Water photolysis by molecular biomimetics

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Résumé **La photolyse de l'eau par biomimétisme moléculaire**

L'enzyme capable d'oxyder l'eau lors de la photosynthèse est le seul catalyseur qui réalise cette réaction de manière efficace d'un point de vue énergétique (i.e. avec un faible surpotentiel). Un catalyseur chimique présentant cette propriété serait une percée scientifique majeure tant au niveau de l'électrolyse que de la photolyse de l'eau. Il y a par conséquent un intérêt croissant pour la compréhension du mode de fonctionnement de cette enzyme de même que pour le développement des systèmes moléculaires traduisant une même réactivité. Dans un même élan, les chimistes s'efforcent d'obtenir des catalyseurs à base de métaux non nobles capables de réduire les protons en hydrogène. Cette quête est cruciale pour remplacer le platine au sein des électrolyseurs et piles à combustible. L'élaboration des électro- et photocatalyseurs bioinspirés peuvent de surcroît conduire à la transformation de produits organiques de base en matière à haute valeur ajoutée. Les connaissances récentes et plus affinées sur l'enzyme d'oxydation de l'eau et les hydrogénases rendent la recherche dans ce domaine plus réaliste. Les avancées de la chimie inorganique, de la photochimie et des nanotechnologies contribuent à l'importance de ces recherches. Cet article présente un aperçu des connaissances actuelles sur l'enzyme et des systèmes artificiels qui en sont inspirés.

Mots-clés **Énergie, photosynthèse naturelle, biomimétique, catalyse, hydrogène.**

Abstract The water oxidizing enzyme of photosynthesis is the only catalyst known as doing this reaction in an energetically efficient way (i.e. with a small over-potential). A chemical catalyst that shares this property could greatly improve the efficiency of water electrolysis and photolysis. There is therefore great interest in understanding the mechanism of this enzyme (and enzymes that catalyse the reverse reaction) and in reproducing aspects of its function in artificial systems. A similar interest exists in producing artificial proton-reducing systems to replace platinum as a catalyst in the current electrochemical systems for H_2 production. Such new catalysts could also help to improve the efficiency of fuel cells. In addition, bioinspired photochemical and electrochemical catalysts could well contribute to energy efficient synthesis of other high value chemicals and fuels. The recent improved understanding of the water oxidizing enzyme and of hydrogenases has made research in this area much more realistic than even in the recent past. Improvements in inorganic chemistry, photochemistry and nanotechnology all contribute of making research in this area timely. This article presents a brief overview of the current knowledge of the enzyme and some of the artificial systems that it has inspired.

Keywords **Energy, natural photosynthesis, biomimetics, catalysis, hydrogen.**

The input of energy to the biosphere is from sunlight. The biological process that is responsible for this is called photosynthesis and it entails the absorption of light by the green tetrapyrrole pigment, chlorophyll, and the use of chlorophyll photochemistry to drive chemical reactions that would otherwise be thermodynamically unfavourable. The "synthesis" part of "photosynthesis" involves the reduction of CO_2 from the atmosphere, producing high energy chemicals (such as sugars) that act both as the fuels and the building blocks needed for life. The electrons needed for reducing CO_2 are taken from water, a low energy substrate that is one of the most abundant chemicals on the planet. It takes a lot of energy to remove electrons from water and put them onto CO_2; this energy comes from light.

As a side product of this process oxygen is produced. Photosynthetic water oxidation is the origin of virtually all of the oxygen in the atmosphere, providing the substrate for the UV-driven conversion of oxygen to ozone producing the ozone layer that protects the surface of the earth from UV radiation. The oxygen in the environment allowed for the development of a bioenergetic mode of life based on respiration with oxygen as the terminal electron acceptor: a process so efficient that it was a key factor for the development of multicellular life.

Aerobic life on the planet can be seen as being made up of two major symmetrical energy transduction processes which work in a sustainable cycle: a) energy input *via* light-driven photosynthesis in which electrons are taken out of water and put onto CO_2 forming sugar with the release of oxygen, and b) energy usage *via* respiration in which the sugar (the fuel) is oxidised (burned), its electrons put onto oxygen forming water and CO_2 with the energy that was stored in the sugar released in a usable form for sustaining life.

Over the millennia, this photosynthesis/respiration cycle resulted in the removal of CO_2 from the atmosphere trapping it in biological material that was deposited as reduced, carbon-rich material that became fossil fuels under the Earth's surface. In the last hundred years or so, humans have built the modern industrial society based on using the energy trapped in fossil fuels. It is becoming ever clearer that this is an unsustainable activity which will not only use up this ancient energy resource but more importantly it is in the process of returning the CO_2 to the atmosphere resulting in the current accelerating climate change crisis.

