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Photocatalytic reactions of porphyrin-based multielectron transfer sensitizers[1]

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Contents

Abstract

Individual metal centers assisted by redox-active ligands can serve as active sites for photocatalytic multielectron transfer (MET) substrate transformations. In porphyrin-based mononuclear systems, the primary steps of excitation and charge stabilization are mediated by the tetrapyrrole ligand acting both as photosensitizer and intermediate charge reservoir. Accumulation and transfer of multiple redox equivalents requires a binding site that provides at least two stable oxidation states separated by more than one unit. The reversible photoconversion between low- and high-valent antimony porphyrins is described as an example of MET sensitization. © 1998 Elsevier Science S.A.

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1. Introduction

Multielectron transfer catalysts are the desired key components in several current fields of coordination compound research including small molecule activation,

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[1] Dedicated to Professor Arnd Vogler on the occasion of his 60th birthday.

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Table 1
Calculated redox potentials of some reactions relevant to water oxidation [8]

Elementary reaction	E_c (V)
$H_2O \rightarrow {}^{\cdot}OH + H^+ + e^-$	3.225
$OH^- \rightarrow {}^{\cdot}OH + e^-$	2.191
$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	1.931
$2OH^- \rightarrow H_2O_2 + 2e^-$	0.896
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	1.401
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	0.367

electrocatalysis, fuel cell applications and chemical conversion of solar energy [1–7]. The crucial advantage of collecting redox equivalents is to *avoid free radical reaction pathways*, as these processes decrease both the long-term stability and the overall efficiency of any catalytic redox system. This is illustrated for water oxidation chemistry by the pH independent configurational potentials E_c [8] given in Table 1. As can be seen, the energetic situation improves with the number of electrons exchanged. The single electron transfer reactions demand the highest redox potentials, while at the same time destructive hydroxyl radicals are formed. Pathways involving a two- or four-electron oxidation of deprotonated water molecules are thermodynamically most favored.

Light-induced substrate transformations in natural and artificial photosynthesis depend strongly on the feasibility of multielectron transfer catalysis. For example, the fixing of carbon dioxide by the following four-electron process allows for long-wavelength spectral sensitization down to a photon energy of 1.3 eV [9] corresponding to a threshold absorption at about 950 nm:

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad (1)$$

In contrast, a minimum energy of 3.6 eV (340 nm) is needed to drive the reaction in highly unfavorable one-electron couples [4], and two thirds of the solar irradiation suitable for fixing CO_2 is wasted.

The basic principles and limiting constraints of biological energy conversion [10,11] can serve as a guideline for the development of artificial photosynthetic redox systems. A perfect coupling of *light-absorption, energy transfer* to a photoreactive center, as well as *separation, stabilization and accumulation of charges* is necessary in order to induce multielectron reactivity at a substrate recognition site (Fig. 1). As will be shown, coordination compounds offer a broad range of potentialities for modeling all of these functions.

2. The design of multielectron transfer (MET) reagents

Evolution of life on earth has resulted in a diverse array of inorganic cofactors and prosthetic groups that enable redox enzymes to overcome the difficulties of MET catalysis [12–14]. In Fig. 2, the various ways in which metal ions (M) may

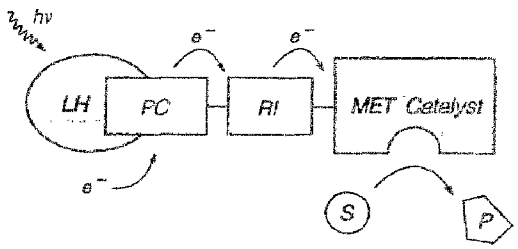
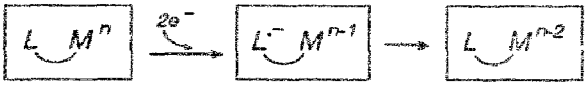


Fig. 1. Schematic representation of a photosystem combining a light-harvesting subunit (LH), a photoreactive core (PC), a redox interface (RI) and a multielectron transfer (MET) catalyst to mediate the selective transformation of substrate molecules (S) into permanent photoproducts (P).

