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Review

Artificial systems related to light driven electron transfer processes in PSII

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Abstract

The water oxidising enzyme, photosystem II, performs one of the most important reactions for life on Earth. Today, in the context of finding renewable sources of energy as alternatives for fossil fuels, the four-electron oxidation of water using light energy stands as one of the most challenging reactions for scientists to understand and reproduce. Mastering this reaction is considered to be a key step towards the use of water and sunlight to produce renewable hydrogen. It is therefore not only timely but also urgent to understand the mechanism of this enzyme so that this understanding can be used to design artificial catalysts. A chemical catalyst that shares the property of the enzyme in its ability to oxidize water with a low overpotential, could greatly improve the efficiency of water electrolysis and photolysis. Here we briefly describe aspects of the enzyme focusing on the essential cofactors involved in the light driven oxidation of water and provide an overview of the work done to produce a biomimetic photocatalyst for water oxidation. The development of such a device can be conceptualized as the association of two chemical modules, a photoactive unit and a catalytic unit. The candidate of choice for the photoactive unit, at least on a proof-of-principle basis, is $[Ru(bpy)_3]^{2+}$. This is due to its robustness, its synthetic flexibility and its unique photophysical properties. The elusive manganese catalyst acting as the catalytic site is dealt with in the previous chapters of this issue. In this review we discuss the different challenges that must be met to develop a synthetic system for water photolysis. These include (1) efficient light absorption by a sensitizer, (2) development of a stable charge separating device, (3) vectorial

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Abbreviations: Bpy, 2,2′-bispyridine; CB, conduction band; CPET, concerted proton electron transfer; DFT, density functional theory; EDTA, ethylenediaminetetraacetate; EPR, electron paramagnetic resonance; ET, electron transfer; His, histidine; MLCT, metal to ligand charge transfer; MV, methylviologen; NMR, nuclear magnetic resonance; OEC, oxygen evolving complex; P_{680}, pigment absorbing at 680 nm; PD1, protein D1; PhD1, pheophytin in protein D1; PQ, plastoquinone; PSII, photosystem II; PTZ, phenothiazine; SCE, saturated calomel electrode; TEA, triethylamine; TD-DFT, time-dependent density functional theory; TW, terawatt; Tyr, tyrosine.

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electron flow to/from, (3a) a donor site that must be capable to accumulate charges for consequent catalytic reactions, and (3b) an acceptor system that allows a multi-electron process.

Keywords: Energy; PSII; Electron transfer; Biomimetic models; Photocatalyst

1. Introduction

One of the most pressing challenges society is facing today is the transition to a new energy scenario. Increases in world population and the rise of emerging economies have projected an increase in energy consumption from 13 TW today to 30 TW by 2050 [1–3]. If we couple the fact that 86% of this energy comes from fossil fuels to the fact that CO_2 levels are the highest they have been for the past 650,000 years, it is clear that the burn rate that will be needed in 40 year's time is unacceptable. In order to fill the gap of needed energy we must look for complementary sources that will be reliable enough to meet the demand and sustainable enough so their use will not be deleterious to life on earth. Obviously, solar power presents itself as the most promising source of renewable energy available. The goal of artificial photosynthesis is to harness this energy to drive the production of high-energy chemicals from low energy source compounds.

Nature has given us the guidelines for such a process. During photosynthesis, absorption of light by phototrophic organisms initiates a series of energy and electron transfer processes that lead to the oxidation of water (Eq. (1)) to reducing equivalents that can then drive the reduction of CO_2 into higher carbohydrates (Eq. (2)).

$$2H_2O + 4h\nu \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

$$nCO_2 + 2ne^- + 2nH^+ \rightarrow (CH_2O)_n \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

Artificial photosynthesis, thus, aims to imitate the above-mentioned processes of light absorption, catalysis, and energy conversion. Photo-driven water oxidation to generate reactive species is in itself a very hard task, but only half of the goal. The long-standing project has been to reuse the electrons and protons generated to drive the production of high energetic fuels such as H_2 (Eq. (3)), or reduced forms of carbon (Eq. (2)). Over the last two decades several advances have been made in this field. Examples of light induced long-lived charge-separated states [4–7], electron transfer from chromophores to catalytic sites [8,9] and water oxidation catalysis by chemical or electrochemical means [10–17] have been reported in the literature. Nevertheless, little success has been attained when trying to combine all these required processes into one complex. In the following, we present a review of the work done up to date in the field of molecular artificial photosynthesis by briefly describing the essential cofactors involved in natural systems and drawing parallels between these components and the synthetic equivalents that could be used as their artificial counterparts. While nature might provide us hints for a solution, trying to chase its mechanism too closely might impede the development of alternative methods which could perform better in an artificial system. The pursuit of such a monumental task will serve to advance the knowledge of the mechanisms at work in the natural systems as well as lead to significant improvements within each of the disciplines involved in the research process.

2. Map of the redox-active cofactors of PSII and their role

The water oxidising enzyme is a membrane-spanning, pigment-containing protein made up of several subunits. 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 oxygen. Since the chlorophyll photochemistry is a high quantum yield, univalent charge separating process, the enzyme must interface the one-electron processes with the multi-electron chemistry occurring at each side of the enzyme. The enzyme is often conceptualized 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 device in which the oxidising power is accumulated in the form of increases in the valence of a cluster of manganese ions. A view of the main cofactors is given in Fig. 1 and the sequence of electron transfer processes after a photonic excitation of the chlorophylls is indicated.