A potential solution to this crisis is to look to Nature for inspiration. While photosynthesis is responsible for energy input into the biosphere, it uses only a small fraction of the solar energy that reaches the Earth's surface. Indeed the amount of solar energy reaching the planet is so great that many scientists consider that its capture and usage provide the best long-term solution to the energy problem and the associated climate change crisis. Can a sustainable solar energy-driven cycle (without net CO_2 production), like that of photosynthesis (energy input)/respiration (energy usage), be mimicked on a scale sufficient to support human activities? In this short article, we look at a chemical biomimetic approach to the energy problem, a kind of artificial photosynthesis in which chemists aim to use aspects of the biological processes as inspiration for the design and synthesis of chemical catalysts and processes for sustainable energy generation. In particular we will focus on water oxidation and the use of the electrons obtained to produce H_2 (or other fuel).

For water oxidation, there is only one enzyme in Nature in which this process occurs and that is the water/plastoquinone photooxidoreductase, or the water oxidizing enzyme of photosynthesis, which is found in plants, algae and cyanobacteria. For hydrogen production (where protons are reduced to H_2) this occurs in several different kinds of hydrogenase enzymes and also in nitrogenase. In some microbial species, H_2 formation is closely linked to photosynthesis and indeed many groups world-wide are trying to obtain economically viable algal or bacterial bioreactor systems for photosynthetic hydrogen production. Rather than this purely biological approach, we focus here on the molecular mechanisms of the enzymes responsible for water oxidation and hydrogen formation in Nature and some of the chemical approaches attempting to produce useful catalysts inspired by these enzymes.

Natural systems

The water oxidising enzyme

The water oxidising enzyme (*figure 1*) is a membrane-spanning pigment-containing protein made up of many subunits [1]. It reduces plastoquinone to plastoquinol on one side of the membrane ($PQ + 2e^- + 2H^+ \rightarrow PQH_2$) and at the other side it oxidizes water, producing molecular oxygen ($2H_2O \rightarrow 4e^- + 4H^+ + O_2$). The first of these processes is a two-electron, two-proton reaction while the second is a four-electron oxidation of two molecules of water, producing four protons and a molecule of O_2. Since the chlorophyll photochemistry is a high quantum yield, univalent charge separating process, the enzyme must interface the 1-electron processes with the multi-electron chemistry occurring at each side of the enzyme. The enzyme is often conceptualised as being made up of two parts: 1) a photochemical charge separating device which produces a reductant and a strong oxidant on opposite sides of the membrane, and 2) a catalytic part in which the oxidising power is accumulated in the form of increases in the valence of a cluster of Mn ions.

Light induced charge separation

Charge separation takes place between pigment molecules very rapidly after excitation of the chlorophylls in the enzyme (step 1 of *figure 1*). A radical pair is detected a few picoseconds after excitation and this appears to be made up of a chlorophyll (P_{D1} in *figure 1*) cation and a pheophytin (Ph_{D1} in *figure 1*) anion (a pheophytin is the free base form of chlorophyll). The pheophytin anion radical rapidly donates an electron to a quinone (Q_A) thereby stabilising the charge separated state. The semiquinone anion formed is further stabilised by a lateral electron transfer step to a second quinone, Q_B. In the meantime the highly oxidising chlorophyll cation extracts an electron from a tyrosine residue (Tyr_Z). The tyrosine's phenolic carbonyl group loses a proton as the tyrosyl radical forms. The neutral tyrosyl radical then goes on to oxidise the Mn ions of the Mn complex (designated OEC, "oxygen evolving complex", in *figure 1*). The final state formed after the excitation of the enzyme by one photon contains a semiquinone (Q_B^-) and a high valence form of the Mn cluster. This is stable for tens of seconds at room temperature and contains more than half of