(a) polynuclear systems with cooperating metal sites

(b) redoxactive ligands as intermediate charge reservoirs



(c) atom or group transfer reactions

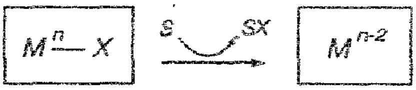


Fig. 2. Representation of the possible strategies to accumulate multiple redox equivalents using polymetallic (a) or mononuclear coordination compounds (b,c).

perform this task are sketched for an arbitrary two-electron oxidation process. A widespread strategy followed in both biological and artificial systems is the storage of charges at polynuclear active sites [2,6,14–21]. On the other hand, mononuclear metal complexes can act as efficient MET reagents whenever additional redox equivalents are supplied by an organic ligand (L) [14,22–24], or when the complete transfer of a coordinated fragment (X) is possible [25–27]. Frequently the substrate molecules (S) themselves are involved as ligands or are attached by hydrogen bonding in the course of their transformation.

The catalytic disruption and formation of chemical bonds resulting in permanent redox products requires a *reversible cycling between at least two stable formal oxidation states* of the system, while at the same time the cage-escape of metastable radical intermediates must be suppressed. In metalloenzyme catalysis this delicate kinetic balance is thought to be controlled by additional strain energy imposed by the protein fold [28]. A comparable situation may be achieved by the photochemical

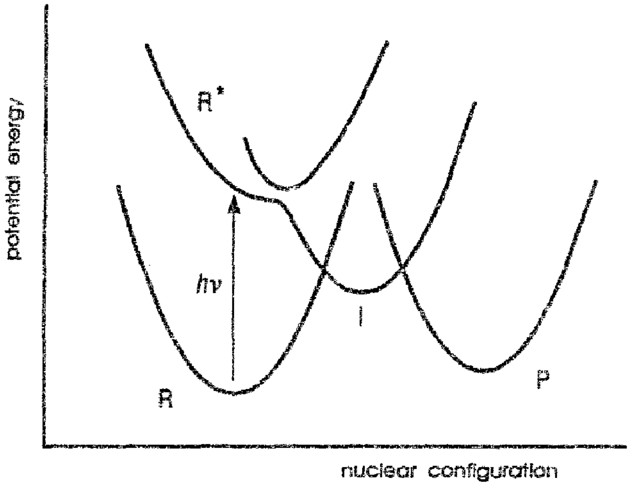


Fig. 3. Three-welled potential energy diagram for a net two-electron transfer process between reactants (R), metastable one-electron intermediates (I) and products (P). Activationless photoinduced electron transfer is facilitated by a strong electronic coupling between the surfaces of the excited reactant assembly (R*) and the intermediate state.

activation of a light-sensitive metal complex. The promotion of an electron in a transition involving predominantly metal-localized orbitals of a coordination compound [29,30] can be regarded as a straightforward method to change the formal oxidation state at a certain substrate binding site. However, an overall double electron transfer [31] may be triggered only when the photoinduced primary step leads to an energy-rich intermediate state that tends to undergo rapid stabilization by a second ET process competing with back electron transfer. This situation is visualized in Fig. 3, following the established concepts of single electron transfer theory [32]. A maximum probability for the desired MET cascade should occur when the reacting centers are in close proximity, the orbital symmetries are favorable, and the nuclear coordinates of the excited state involved are already distorted toward the product geometry (adiabatic electron transfer [15,32]).

Photoactive *main group metal centers* [33] are the smallest of all possible building blocks for the design of redox systems that can be characterized by the type of potential energy diagram depicted in Fig. 3. In *combination with charge stabilizing ligands* the thermodynamic accessibility and kinetic reactivity of odd-electron intermediates in main group chemistry [34,35] allows the tailoring of mononuclear multielectron transfer catalysts.

3. Porphyrin-based MET photosensitizers

Porphyrins and related tetrapyrrole compounds represent the most important class of sensitizers in both natural and artificial photosynthesis [36]. In addition to

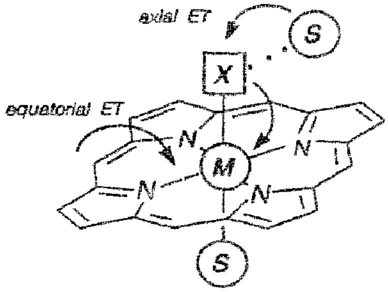


Fig. 4. Substrate binding sites and electron transfer pathways in metalloporphyrin complexes.

their excellent light-absorption properties, they are very versatile chelating reagents. Porphyrin ligands are able to complex almost every metal and several other elements of the periodic table [37]. In many cases low- and high-valent states of a coordinated central atom are stabilized. The axial positions of metalloporphyrin complexes play a crucial role in the reversible binding and activation of substrates (Fig. 4). By a variation of substituents the redox properties of synthetic porphyrin derivatives are readily tuned over a broad range of potentials [38–40]. The relative rigidity and the extensive delocalization of the macrocyclic ring tend to minimize the inner-sphere reorganization energy [31] associated with an equatorial electron transfer (Fig. 4), which therefore is a very rapid process [41]. Acting as intermediate charge reservoirs, porphyrin ligands are predestined to support multistep redox reactions involving electrons of the central atom and its axial coordination sphere. Many of these features have been exploited in synthetic MET catalyst systems based on mono- or polynuclear tetrapyrrole derivatives [6,22,24,42–45].

