically reasonable spectral regions including the improvement of two-photon absorption cross sections or NIR-photosensitivity. The structures of two recent examples of a photoactivated NO-delivering transition metal complex sensitive to NIR light (**26**) and a water soluble organometallic compound (**27**) which was tested for the controlled photorelease of CO are shown in Fig. 23. Efforts in our own group currently focus on



26



27

f0115 FIG. 23. Examples of photolabile nitrosyl (**26**) and carbonyl complexes (**27**) that have been suggested for the light-triggered release of nitric oxide (212) and carbon monoxide (210).

the sensitization of related CO-releasing molecules (CORMs) into the red and NIR spectral region to be able to better match the phototherapeutic window of mammalian tissue (213).

s0130

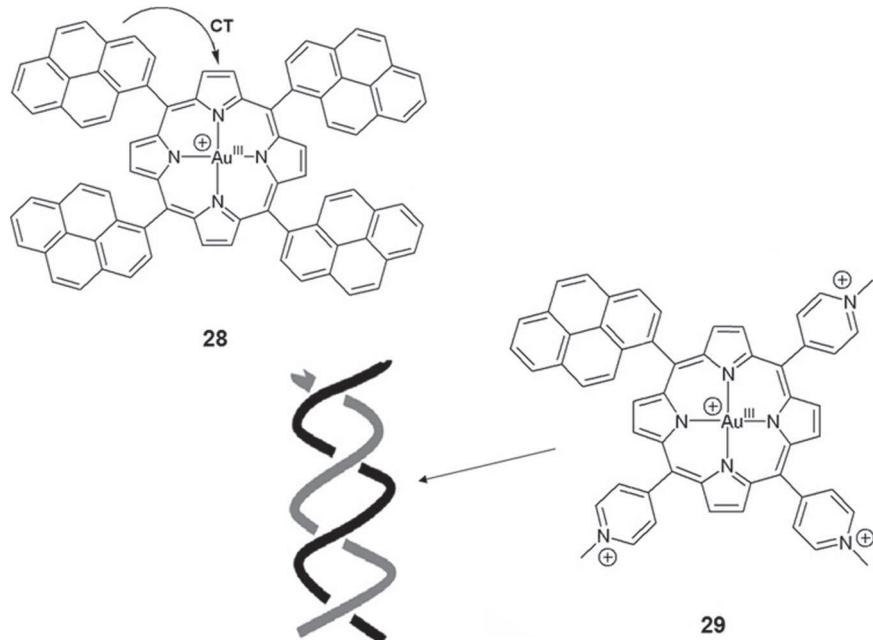
IV. Selected Applications

p0485 Despite the obvious versatility of light-activated key steps and their numerous advantages for the biomimetic modeling of natural systems, up to now, only very few examples are known, where such types of photosensitized processes have been successfully combined to complete reaction cycles with reasonable catalytic turnovers (6). In the last section, we are therefore briefly presenting two case studies which describe some recent work performed in our own group focusing on bioinspired catalytic systems that can be controlled and driven by visible light.

s0135 A. TOWARD ARTIFICIAL ENDONUCLEASE ACTIVITY

p0490 Synthetic compounds able to induce selective damage or scission of DNA strands in a controlled fashion are of prime interest for molecular biology and genetic engineering and for the design of specific diagnostic or chemotherapeutic agents. Therefore, chemical nuclease mimics have actually been among the first examples of bioactive model compounds triggered by light (214). The interactions with DNA or nucleobases observed with most of these systems, however, are not operating in a catalytic way, and a reversible regulation of DNA strand cleavage activity with chemically modified restriction enzymes has only recently been reported (215). Natural endonucleases are acting as a kind of molecular scissors which can recognize short DNA sequences and cut the phosphodiester bonds of the double helix close to their target sites, which leads to a complete double-strand cleavage.