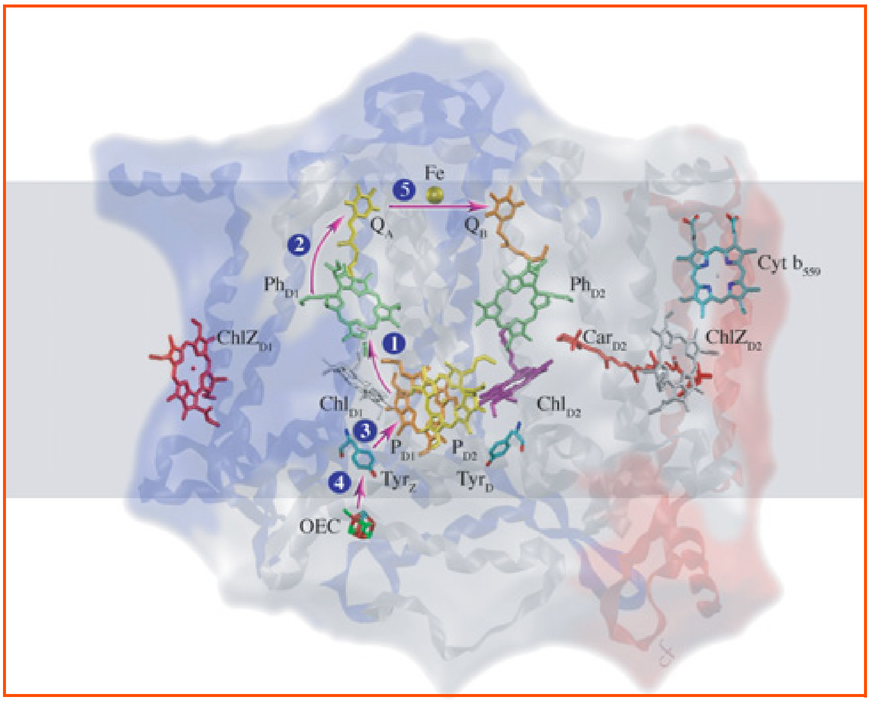

Figure 1 - Photosystem II only showing the protein subunits that bear the electron transfer cofactors. The structure shown was drawn using the protein data base [4].

The figure was made by Christian Fufezan (currently at New York City College) in Saclay and he is gratefully acknowledged for allowing us to reproduce it here. The arrows show the electron transfer steps and their numbers indicate the order in which the steps occur. The abbreviated names of the cofactors are explained in the text, at least for those involved in main electron transfer reactions.

the energy (approx. 1 eV) of the absorbed photon. In order to complete the reduction of plastoquinone a second turnover must occur and in order to oxidise water a total of four photochemical turnovers must occur, with each one resulting in a higher number of accumulated oxidation steps corresponding to increases in Mn valence (in fact there is still some debate concerning whether all of the charge accumulation steps involve Mn oxidation, [2]).

Tyrosyl radical chemistry

Tyrosyl radical chemistry may be directly involved in water oxidation. Rather than a simple electron transfer component as previously thought, it was suggested that the tyrosyl radical may act as a hydrogen atom abstractor [3]. This would require proximity between the substrate water and the tyrosyl radical and the evacuation of the tyrosine's proton away from the active site. While the crystal structure confirmed that the distance between the tyrosine and the Mn_4Ca cluster would allow H-bonding from the phenolic oxygen to a putative Ca-liganded water [4], there was no discernible H-bonding pathway for proton evacuation [4-5]. Given the ambiguities in the structural model and the attractions of the H atom transfer mechanism, a direct role for the tyrosyl radical in water oxidation has not been ruled out.

A mixed valence tetra nuclear Mn cluster with a Ca ion

The structure of the active site remains to be fully defined. The X-ray structural model is impeded by lack of resolution and by reduction of the Mn ions back to Mn(II) by the X-ray beam [6]. The models from X-ray crystallography [4-5] are similar to those developed from spectroscopy [7-8], namely four Mn ions and a Ca ion in which three Mn ions are closely associated with the fourth Mn ion somewhat less tightly associated: a 3+1 Mn tetramer. X-ray absorption studies have put further restrictions on the model and related structure shown in *figure 2* is currently the best model [9]. While the geometries shown in the model are likely to be close to that in the enzyme, the ligand sphere of the metal cluster remains poorly defined. In particular it is not clear where the substrate waters are bound. Indeed the Mn ions are thought to be linked by oxo or hydroxo groups (which are potential substrates) but the current models for the protein show the Mn ions and the Ca ion incompletely liganded [4-5]. It is likely that the coordination sphere of the metal ions is completed by water molecules and each of these waters is a potential substrate.

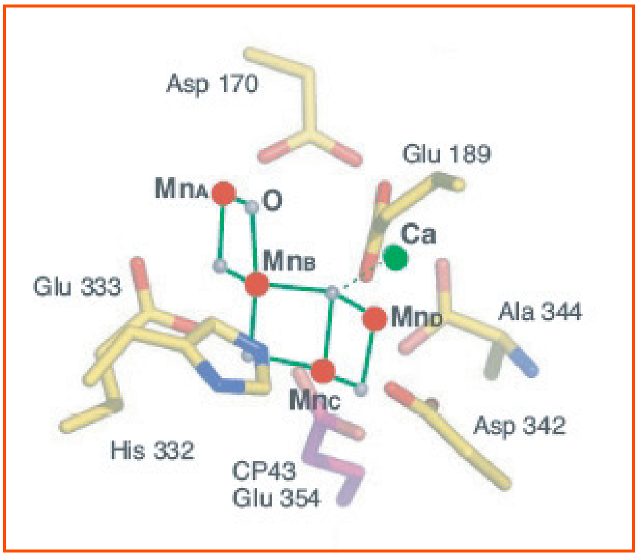

Figure 2 - The geometry of the Mn_4Ca structure: one of the current "best" models.