1. Light induced charge separation: charge separation takes place between pigment molecules very rapidly after excitation of the chlorophylls in the enzyme (step 1 in Fig. 1). A radical pair is detected a few picoseconds after excitation and this appears to be made up of a chlorophyll (P_{D1} in Fig. 1) cation and a pheophytin (Ph_{D1} in Fig. 1) anion.
2. The pheophytin anion radical rapidly donates an electron to a quinone (Q_A) thereby stabilising the charge-separated state.
3. 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.
4. The neutral tyrosyl radical then goes on to oxidize the Mn ions of the Mn complex (designated OEC, oxygen evolving complex, in Fig. 1).
5. The semiquinone anion formed is further stabilized by a lateral electron transfer step to a second quinone, Q_B.

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 state is stable for tens of seconds at room temperature and contains more than half of the energy

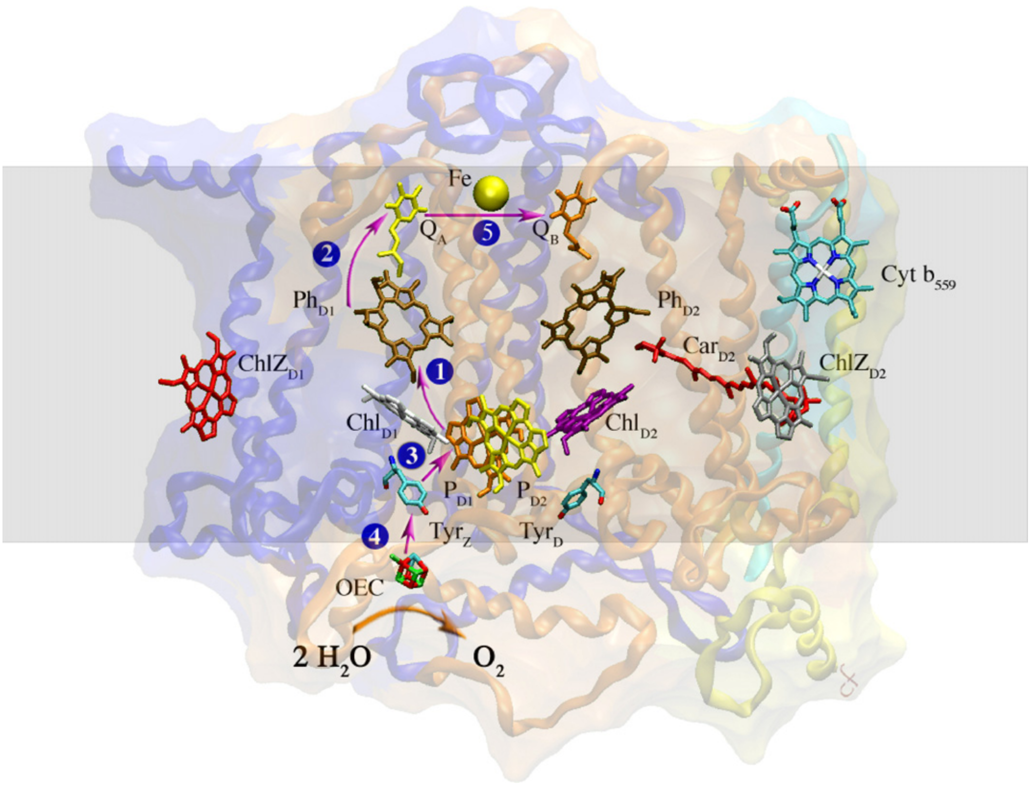

Fig. 1. Map of the main cofactors of PSII. The arrows show the electron transfer steps and the numbers indicate the order in which they occur.

(approx. 1 eV) of the absorbed photon. In order to complete the reduction of plastoquinone, a second turnover must occur. In order to oxidize water, a total of four photochemical events must take place, with each one resulting in an increase in the manganese cluster's valence.

3. Chemistry at the water oxidizing complex

The core complex of PSII described above contains six chlorophyll *a*'s and 2 β-carotene pigments [4,18]. In order to increase the collection of light, several antenna proteins containing a large number of chromophores are associated with the core complex to harvest light of various wavelengths. These antenna systems are capable of funnelling the photon energy through a series of energy transfer steps to the primary electron donor P_{680} which is probably made up by the four excitonically coupled chlorophyll molecules of the PSII core (P_{D1}, P_{D2}, Chl_{D1}, Chl_{D2} in Fig. 1). After excitation of P_{680}, a charge-separated state is created and a chain of well-positioned and optimally tuned redox cofactors makes up a pathway for efficient transfer of the electrons away from the oxidized primary donor $P_{680}{}^{+}$ (probably P_{D1} in Fig. 1). The efficiency of this process is virtually independent of the oxidation state of the Mn cluster, giving us an idea of how evolution has resulted in a high level of sophistication of the natural enzyme, which is capable of controlling the electron transfer away from the active catalytic site even if the latter is in a high valence state. The resulting $P_{680}{}^{+}$ is then reduced to its initial state upon oxidation of a tyrosine residue. Interestingly, recent crystallographic data [18,19] show that the phenolic oxygen of the tyrosine (Tyr_Z) is hydrogen bonded to the imidazole ring of a histidine residue (His_{191}). Babcock et al. [20,21] suggested that rather than being a simple intermediate in an electron transfer process as had been previously thought, the tyrosyl radical might act as a hydrogen atom abstractor. 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 cluster would allow H-bonding between the phenolic oxygen and a putative Ca-bonded water, there was no obviously discernible H-bonding pathway for proton evacuation [18,19]. Given the ambiguities in the structural model and the H atom transfer mechanism, a direct role for the tyrosyl radical in water oxidation has not been ruled out.