p0495 Several years ago, we have started to explore the possibilities of selective catalytic nucleic acid damage and light-triggered DNA cleavage with bioinspired metalloporphyrin photocatalysts (216). In this context, the cationic porphyrinato gold complex **28** shown in Fig. 24 was synthesized as a novel type of potentially tumor localizing electron transfer sensitizer. The choice of the high-valent central metal and the additional aromatic substituents was guided by several reasons. First of all, gold(III) porphyrins were already established as excellent electron acceptors, which should make their low-lying excited states



f0120 FIG. 24. Structures of cationic gold porphyrins which can bind to DNA and display photocatalytic nucleobase damage and double-strand cleavage controlled by visible light absorption (216,217).

well-suited for an oxidative nucleobase damage involving PET steps. Further, we speculated about possible synergistic effects, as the biological activity of gold-based drug compounds had already been studied for more than one century (218). Indeed, it turned out in the mean time that gold porphyrin complexes depending on their detailed ligand structures display several promising *in vitro* properties, which seem to indicate a bright future as drug candidates for variety of therapeutic applications (219).

p0500 The attachment of the pyrenyl substituents in the ligand periphery of **28** was chosen to supply a functional domain that could act as an anchor group with a pronounced affinity for DNA binding and intercalation. This kind of functionalization of the gold(III) porphyrin core structure also introduced novel excited state levels, which led to the occurrence of additional intramolecular CT interactions (216). Thus, excitation of the complex **28** with visible light resulted in a direct optical electron transfer process generating a charge-separated state with a pyrenyl radical cation functionality in the molecule periphery and a reduced gold porphyrin center. The redox properties of this

excited state opened the possibility of a selective photodamage of the purine nucleobase guanine (G) under long-wavelength irradiation which should also operate well under hypoxic conditions. When **28** was irradiated in the presence of nucleobase substrates, a photocatalytic oxidative degradation of guanine could be demonstrated. A quantum yield of $\phi=0.03$ measured for 436-nm photolysis and an initial turnover frequency of $TOF=66 \text{ h}^{-1}$ was estimated for guanine degradation. At the same time, a maximum number of approximately 700 turnovers for each photosensitizer molecule were observed (216).

p0505 Despite these very interesting photocatalytic properties of the gold complex **28**, this compound still had several disadvantages such as moderate water solubility and the existence of atropisomeric mixtures under physiological conditions due to a hindered rotation of the pyrenyl substituents. Therefore, we decided to improve some crucial properties of the system and synthesized the novel gold(III)porphyrin complex **29** (217). This compound no longer can form isomeric mixtures and exhibits an excellent water solubility, while keeping one functional pyrenyl group attached. The presence of four positive charges leads to a modification of the possible electrostatic interactions with nucleic acids. Spectroscopic studies revealed that **29** interacts with A-DNA and B-DNA and displays outside binding with self-stacking to DNA duplexes. The modified gold(III) porphyrin sensitizer shows light-induced guanosine and 5'-dGMP oxidation under aerobic and anaerobic conditions. Light-triggered plasmid DNA nicking and photocatalytic double-strand cleavage of oligonucleotide duplex DNA are possible with this artificial photonuclease (217). Tumor cell line tests and related studies on other gold(III) tetrapterroline photosensitizers including substituted corrole complexes are currently underway.

s0140 B. LIGHT-DRIVEN MODEL ENZYMES IN CATALYSIS

p0510 One of the most challenging areas in inorganic photochemistry is to catalyze the synthesis of valuable and energy-rich compounds from abundant raw materials and sunlight. In this context, the development of homogeneous photocatalysts which are able to completely replace the function of natural enzymes for synthetic applications is a highly desirable goal (5,18). As one of the rare examples of such a synthetic model photoenzyme system controlled and driven by visible light, we have chosen an artificial oxidoreductase catalyst investigated in our own group which has already been described in detail elsewhere (3,6).