This model is based on the poorly resolved X-ray crystallographic studies and a series of X-ray absorption spectroscopic studies, some of which were done on crystals [9]. The figure was kindly provided by Junko Yano.

Water oxidation

Water oxidation seems not to occur until all four of the oxidation increases have occurred and the oxidation of the two waters occurs either as a concerted 4-electron process or *via* a short-lived 2-electron peroxo-intermediate. This assertion is made based on the observation that both substrate waters are exchangeable even in the state where three of the four oxidation increases have been accumulated as measured by time resolved mass spectrometry [1]. The substrate waters almost certainly undergo deprotonation as the valence state of the Mn cluster increases, compensating for charge accumulation and preventing big increases in the redox potential.

The valence state of the Mn ions when the water oxidation occurs is not known. X-ray absorption studies taken with some electron paramagnetic resonance (EPR) studies indicate that the Mn cluster is in Mn(III) and Mn(IV) even at its most reducing step in the cycle [1]. Several models consider that a Mn(V) oxo state (or the formally equivalent Mn(IV) plus oxyl radical state) is present but hard evidence for this is lacking.

The role of the Ca^{2+} ion is unclear. Its removal from the complex leads to a block in the charge accumulation cycle after the Mn accumulated two oxidations plus formation of what is probably the Tyr_Z tyrosyl radical. The redox chemistry of the tyrosyl radical appears to be affected by the absence of the Ca ion, being more slowly oxidised by the chlorophyll cation. The only ion that can replace the Ca^{2+} is Sr^{2+} and this leads to the enzyme turning over more slowly, with slower Mn oxidation and slower water oxidation [1]. It has been suggested that Ca^{2+} plays an important role in water oxidation [10].

Water oxidation mechanisms

Based on the structural model, theoreticians are now able to test the feasibility of chemical mechanisms of water oxidation. At present the ambiguities in the structure are probably still too great for the results of these theoretical studies to be seen as other than a means of ranking possible scenarios. However interesting chemical insights have been obtained from this approach. *Figure 3* shows a simplified version of a reaction mechanism based on such modelling [10-11]. The S prefix stands for the number of charge accumulation at the active site (S_0: 0 and S_4: 4). The main features of this proposal are i) a crucial role of the side chain of an arginine residue (R357) in orienting the two water molecules by means of hydrogen bonds and acting as the starting point for proton evacuation route, ii) formation in the S_4 state of a high valent Mn-oxo moiety which undergoes a nucleophilic attack from an activated water molecule bound to the Ca^{2+} leading to the formation of the O-O bond.

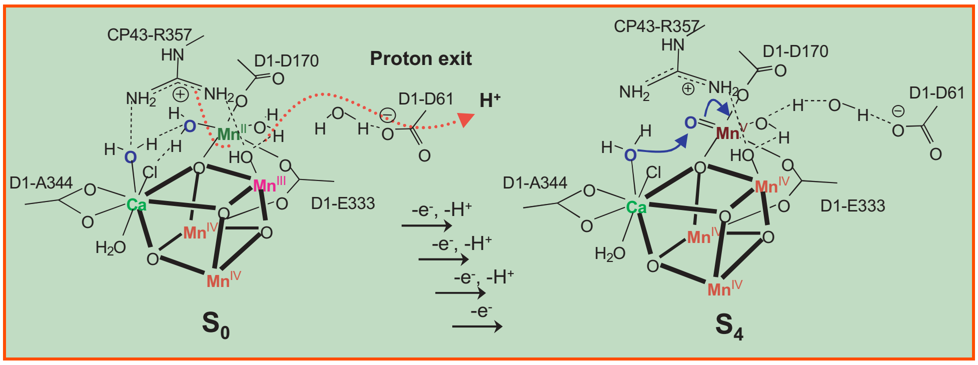

Figure 3 - Simplified version of the proposed mechanism by the Batista/Brudvig group based on theoretical and structural data. S_0 and S_4 stand for the states with 0 and 4 oxidising equivalent(s) respectively.
The doted arrow represents the proposed rote for proton exit from the OEC.

Hydrogenases as proton reducing enzymes

Hydrogenases are enzymes that catalyse the production or consumption of H_2. They are found in many different microorganisms living in essentially anaerobic environments [12]. The main hydrogenases can be grouped into two classes according to the metal composition of their catalytically active site: [NiFe] and [FeFe] (or Fe-only) hydrogenases. Their physiological role is to either evacuate excess reducing equivalents from, e.g. fermentation, by reducing protons and producing H_2, or to take up H_2 from the environment to obtain low potential electrons for a range of metabolic processes. In general, [FeFe] hydrogenases show much higher activity for H_2 formation than the more reversible [NiFe] hydrogenases, but they are also much more sensitive to O_2. The differences in activity are believed to be related to the different affinities for H_2. Depending on the species, hydrogenases interact with small redox active proteins like cytochromes or ferredoxin to couple the enzyme to the metabolism of the cell.