The manganese cluster, known as the oxygen evolving complex (OEC) catalyses the water oxidation reaction. It is composed of four manganese ions, bridged by oxo ligands. Calcium chloride and carbonate ions are known to be present at the OEC but their roles are unclear yet. The mechanism for the removal of four electrons and four protons from two substrate water molecules is still subject to speculations [22]. The main obstacle to the understanding of this mechanism is the lack of knowledge concerning the structure of the OEC. Recent X-ray diffraction structures [18,19] are impeded by lack of resolution and by reduction of the high valence Mn ions back to Mn^{II} by the X-ray beam [23]. A different proposal has incorporated the use of both theoretical modelling and X-ray absorption techniques [24]. New theoretical proposals based on experimental findings are providing possible scenarios for the functioning of the OEC

[25]. While the electronic structure of the different S-states, substrate binding, calcium/chloride binding, and function of amino acid side chains are still a matter of debate, it is widely admitted that the substrate waters undergo deprotonation as the valence state of the Mn cluster increases [26], compensating for charge accumulation and preventing large increases in the redox potential. Different possible pathways for the eventual formation of the oxygen–oxygen bond have been proposed (see previous chapters).

4. Construction of an artificial photosynthesis device

The most basic molecular device relevant to natural photochemical processes should be composed of a photosensitiser linked to an electron donor on one side and to an electron acceptor on another side. This triad should undergo the following steps:

1. $D–S–A \rightarrow D–S^*–A$ Light absorption by antenna system or sensitiser
2. $D–S^*–A \rightarrow D–S^+–A^-$ Electron transfer to an acceptor
3. $D–S^+–A^- \rightarrow D^+–S–A^-$ Electron transfer from donor (charge-separated state)

Triads have been published which show long lifetimes for a charge-separated state and multi-electron cascades have been observed [27,28]. These examples show that transformation of light energy into chemical energy in the form of a charge-separated state can be achieved. The next step towards water decomposition would require the coupling of the pertinent reduction and oxidation catalysts to a triad. The basic requirements for such a particular photocatalytic system to work are the following: (i) directionality of the electron transfer process for each individual charge separation step, (ii) tuning of the electronic coupling between the donor/acceptor and the photosensitiser in order to maximise electron transfer efficiency, (iii) a long-lived charge-separated state and (iv) catalysts (donor/acceptor) capable of storing oxidising/reducing equivalents.

Coupling two catalytic reactions involving the same number of electrons on a single molecule requires the rates for the catalytic reactions to be faster than the recombination rates. This challenge is even harder when the two reactions performed do not involve the same number of electrons. Decomposition of water belongs to the latter case. This reaction would require coupling a $2e^-$ reduction reaction (H^+ reduction) to a $4e^-$ oxidation reaction (H_2O oxidation). After accumulation of two charges, protons would be reduced, while the oxidation of water would still require two other oxidizing equivalents. In order to maintain the efficiency of the early photophysical events independent of the redox state of the catalysts, the charges accumulated have to be compensated for. Another point of importance is the condition under which a reaction is conducted, which might be different for the oxidation and the reduction sides.

These obstacles can partly be solved by designing a photochemical cell in which the oxidation and reduction reactions are separated. In such a system we could imagine the oxidation catalyst (Cat_{ox}) linked by a photosensitiser to an anode and a reduction catalyst (Cat_{red}) grafted to a cathode [29] (see Fig. 2). Through an electrical connection between both electrodes, the electrons from the oxidation half-cell could be transferred to the reduction half-cell, while protons would move in the opposite direction through a selective membrane. Of course, the four requirements (i–iv) mentioned above for the efficiency of a photoactive molecular catalyst still hold true for both components of such a photochemical cell. However, the use of two separated compartments with the catalysts bound to a surface prevents the intermolecular short-circuit reactions between i) the photocatalysts and ii) the photocatalysts and the reaction products. Another advantage of fixing the photocatalysts, notably the oxidation half, to an electrode resides in the properties of large bandgap semiconductor surfaces like TiO_2. These offer very fast injection rates for electrons from the excited state of attached chromophores in their conduction band [30] (see Section 4.3) contributing to the necessary control of directionality of electron transfer.

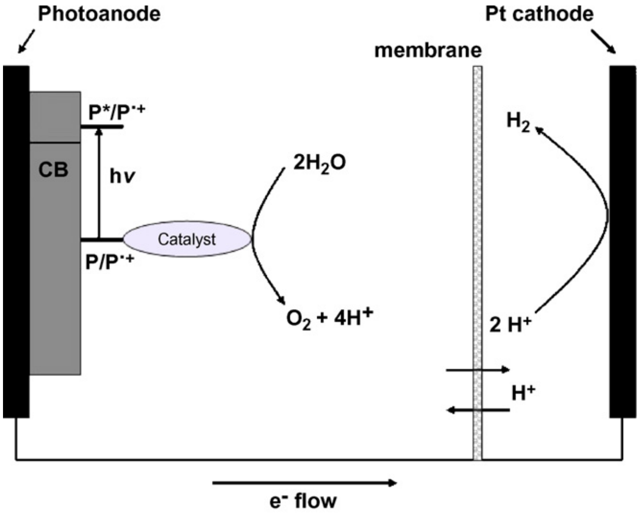

Fig. 2. Schematic of a water-splitting photochemical cell.