Certain metalloporphyrins achieve an efficient fusion of the complementary functions of a light-harvester, a photoredox interface, a substrate recognition site and a mediator of chemical reactions. In this case a single catalyst molecule combines all the components needed for the development of an artificial photosynthetic reaction center (Fig. 1). Such compounds that rely on static spectral sensitization [46] in order to trigger the homogeneous photocatalytic [47–49] multiple electron redox transformation of substrate molecules have been termed *multielectron transfer (photo)sensitizers* [22]

4. Antimony porphyrins in photocatalytic MET reactions

Considering the accessibility of their formal oxidation states [50], tin, lead or antimony porphyrins are the logical starting points for the design of MET photosensitizers using tetrapyrrole type ligands and redox-active main group elements. The antimony complexes are ionic, either $[(L)Sb^{III}]^{+}Y^{-}$ or $[(L)Sb^{V}(X)_{2}]^{+}Y^{-}$, where X^{-} denotes an anionic axial ligand, Y^{-} is a counterion, and L^{2-} stands for the corresponding porphyrinato ligand.

While long-term photocatalytic applications of tin and lead porphyrins are ham-

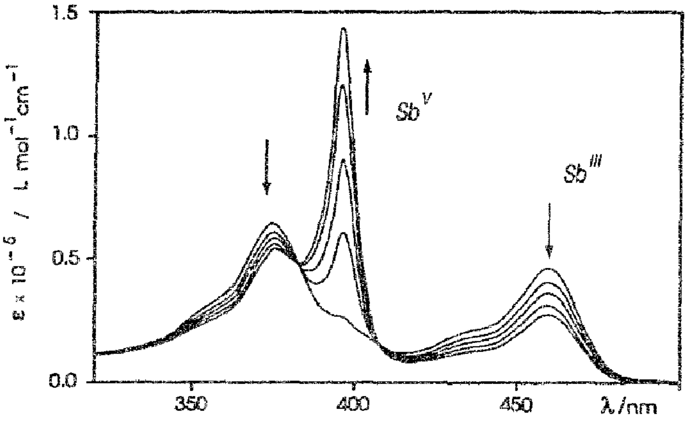


Fig. 5. Typical absorption spectral variations during the net two-electron interconversion between low- and high-valent antimony octaethylporphyrin complexes in ethanol solution at 298 K [53].

pered by their less stable Sn(II) and Pb(IV) oxidation states, a reversible switching [22,51–53] between the low-valent (s^2) and high-valent (s^0) electron configurations of antimony porphyrins is possible over many redox cycles (Fig. 5). In the course of this photoassisted [48] process, various permanent products resulting from bimolecular two-electron transfer reactions with substrate molecules can be accumulated (Table 2). A consecutive transformation of primary products has also been achieved [51,55], leading to the following four-electron reactions:

$$\text{cyclohexene} + H_2O \rightarrow \text{2-cyclohexen-1-one} + 4H^+ + 4e^- \qquad (2)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (3)$$

The formation of secondary redox products can be controlled and widely suppressed by a variation of the substrate to photocatalyst ratio. This is illustrated in Fig. 6 and Fig. 7 for the non-radical activation of dioxygen sensitized by antimony(III) porphyrins [51]. Due to some secondary photolysis, the quantum yield for the formation of the initial two-electron product, hydrogen peroxide, typically decreases in the course of the reaction (Fig. 6). While the yield of H_2O_2 formed can be optimized at low metalloporphyrin concentrations (Fig. 7), an overall four-electron

Table 2
Some photochemical redox reactions sensitized by antimony porphyrins

Substrate transformation	Ref.
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	[51]
$3Br^- \rightarrow Br_3^- + 2e$	[53]
$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e$	[53]
cyclohexene $+ H_2O \rightarrow$ 2-cyclohexen-1-ol $+ 2H^+ + 2e$	[54]
$2OH^- \rightarrow H_2O_2 + 2e$	[22]