For both classes of hydrogenases structures obtained by protein crystallography have been published [13-15]. The active sites are bimetallic centers, bridged by two sulfur atoms and one or both of the metals ligated by CO and CN (*figure 4*). In [FeFe] hydrogenases a [4Fe-4S] cluster is closely connected to one of the Fe atoms making up a [6Fe6S] structure (the H cluster). In most but not all cases further FeS clusters are present and form an electron transfer pathway from the active site to the surface. In addition there are pathways for transport of substrate and product to and from the active site with hydrophobic channels for H_2 transfer and a chain of histidine and glutamate side-chains for proton transfer.

The model of the active site (*figure 4*) shows a possible substrate binding site between the distal (to the [4Fe-4S] cluster) iron and the bridge over the two sulphur atoms, the central atom of which is probably nitrogen. The reaction of a formal metal hydride on the distal iron with a nearby proton on the bridging secondary amine may lead to H_2 formation.

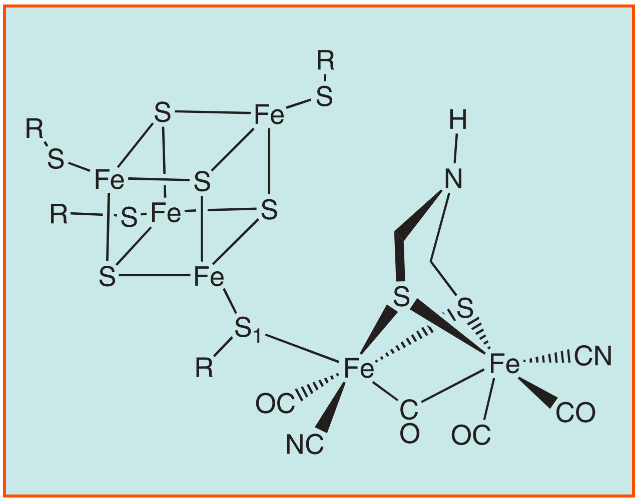

Figure 4 - Structural view of the catalytic centre of Fe-Fe hydrogenase. R stands for cysteine residues.

Artificial systems

There is an extensive literature where chemists have synthesised metal clusters that have been put forward as being of potential structural relevance to the active sites in these enzymes. For decades this was a relatively straightforward thing to do because the structures of the active sites were unknown. Good structural models have made this a more rigorous task (although the structural ambiguities of the water oxidising enzyme still make it a somewhat fuzzy target). For hydrogenases chemists have come close to reproducing the complex geometry and yet they have performed poorly as a catalyst. This is not surprising from a biological perspective since eons of evolutionary pressure have refined the enzymes by balancing factors like substrate access, redox (electronic) tuning, geometrical tuning, conformation effects. The aim of the biomimetic chemist is not to reproduce all the complexity of the enzyme, rather to learn from the enzyme and pick out key features that would be less obvious in standard strategies for the synthesis of catalysts.

An attractive approach has been to attempt to engineer the photocatalysts rather than catalysts alone. This may give specific advantages since it can in principle allow detailed characterisation of the catalyst in terms of electron-by-electron redox reactions and kinetics. And if it worked as a catalyst then it could be a winner. The problem is that while the fabrication of high-yield charge-separating devices has been achieved (still not a trivial achievement), there are no good catalysts ready to be connected. Furthermore linking a charge separating device with a metal catalyst is no easy matter and it is even more difficult to achieve multiple redox reactions and maintain directionality in such a complex. These difficulties have not deterred research into photocatalysts. Here we describe briefly some approaches aimed at producing both catalysts and photocatalysts.

Water oxidation catalysts inspired by Nature

The construction of a molecular catalyst for water oxidation is a particularly challenging task since the structure of the biological catalyst is not fully defined and the mechanism of water oxidation remains the subject of speculation. However ambiguities concerning the structure of the complex are gradually being eliminated and target structures for modelling can already be set despite the lack of detailed structural knowledge. Manganese complexes reporting water oxidation have been published [16-19], but the catalysis activity has at best been disappointing and difficult to demonstrate unambiguously. In contrast ruthenium complexes have been shown "bone fide" water oxidation [20-22].

Based on the mechanistic proposals for O-O bond formation coming from the water oxidizing enzyme and from coordination metal complexes, strategies for the synthesis of artificial catalysts have been obtained. We consider here a few representative strategies based on manganese complexes.