Examples of such devices have been developed with porphyrin-sensitised photoanodes [31,32], which drive oxidation of sugar via a natural enzyme, delivering sufficient reducing potential for H_2 production at a platinum electrode [33]. As far as we know, the use of a synthetic molecular photocatalyst has not been reported yet for such a system.

Following, we will review the research done in the field of each of the molecular constituents used in artificial photosynthesis devices: antennas, photoactive chromophores, acceptor groups and donor groups including manganese complexes. We will present the progress made in order to connect some of these modules together on the way to photodecomposition of water.

4.1. Antennas

The development of synthetic antenna systems is an active field [34–36], this for obvious reasons of collecting and harvesting solar energy in an efficient manner. The role of an antenna is to increase the absorption cross-section of the complex and, through a series of energy transfer steps, funnel that energy to a reaction centre where a charge-separated state is initiated. The solar spectrum has a maximum intensity just below 500 nm [37] and extends well into the infrared region where a photon with

$\lambda = 1000$ nm still has 1.2 eV energy. In nature, the efficient geometrical arrangement of the pigments is related to the tertiary structure of the PSII antenna subunits (light-harvesting complexes) [38]. In artificial photosynthesis this spatial arrangement is not easily achievable. The distance between the pigments to be used, their respective angle, and electronic coupling, must be engineered by the covalent bonds that unite them. Two mechanisms are responsible for energy transfer processes. Förster energy transfer occurs in cases where the distance between the chromophores is larger than their transition dipole strength, the dipoles have sufficient strength, and the lifetime of the emitting chromophore is sufficiently long. Dexter energy transfer takes place when the chromophores are brought into van der Waals contact and there is orbital overlap between them. Systems such as carotenoid–tetrapyrrole triads [39], diads [40,41], and (phenylethynyl) anthracene–porphyrin–fullerene heptads [42] have been shown to combine large absorption spectral range (350–700 nm), high extinction coefficients (10^5 M^{-1} cm^{-1}), and quantum yields for energy transfer of close to 100% [43]. Different approaches, such as the use of dendrimers [44] or self-assembled π-stacked arrays [36,45] have also been reported in the literature. However, the connection of antenna pigments to a photochemically active chromophore to trigger a catalytic reaction has not been realised yet.

4.2. *Photoactive chromophore*

Several types of molecules have been used as photosensitisers, going from tetrapyrrole [6,7,46] systems to transition metal complexes (Ru, Re, Ir, Os) [44,47,48]. Synthetic porphyrin derivatives have been widely used to mimic the natural chlorophyll pigments in order to convert light energy into chemical energy [49]. However, their syntheses are long and tedious, therefore preventing their common utilisation as the photoactive module. Another well-known chromophore is the $[\mathrm{Ru(bpy)_3}]^{2+}$ complex [50–52]. This complex is robust and can be easily prepared, therefore making it a better candidate. It presents an absorption band in the region around 450 nm corresponding to a metal to ligand charge transfer (MLCT) band with an extinction coefficient of about 13,000 M^{-1} cm^{-1} [53]. Upon irradiation in the MLCT band, the input light energy is converted into a $1(\mathrm{d}\pi^6) \rightarrow 1(\mathrm{d}\pi^5\pi^*)$ excited state, which in turn relaxes to form the lowest triplet state (^{3}MLCT) in less than a picosecond [54–56]. This state is sufficiently long-lived to allow reductive or oxidative electron transfer processes to occur before regeneration of the ground state [57]. The oxidation potential of $[\mathrm{Ru(bpy)_3}]^{3+}$ is around 1.2 eV [51,55] which is close to that of the primary donor of PSII, $\mathrm{P_{680}}^+$ [58,123], therefore making it a suitable candidate to reproduce the oxidation reactions performed by the natural system.

Two different proposals describe the nature of the triplet state of the parent ruthenium(II) trisbipyridine complex [44]. On one hand, a localised description where the metal promoted electron is present on only one bipyridine moiety, on the other, a delocalised view where the excited electrons are extended on all three bipyridines. A recent DFT study [59] described the electronic properties of the ground and excited states of the $[\mathrm{Ru(bpy)_3}]^{2+}$ complex. The lowest triplet state calculated $^3\mathrm{A}_2$, as represented in Fig. 3, was the symmetric $[\mathrm{Ru^{III}(bpy^{[\bullet-]1/3})_3}]^{2+}$.

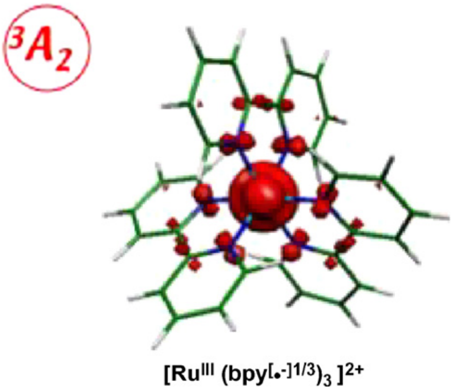

Fig. 3. Spin density distribution map of $[\mathrm{Ru(bpy)_3}]^{2+}$ in the $^3\mathrm{A}_2$ state.

In the computational methodology used, no asymmetry was introduced in the bipyridine ligands that could alter the transition moments. This calculated electronic snapshot may result from the statistical mean of three equivalent and equiprobable situations in which the electron is localised on one of the ligands. However, the computed data for the singlet state $^2\mathrm{A}_1$ of the oxidized species after relaxation are in agreement with experimental data.