p0515 The conception of this functional enzyme mimetic is based on a combination of several individual key steps already discussed in the previous sections. A closed photocatalytic reaction cycle in homogeneous solution could be successfully constructed by coupling a series of complementary functions including bioinspired dioxygen activation with photoexcited main group metals (Fig. 22), hydrogen atom abstraction, controlled formation of substrate radicals with photoactivated metal-oxo species (Fig. 19), and an efficient long-wavelength spectral sensitization of the catalytic system with tetrapyrrole macrocycles acting as robust antenna chromophores (Fig. 8).

p0520 The selective transformation of alcohols into carbonyl compounds with this kind of artificial oxidoreductases has been directly compared to a series of native enzymes performing under identical reaction conditions (3). In the dark-adapted form of the photocatalyst, which is a high-valent antimony porphyrin complex, the alcohol substrates are already preorganized by hydrogen bonds in the second coordination sphere of the active site. The system displays a certain extent of pH-controlled substrate selectivity, which makes competitive secondary reactions involving the reaction products less favorable. Substrate conversion can be completely switched off in the dark and is readily regulated by variations of light intensity. The system performs under very mild reaction conditions at room temperature and ambient pressure in aqueous solution utilizing dioxygen from air as a two-electron acceptor. Sunlight or even diffuse daylight with a threshold wavelength of approximately 600 nm is activating the catalyst for substrate conversion, which occurs at a rate of $k_{\text{cat}} = 0.05 \text{ s}^{-1}$ corresponding to a turnover frequency of $\text{TOF} = 180 \text{ h}^{-1}$ under $\text{AM} = 2.0$ solar irradiation conditions (3). A product formation quantum yield of $\Phi = 0.02$ has been determined for monochromatic visible light irradiation at 546 nm. Gradual degradation of the quite robust photocatalyst occurs with a quantum yield of $\Phi \leq 3 \times 10^{-5}$, which is in a typical stability range of natural tetrapyrrole pigments such as chlorophylls and corresponds to an average turnover number of at least 4000 productive photoredox cycles for each catalyst molecule.

p0525 The most significant and surprising result of this proof of principle study was the fact that even with such a simple MET photosensitizer system powered by sunlight, a very promising biomimetic performance with reaction rates up to three times higher than that of the natural metalloenzymes catalyzing exactly the same process in the absence of light could be achieved (3,5). Further systematic activities heading in this direction are therefore certainly worthwhile.

s0145

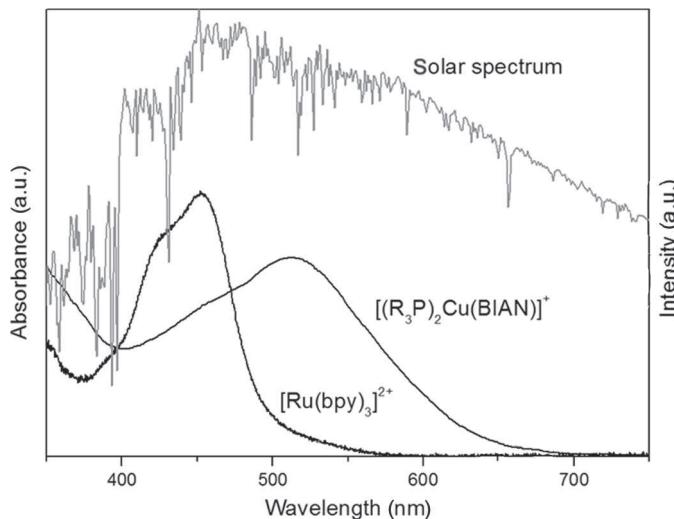
V. Concluding Remarks

p0530 Photoreactivity is a common feature of many components of biological systems and their synthetic functional counterparts. The important role of inorganic photochemistry and photocatalysis as a versatile tool for triggering, driving, and controlling molecular processes by light will therefore certainly be further increasing in the near future.