Radical coupling between oxo groups

Formation of the O-O bond could result from activation of two close-by, well oriented Mn-ligated water molecules following a two-electron, two-proton abstraction process for each water (*figure 5a*). Such a mechanism has been postulated many times in the biological literature. An artificial complex aimed at doing this requires a ligand that can hold the two metal ions at the right relative geometry and distance. Each of the metal centres must be surrounded by a pentadentate ligand leaving an exchangeable liganding site for substrate water binding and the ligand must be robust enough to withstand the formation of high-valent Mn states. The cofacial bisporphyrin complex of Naruta [18] is an example of such a geometry and while this was reported to act as a catalyst for water oxidation, the work has not been followed up nor repeated and so doubts about its validity remain. We are synthesising a novel family of face-to-face biscompartmental salen-type ligands holding two manganese ions as shown in *figure 6* [23]. The challenge now is to adjust the Mn coordination spheres in order to generate reactive oxo species.

Nucleophilic attack of an activated H_2O molecule on a highly oxidised Mn-oxo species

This type of mechanism has been under consideration for several years for the water oxidising enzyme (see above and [16]). Salen- or porphyrin-based manganese complexes are known to generate high-valent manganese-oxo species that can oxidise alkene to epoxide in a two-electron process. If the C-C double bond of the alkene were to be replaced by an activated form of water (e.g. OH^-), then it may be possible to use this chemistry to create the O-O bond. However, a 4-electron process is required for the liberation of O_2 and an elegant synthetic option to do this would be to share the oxidising power on a multi-centred complex (*figure 5b*) that can provide the necessary two additional oxidizing equivalents upon the nucleophilic attack through electronic communication between the metal centers. One on-going strategy for the synthesis of such a system is to design dissymmetric dinuclear Mn complexes, where one of the Mn ions is coordinatively saturated, while the other is 5-coordinated with one exchangeable site to bind and activate a substrate water molecule.

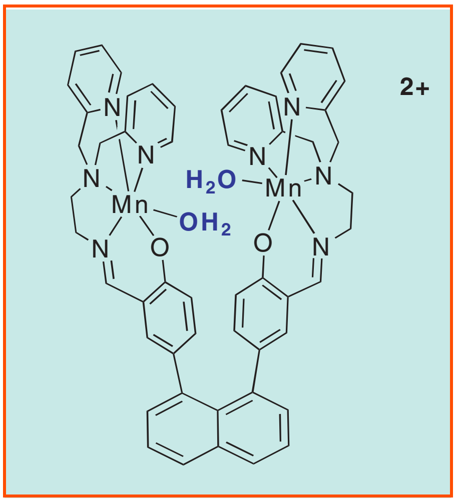

Figure 6 - Dinuclear face-to face Mn(II) complex.

O-O bond formation by the coupling of radical µ-oxyl bridges

The Mn cluster in PSII is thought to have four µ-oxo bridges and a possible route for O-O bond formation involves the reaction of two radical µ-oxyl bridges (*figure 5c*) [8, 24]. Relevant synthetic complexes exhibit some catalytic activity for water oxidation in the heterogeneous phase but not the homogeneous phase [25]. Such a reaction leading to the formation of a O-O bond was reported for a bis-copper complex showing an equilibrium between a (bis µ-oxo)dicopper(III) and a (µ-η^2:η^2-peroxo) dicopper(II) unit [26]. This option is worth considering in Mn chemistry provided that each Mn centre is kept in close proximity during all steps of the oxidation process.

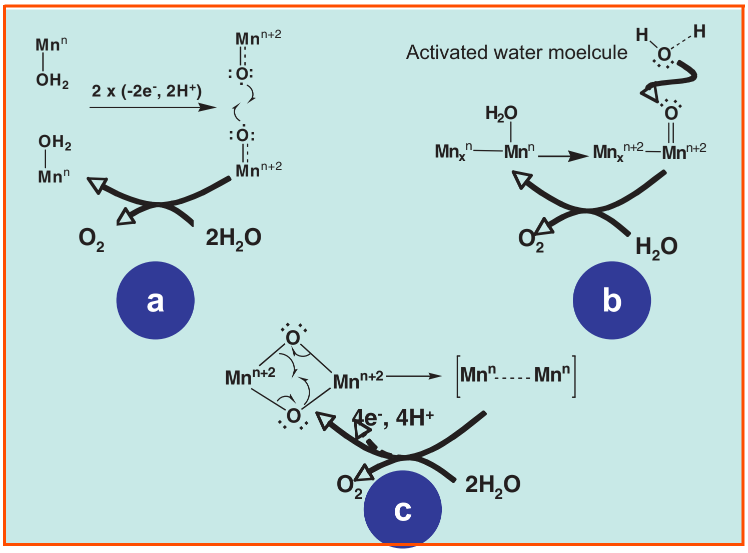

Figure 5 - Different synthetic approaches for the formation for the oxygen-oxygen bond.