Synthetic methods are available [52,60] for the modification of the bipyridine ligands surrounding the ruthenium atom. In this manner it is possible to obtain mono and di-substituded ligands with either electron donating or withdrawing groups [53,60,61], as well as synthetic handles either for further synthesis [47,52,62,63] or for grafting [55,63–65] onto surfaces. Oxidation potentials for this group of molecules range from 1.20 to 1.40 V versus SCE, depending on the nature and number of substitutions [53,55,60].

These structural changes on the ligand allow the modulation of the photophysical properties of the complex. For instance, direct changes in the relative energies of the dπ and π* orbital levels observed as bathochromic shifts of up to 50 nm [48,53,60,66] are achieved by the addition of ester or carboxylate groups to the bipyridine ligands. The emission lifetimes of these compounds are also affected by substitution patterns on the bipyridines [53,60,67,68]. Electron withdrawing substituents diminish the fluorescence lifetimes and intensities by as much as 70% compared to the parent $[\mathrm{Ru(bpy)_3}]^{2+}$ [55,60]. For all the above-mentioned reasons, we will focus in this review on the derivatives of the $[\mathrm{Ru(bpy)_3}]^{2+}$ complex as the photoactive chromophore unit.

4.3. *Acceptor side*

A vectorial electron flow is established in PSII, that moves electrons coming from the excited $\mathrm{P_{680}}^*$ pigment away from the catalytic oxidative site. Pheophytin and quinones are the main cofactors that drive the electrons in order to stabilize the charge-separated state. An important issue in the development of artificial photosynthesis devices is to borrow features of this type to control the directionality of electron transfers. Current work

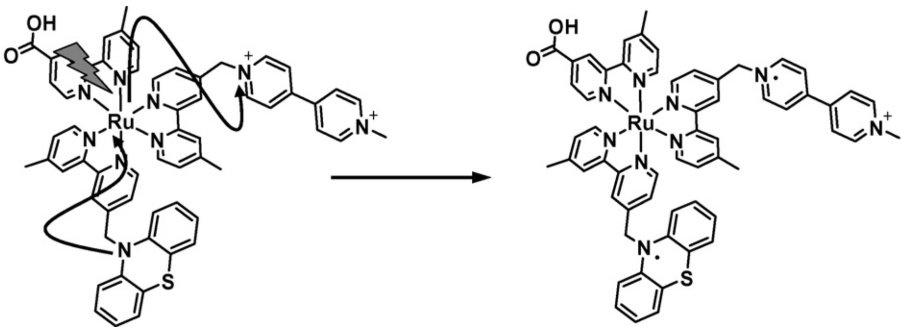

Fig. 4. Meyer's chromophore–quencher system.

in this field utilises external electron acceptors as the recipients of the first electron transfer. The more commonly utilized external electron acceptors are methyl viologen (MV) and cobalt(III) pentamine. The main disadvantage of external acceptors is the fact that the electron transfer rate is limited by diffusion. In order to overcome this problem, acceptors have been covalently linked to sensitisers [4,69–71]. Meyer et al. [72] have described an elegant example termed chromophore–quencher to illustrate the feasibility of controlling the directionality of a photo-induced electron transfer within a molecular assembly in solution. The synthetic strategy involved the linking of an acceptor (MV) and a donor (10-methylphenothiazine, PTZ) to the periphery of the bipyridine ligands, thus developing the synthesis of trisheteroleptic ruthenium(II) complexes. In order to be operational, the thermodynamics of each component must be adjusted so as to provide a free energy gradient to drive the electron in the right direction. In the case of the donor–chromophore–acceptor complex, as shown in Fig. 4, upon irradiation in the MLCT band, the primary excited electron transfer occurs to the appended MV^{2+} ($k \sim 6 \times 10^{10}\ s^{-1}$) and is followed by a rapid intramolecular PTZ to Ru(III) electron transfer ($k \sim 1 \times 10^{10}\ s^{-1}$) leading to the formation of the redox charge-separated state described as oxidized $PTZ^{\bullet +}$ and reduced $MV^{\bullet +}$. Back electron transfer occurs on the range of $\sim 10^6\ s^{-1}$.

Recently a ruthenium dimer bridged by a fused aromatic system containing two phenanthrolines at each end together with two pyrazines and a quinone was reported [73]. It was shown that the central part of the ligand acts as a reversible reservoir for four electrons upon irradiation in the visible region and in presence of a sacrificial electron donor (triethylamine) (Fig. 5). Experimental facts tend to support that the first UV–visible spectral modification corresponds to a two-electron reduction process leading to the formation of the doubly reduced form of the quinone fragment, followed by two consecutive one electron transfers. More importantly, each electron transfer step is coupled with the protonation of the reduced species.

Other examples of suitable electron acceptors are perylenes [74] and fullerenes [75–77]. The latter show first reduction potentials similar to those of the biomimetic quinones, and additionally, the ability to accept multiple electrons (accumulation), rapid charge separation rates and low reorganization energies. Diads and triads involving C_{60} modules have been reported to have up to ~1 μs lifetimes [49,77].

The more challenging case is where the acceptor is itself a catalyst. Systems comprising heterobinuclear ruthenium–platinum [9] and ruthenium–palladium [8] have been described. These compounds photocatalyse the reduction of protons into molecular hydrogen using light ≥390 nm, albeit low quantum yields and turnover numbers. The Ru–Pd complex is capable of reducing diphenylacetylene to *cis*-stilbene under mild conditions (25 °C, 470 nm). Although the mechanism is not fully understood, it is clear that the reaction is photo-induced and that the palladium is responsible for the catalytic activity. These examples of photocatalised reduction reactions are of utmost importance since they would be a potential couple to the water oxidation reaction.