p0535 In this chapter, a unifying description of the most important bioinorganic chromophores and their light-induced properties has been provided. An attempt has been made to collect some general guidelines for the rational design of biomimetic and bioinspired systems based on photoreactive inorganic compounds, which are key constituents of artificial photosynthetic devices, functional enzyme mimetics, and light-sensitive reagents for the controlled release of physiologically active species. Processes based on this kind of photoresponsive molecules inspired by nature are of crucial relevance for many cross-disciplinary research fields and provide a solid foundation for numerous applications at the borderlines of chemistry, biology, and medicine (5,6). At present, however, there are only a few pioneering studies demonstrating the power of this novel approach, which have already supplied a convincing proof of principle for the fascinating new research fields of *bioinorganic photochemistry* and *biomimetic photocatalysis* founded about a decade ago (3,8). We hope that our current review will be able to stimulate further research efforts in this direction.

p0540 Besides novel frontiers in photosensitization and photocatalysis in the context of bioinorganic systems, the photophysics and photochemistry of inorganic materials also continue to be the central discipline in the field of solar energy conversion and renewable fuel production (87,220). One of the main future challenges in this direction will be the search for much more versatile types of photosensitizers with improved properties such as intrinsic MET reactivity and light-absorption characteristics optimized for solar chemistry. Further, in the long run, the construction of more efficient systems for powering photocatalysis and artificial photosynthetic energy storage has to be achieved with sustainable, environmentally benign and earth-abundant building blocks (220,221). An example illustrating the suggested way to follow (138) is given below (Fig. 25).

p0545 The widely applied class of photosensitizers derived from the tris(2,2'-bipyridyl)ruthenium(II) cation $[\text{Ru}(\text{bpy})_3]^{2+}$ (101) is based on one of the rarest metals on earth. Many high-valent compounds of the platinum group metal ruthenium are further



f0125 FIG. 25. Comparison of the sunlight harvesting features of tris(2,2'-bipyridyl)ruthenium (**9**) and a copper-based multielectron transfer photosensitizer (**138**) carrying a π -acceptor ligand of the BIAN-type (**13**) already described in Fig. 16.

regarded as toxic or carcinogenic, and reactions involving ruthenium complexes should therefore be considered at least as environmentally problematical. Moreover, $[Ru(bpy)_3]^{2+}$ derivatives absorb only a limited share of the photochemically relevant region of the solar spectrum, and the photoinduced primary processes of such compounds are typically limited to one electron chemistry, which requires further coupling to other redox-active components acting as mediators for multielectron transformations (173).

p0550 In contrast, bioinspired compounds such as the copper diimine complex shown in Fig. 25 have been suggested as a versatile and readily tunable alternative to conventional sensitizers used today for various photocatalytic applications, artificial photosynthetic devices, and dye-sensitized solar cells (138). It combines some of the highly desirable features such as long-wavelength absorption well adapted to the solar spectrum and intramolecular coupling of the low-lying excited states to an acceptor ligand providing a preponderance for multielectron reactivity. Further, the compound exclusively consists of abundant and environmentally benign building blocks including a biocompatible redox-active transition metal.

p0555 The current state of the art in inorganic photochemistry already offers a large number of possibilities for the development of such alternative approaches. Additional inspiration from natural systems collected in the novel field of bioinorganic photochemistry will certainly lead to further valuable input in this direction. Many other important aspects of biological systems such as the development of self-repair mechanisms to assure a prolonged catalyst lifetime or the control of the microenvironment of active sites by second coordination sphere interactions should also be considered to create robust, selective, and environmentally benign photosensitizers and photocatalysts (3,5).

p0560 One of the most fascinating aspects of the photochemical approaches in biomimetic chemistry presented in this review is that abiotic reagents are able to accelerate the same overall reactions as biocatalysts in a very promising way. This type of chemistry might even allow to develop systems “realizing processes that enzymes do not perform while displaying comparable high efficiencies and selectivities” (222). In the context of artificial photosynthesis and solar fuel production, scientists are now collaborating to find out if they can “beat nature at her own game” (223). Bioinorganic photochemistry has already set the stage for this demanding goal, and we are looking forward to the photochemistry of the future (224).

st0160

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