Other aspects of catalyst design: charge compensation effects

In the natural system four univalent oxidation steps occur before the enzyme accumulates the oxidising power needed for the removal of four electrons from two molecules of water. Some of these oxidation steps are accompanied by proton release from the active site and this prevents the build up of excess charge at the active site and thus allows the same oxidant (i.e. a chlorophyll cation with an E_m of around 1.1-1.2 eV) to achieve four successive oxidations at the same site. While deprotonation of water may be expected to occur as the Mn ions increase in valence, specific design features may facilitate the process and attempts have yet been made to do this in synthetic models. This probably requires efforts to engineer functional roles for the second coordination sphere of the catalytic metal centres with hydrogen-bonding interactions being the most important chemical parameters needed.

Proton reduction catalysts for H_2 production

H_2 generation by electrolysis and hydrogen oxidation in a fuel cell are catalysed by Pt electrodes. This occurs at a small over-potential and so is relatively efficient. The task for chemists here is to replace the expensive Pt metal by cheaper coordination metal complexes using first row transition metal ions. Two approaches are currently investigated: biomimetic models of the hydrogenase active site and coordination metal complexes for electrocatalysis.

In Nature Fe or Ni ions are present at the active sites of the hydrogenases. However these metal ions have unusual CO and CN ligands which are thought to confer a "noble character" on these ions by stabilising their low valent oxidation states. Since the structures of [FeFe] and [FeNi]-hydrogenases have been elucidated, a number of biomimetic models of the active sites have been synthesised [27]. Although a high degree of resemblance has been reached between the active site particularly for the [Fe]-only hydrogenase, the catalytic activity for the production of H_2 of such complexes is mediocre and needs a high overpotential. Work in this field is focussed on the fine-tuning of the redox potentials of the metal ions with a set of different monodentate ligands in their coordination spheres.

Other non-biomimetic coordination metal complexes based on Pt, Fe, Ni, Rh, Co… are active in H_2 production either by electrocatalysis or photochemically in the presence of an external electron donor. We are interested in revisiting the electrochemical properties of a family of Co-glyoxime complexes. $CoDMGBF_2$ (DMG: dimethylglyoxime) can catalytically evolve H_2 in an aqueous acidic solution in presence of an exogenous electron donor [28]. Electrochemical studies exhibited a catalytic reduction wave in organic solvents and in presence of an acid [29-30]. We have dispersed these complexes in a conducting medium (e.g. black carbon) and immobilised them at the surface of a glassy carbon (GC) electrode in a H^+-conducting matrix (Nafion®). In comparison with the reference electrodes (GC with or without black carbon), a significant improvement in the hydrogen evolution reaction (HER) was found for the modified electrodes containing the Co catalysts [31]. Although the current densities observed with these confined complexes are well below that of platinum, these results are encouraging.

The main tasks for the chemists are: i) to reduce the cathodic over-voltage by a fine-tuning of the ligand around the metal centre, ii) to increase the electrical contact of the non-conducting molecular catalyst with appropriate conducting substrates for efficient supply of electrons and iii) to provide access for the protons to the metal centre and also to allow the rapid evacuation of the H_2, i.e. optimizing transport to and from the catalyst.

Bridging catalysts to photoactive modules

Molecular organic and inorganic chromophores are known to induce charge separation under light excitation. A classic example is the ruthenium(II) trisbipyridine complex. The robustness, inertness and the unique photophysical and redox properties of this family of complexes make them good candidates for sensitizers. Upon irradiation in the metal-to-ligand charge transfer transition (MLCT) at around 450 nm, a singlet MLCT state is reached which is strongly coupled to a triplet MLCT state. This state relaxes to the ground state with a lifetime at around 800 ns. Adamson and Gaffney [32] showed that the ^{3}MLCT state can be quenched either oxidatively (in presence of an electron acceptor) or reductively (in presence of an electron donor), generating a highly oxidizing Ru(III) complex (+1.3 V *vs* SCE, saturated calomel electrode) or a formal Ru(I) reducing agent (-1.2 V *vs* SCE), respectively. This family of complexes has been extensively used in studies of photoinduced electron transfer (ET).