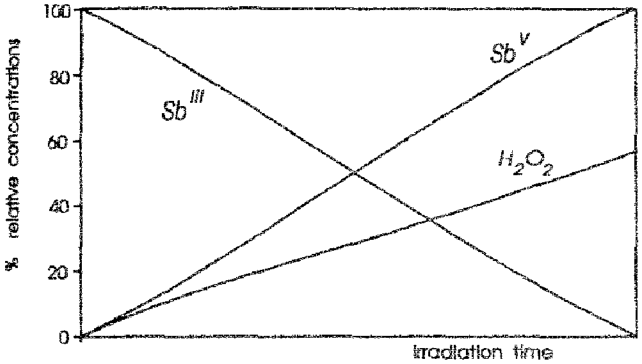


Fig. 6. Reaction profile for the production of hydrogen peroxide from dioxygen during the photolysis of 1.3×10^{-3}M antimony(III) octaethylporphyrin in ethanol at 298 K (irradiation at $\lambda_{exc} = 546$ nm).

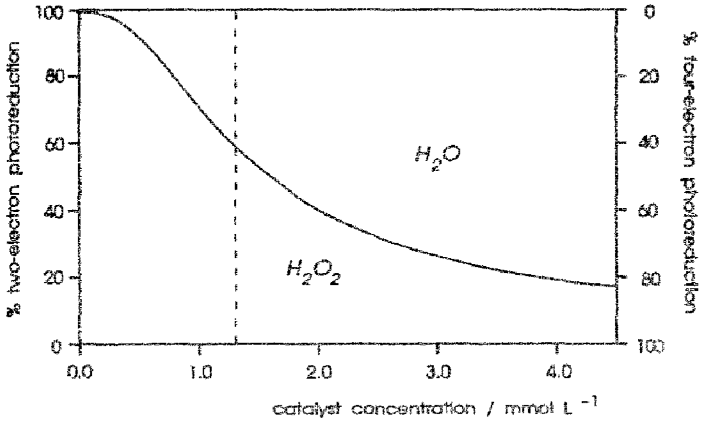


Fig. 7. Calculated product distribution for the photochemical reduction of dioxygen sensitized by antimony octaethylporphyrin. Note that the broken line corresponds to the experimental conditions displayed in Fig. 6.

process that resembles the respiratory O_2 transformation mediated by cytochrome *c* oxidase [10] according to Eq. (3) may also be favored.

A similar sequence of consecutive two-electron transfer steps is observed during the photolysis of antimony porphyrin complexes with axially σ-bonded alkyl substituents [56,57]. For example, the photochemical oxidation of axial methyl ligands can be driven to completeness, according to the following overall stoichiometry:

$$CH_3^- + 3H_2O \rightarrow OH^- + 8H^+ + 8e^- + CO_2 \qquad (4)$$

This process is of considerable interest for the catalysis of low-temperature methane conversion in homogeneous phase, including applications in fuel cell technology.

The overall efficiency of small molecule redox transformations catalyzed by MET photosensitizers such as antimony porphyrin complexes would certainly be much higher if all the consecutive two-electron steps involved could be driven at the same substrate binding site. In fact, this important feature might be achieved simply by a combination of the basic strategies described in Fig. 2. As an example, the two-electron photooxidation of hydroxide ions catalyzed by antimony porphyrins (Table 2) might possibly be changed into a four-electron process by using cofacial diporphyrin ligands [42]. Future efforts in this field therefore should concentrate on the possibilities of incorporating redox-active main group metals into porphyrin dimers or similar cooperating polynuclear assemblies. In this context, it is interesting to note that first attempts to synthesize dinuclear porphyrin complexes bearing antimony and other main group element central atoms have recently been started [58].

5. Concluding remarks

In this review an attempt has been made to provide some general guidelines for the design of homogeneous multielectron transfer (MET) catalysts based on photoreactive metal complexes. It has been outlined that the static sensitization of MET reagents allows a *minimal structural approach* toward artificial photosynthetic and oxidoreductase type reaction centers. Although our knowledge in this exciting field at the crossroads of homogeneous catalysis, bioinorganic chemistry, and the photochemistry and photophysics of coordination compounds is still very limited, a novel concept of *bionic photocatalysis* seems to evolve. This promising strategy tries to apply light-induced instead of protein-mediated energetic and structural changes at a substrate recognition site for the *functional* modeling of difficult chemical transformations that had been restricted to the expertise of metalloenzymes.

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