One last example of an electron acceptor module consists of solid-state semiconducting materials. In recent years the use of nanocrystalline TiO_2-based systems has received much attention [78–80]. Grätzel's group has studied the photo-injection of elec-

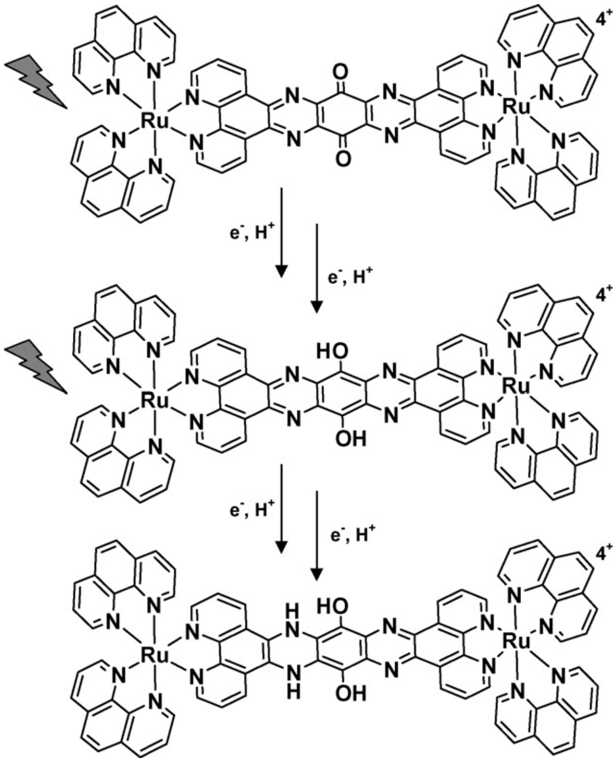

Fig. 5. Example of photo-induced sequential $2e^-$, $2H^+$ transfers.

trons into TiO_2 from the excited state of ruthenium polypyridyl complexes [81]. The resulting oxidized species can be reduced by a redox couple, which in a generic Grätzel cell is an electrolyte such as $I^-/I_3{}^-$, or by electrons coming from a catalytic centre. The advantages of such systems rely in the large surface area of the materials increasing the absorption by orders of magnitude (antenna effect), and the extremely fast rates of electron injection compared to the back electron transfer rates. These properties make the use of such materials is an interesting alternative to external electron acceptors in solution.

4.4. Donor side

The oxidized $P_{680}{}^+$ is reduced by Tyr_z, which in turn oxidizes the OEC. To date, the precise structure of the manganese cluster is not known, therefore preventing the elucidation of the water oxidation mechanism. The literature contains examples of anthracenes [42,82] carotenoids [35,46,83], metallated porphyrins [7,41] or transition metal complexes [84,85] used as electron donors. In the following sections, we will concentrate on examples more closely related to the natural systems. We will give an overview of the progress made into ruthenium systems linked to Tyr_z synthetic equivalents and manganese complexes. Finally, we will discuss the common issues between the oxidation of water by a (manganese) catalyst and the photogeneration of a charge-separated state by a ruthenium chromophore.

4.4.1. Phenol group

In the natural system, electron transfer processes are often accompanied by proton transfer processes. This observation is most important in the PSII system where a $4e^-$ oxidation is coupled to a 4 proton transfer in order to produce molecular oxygen. In PSII, the coupling of both these processes is initiated at Tyr_z, which not only reduces the photooxidised P_{680}, but is also involved in PCET processes [86] that prevent excessive charge accumulation from making the reaction too endergonic, and has even been thought to intervene in the abstraction of protons from the substrate water molecules [20,21]. This charge compensation process allows the OEC to rock within 300 mV between its four-oxidation states, therefore avoiding oxidation potentials that could not be achievable by P_{680} [58,87,123]. The chemical basis for this proton/electron transfer lies within the chemical properties of the phenol moiety. In aqueous solution, the pK_a of a phenol changes from 10 to −2 upon oxidation, with the corollary that these processes will happen concurrently. Whether these steps occur via proton first, electron first, or as a concerted process has been recently investigated by several groups [88–94].

From a synthetic point of view, phenol groups are widely used in the design of multidentate ligands [95,96] for their good ability to bind to a wide variety of metal ions and also for stabilising high oxidation state manganese ions [97–100]. There are several examples in the literature describing the oxidation of phenols by photochemical means, both as terminal groups [79,101,102] and as coordinated ligands [103–105].

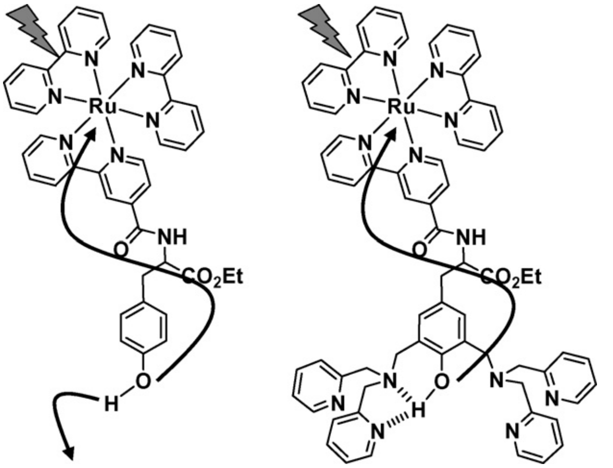

Fig. 6. Ruthenium–tyrosine complexes: free pending phenol (left); coordinating cavity (right).