The high oxidizing power of the Ru(III), photogenerated in the presence of an electron acceptor, makes it a good candidate for mimicking the redox active chlorophyll pigment of PSII. The task of building a supramolecular device to drive the photooxidation of water must deal with several issues including the following:

- The chemical nature and length of the covalent link between the photoactive part and the catalytic site in the supramolecular complex must be controlled. The spatial separation must be tuned to conserve the inherent photophysical properties of the photoactive chromophore (e.g. to avoid quenching of the excited state) and the electrochemical behavior of the linked metal complex while at the same time providing an electronic pathway between the constitutive parts.
- Multiple sequential photoinduced electron transfer processes will be necessary for the multi-charge accumulation at the catalytic unit. In the natural system, a number of cofactors provide a charge relay chain leading to efficient and unidirectional charge transfer. In the case of the artificial construct, charge transfer must be channeled in the right direction to prevent back transfer, which would annihilate the charge accumulation at the catalyst.
- As in PSII, the redox potential of the oxidised artificial chromophore fixes the potential limit available for every oxidation step. To avoid that accumulation of positive charges and the consequent increase in redox potential, a proton-coupled electron transfer mechanism maintains the redox potential of the Mn cluster below the potential of the tyrosinyl radical. An in-depth comprehension of this type of mechanism is necessary to try to incorporate it into future Mn-based photocatalysts.

First attempts at making biomimetic photocatalysts

The Hammarström/Styring group was the first to design and synthesize a series of covalently linked Ru trisbipyridine-Mn complexes (*figure 7*). Single and multi-electron transfers from the Mn core to the photogenerated Ru(III) centre have been demonstrated. It remains unclear whether the phenol fragment linked to the manganese ions acts as an electron relay between the Ru(III) and Mn ions [33]. Wieghardt and his coworkers [34] have also published a mixed Ru-Mn complex where upon excitation of the lumophore in presence of

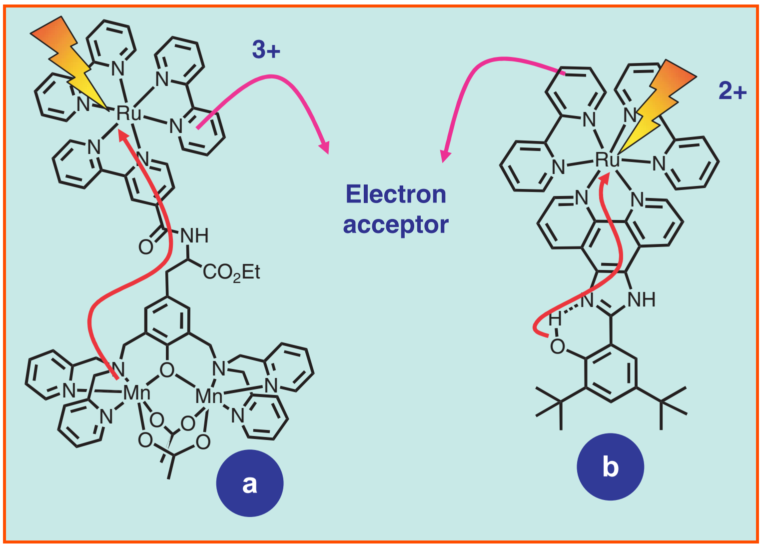

Figure 7 - **a** represents a Ru^{II}-Mn^{II}_2 system from [33] and **b** is a Ru^{II} complex holding a tyrosineZ/imidazole191 model of the PSII elaborated in Orsay.
The arrows indicate the photoinduced charge shifts upon flash excitation in presence of an electron acceptor.

an external electron acceptor an intramolecular electron transfer leads to the formation of a high valent Mn(IV) complex.

Mimicking PSII, we have introduced an imidazole-phenol functionality as the analogue to the tyrosineZ-histidine191 couple between the Mn and P680 as shown in *figure 7* [35]. Upon flash excitation in presence of an electron acceptor such as methylviologen, the formed Ru(III) disappeared much more quickly than the methylviologen radical, showing that the Ru(II) state is recovered by intramolecular electron transfer. Spectroscopic data showed the formation of a phenoxyl-type radical hydrogen-bonded to the nitrogen atom of the imidazole ring. We are now in the process of tethering a Mn cluster to the phenol ring to obtain a supramolecular structure mimicking the main cofactors of the PSII reaction centre.

Electron transfer processes in the above examples are carried out in homogeneous medium with a reversible or sacrificial electron acceptor. The goal of this research is to recover the electrons from the photooxidation reaction to perform reduction reactions such as reductions of protons. Such a device probably requires that the photocatalysts be attached to modified transparent electrodes. Strategies for connecting the photocatalytic systems to semiconductors and to electrode surfaces are under development.

Conclusion

This article is a brief and limited survey of the biomimetic approach for making catalysts based on some of the key enzymes involved in energy conversion processes in biology. Our aim is to provide a flavour of the kind of research that is underway in this area and in particular of the strategies that we have recently adopted in our laboratories. Molecular biomimetics is an exciting interdisciplinary field where synthetic chemistry meets both molecular enzymology and a wide range of physical approaches. The ultimate aim of molecular biomimetics in this area is to obtain devices that will not only be of commercial value but will contribute to one of the greatest scientific challenges of our time: to improve the efficiency of energy use and to achieve sustainable energy production.

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