A synthetic model where a tyrosine was covalently linked to a ruthenium(II) trisbipyridine complex through an amide group was reported [101] (see Fig. 6). The phenol ring was used as a molecular platform to prepare a biscompartmental coordinating cavity (Fig. 6). Prior to metallation of the coordinating cavities, photophysical measurements displayed an emission decay similar to that of the parent $[Ru(bpy)_3]^{2+}$ complex, insinuating that the tyrosine does not quench the excited state of ruthenium and also that the nature of the molecular link does not alter the intrinsic properties of the ruthenium(II) complex. Flash photolysis experiments performed by irradiating at 460 nm in presence of MV^{2+} in water, resulted in the bleaching of the MLCT band of the Ru(II) chromophore at 450 nm (formation of Ru(III)) with concomitant formation of the $MV^{\bullet+}$ radical. The longer lifetime of the $MV^{\bullet+}$ radical compared to that of the recovery of Ru(II) confirmed an intramolecular electron transfer process from the tyrosine to the photogenerated Ru(III). Interestingly, the rate of electron transfer was found to be two orders of magnitude faster in the case where the –OH fragment of the phenol ring was in hydrogen bond to the nitrogen atoms of the pending dipyridyl amine ligand. This behaviour was explained by an increase of electron density on the phenol ring upon hydrogen bonding. This assertion led to a series of studies on the implication of synthetic phenols in CPET processes, when hydrogen bonded to a nearby base [88–94].

Experiments using the above molecule grafted to colloidal TiO_2 in solution showed also the ability to photooxidize the tyrosine moiety using TiO_2 as the electron acceptor instead of an external equivalent [79]. Low yields were explained by the large electron transfer back reaction from TiO_2 to ruthenium, but the ability to use nanoparticles as electron acceptors is promising towards the development of photochemical cells.

A recent synthetic model mimicking the Tyr_Z/His_{191} pair has been reported [102] (Fig. 7). In solution, the existence of a hydrogen bond between the phenol and imidazole groups is supported by ^1H NMR study. Photoexcitation electron transfer studies were realised upon irradiation at 450 nm in presence of MV^{2+} as an electron acceptor. The transient absorption spectrum is dominated by the strong absorption of $MV^{\bullet+}$ and the extinction of

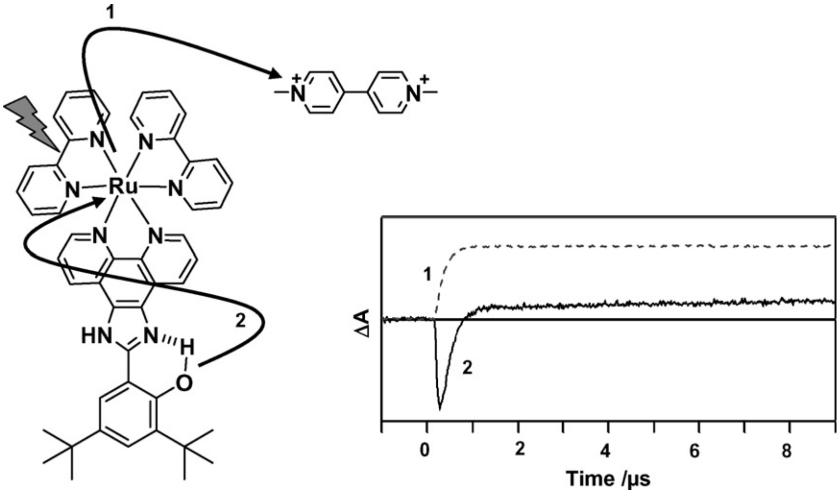

Fig. 7. Tyrosine–histidine couple mimic with its transient absorption spectrum. (1) Formation of methylviologen radical (605 nm) and (2) recovery of Ru(II) MLCT (450 nm).

the MLCT band, indicating the generation of a Ru(III) species. The kinetics shows a recovery of the reduced state of the chromophore within 500 ns (Fig. 7). This is much faster than the decay of $MV^{\bullet+}$, occurring in about 200 μs, meaning that the reduction of Ru(III) to Ru(II) is due to an electron transfer from an electron donating group on the ligand i.e. the phenol. Confirmation of the photooxidation of the phenol group comes from the EPR spectrum of an irradiated sample in presence of an irreversible electron acceptor.

As mentioned above, phenol groups have been used as coordinating groups in a large number of family of ligands [95,96]. An example of such a coordinating cavity is the salophen core [106], being defined by two imino nitrogen atoms and two oxygen atoms coming from phenol groups. A heteroditopic ligand holding both a phenanthroline end and a salophen cavity was synthesised and fixed to the ruthenium(II) ion through the phenanthroline appendix [105] (see Fig. 8). Upon excitation in the MLCT band at 450 nm, a quenching of the MLCT triplet excited state of the ruthenium(II) complex was evidenced (>95% as compared to $[Ru(bpy)_3]^{2+}$). This phenomenon was attributed to an intramolecular electron transfer process, which resulted in the formation of an extremely long-lived charge-separated state of 30 μs. Theoretical data support that both the lowest singlet and triplet states originate mainly from intra-ligand charge transfers within the extended π-ligand. The calculated spin density map of the triplet state indicates that it results from an electron transfer from the $N=CC_6H_4$–OH fragments to the binding phenanthroline moiety (Fig. 8). Therefore, this triplet cannot be considered as the usual charge-separated state in ruthenium(II) polypyridine type complexes. The electron transfer studies upon irradiation at 355 nm in the presence of an irreversible electron scavenger ($[Co^{III}(NH_3)_5Cl)]^+$) lead to the formation of a phenoxyl type radical as evidenced from the EPR spectrum (signal at $g = 2.004$). This suggests that a Ru(III) intermediate is generated that can be reductively quenched by a phenol group. The insertion of a copper ion in the coordinating cavity resulted in a complete extinction of the luminescence and no significant electron transfer process was observed under irradiation in presence of external electron acceptors. The authors explained this phenomenon by a strong electronic coupling between the two metal ions.

4.4.2. Manganese complexes

The outstanding challenge in artificial photosynthesis research is to power a water oxidation catalyst by a photoactive chromophore. Manganese complexes known to perform the four-electron water oxidation reaction are scarce [11–13,16] and intensive efforts are still needed to discover robust molecular

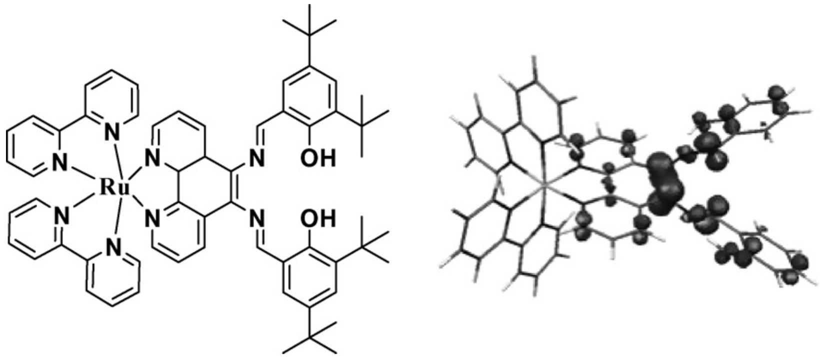

Fig. 8. Structure of a ruthenium bound to a salophen cavity (left), and calculated spin density map of the lowest triplet state (right).

catalysts working at modest overpotential (see previous chapters in this issue). In this section we will discuss about the first attempts in building a molecular system bearing a ruthenium(II) chromophore and a mono- or polynuclear manganese complex as the donor component.

The first published work on a molecule containing a sensitiser covalently linked to a manganese complex dates back to 1997 [107]. It was shown that upon photoexcitation of a binuclear Ru–Mn complex, the ruthenium chromophore could donate an electron to an external acceptor and consequently oxidize a coordinated manganese ion with rate constants ∼50 ns to 10 μs. On the up side, this first work proved the fact that upon light absorption, a chain reaction of ET events could be initiated, on the down side, it already outlined the difficulties intrinsic to manganese chemistry. First, de-coordination phenomena were reported, and biphasic decays corresponding to mono and bimetallic complexes were observed. Additionally, insertion of a manganese ion to a ruthenium complex led to significant quenching of the excited state of the chromophore. The process, identified as energy transfer from ruthenium to manganese, was reported by Abrahamsson et al. [108] and showed that, within this family of molecules, when the metal-to-metal distances were smaller than 10 Å the ruthenium complex was very difficult to photooxidize due to its very short excited state lifetime (∼10 ns). Additionally, this work also showed that chemical modifications in the ligands around the ruthenium could lower this quenching process. The authors found the reorganization energy for the Mn^{II}/Mn^{III} transition to be high, 1.4–2.0 eV, while typical values for electron transfer reactions in polar media are around 1.0 eV. These conclusions pointed out the inherent problems of using Mn^{II} as an electron donor. Therefore, a higher oxidation state of manganese and/or an electron relay intermediate might be needed.

An elegant example by Burdinski et al. [104] presented for the first time the photooxidation of both a $Ru_3(Mn^{II})_3$ complex, and a ligand coordinated to a Mn^{IV} ion via three phenolate groups. In the first case, each manganese(II) ion could be oxidized by one electron only, showing the need for charge compensation. In the second case, one electron could be removed from a phenolate group. This last example raises the issue of the oxidation site in phenolate-containing manganese complexes, which has been barely addressed so far [109,110].

Magnusson et al. [111] showed how a Ru–Tyr molecular dyad was used to power the light driven oxidation of a dinuclear $Mn_2^{III–III}$ complex. In this study, it was shown that the observed one electron transfer process could parallel the first electron transfer sequence in PSII. Indeed, upon light absorption, a chain reaction of ET could be achieved whereby the Ru(III) species, obtained in presence of an electron acceptor, was quenched through an intermolecular ET leading to the formation of the tyrosyl radical. Conclusive evidence that the tyrosyl radical was sufficiently oxidising to abstract one electron from the dinuclear $Mn_2^{III–III}$ came from monitoring the EPR spectrum from the starting silent $Mn_2^{III–III}$ to the formation of a typical 18 lines spectrum for the mixed valence mono-μ-oxo $Mn_2^{III–IV}$ dimer [99]. Time-resolved EPR measurements for the decay of the generated tyrosyl radical in presence and absence of the manganese complex confirmed the results. Furthermore, photo-induced intermolecular ET studies between the parent $[Ru(bpy)_3]^{2+}$ complex and the dinuclear $Mn_2^{III–III}$ compound in the same experimental conditions lead to more oxidized forms of the manganese complex. This example shows that a phenol group can act as an electron relay, by tuning the oxidation potential applied to the manganese complex (Fig. 9).

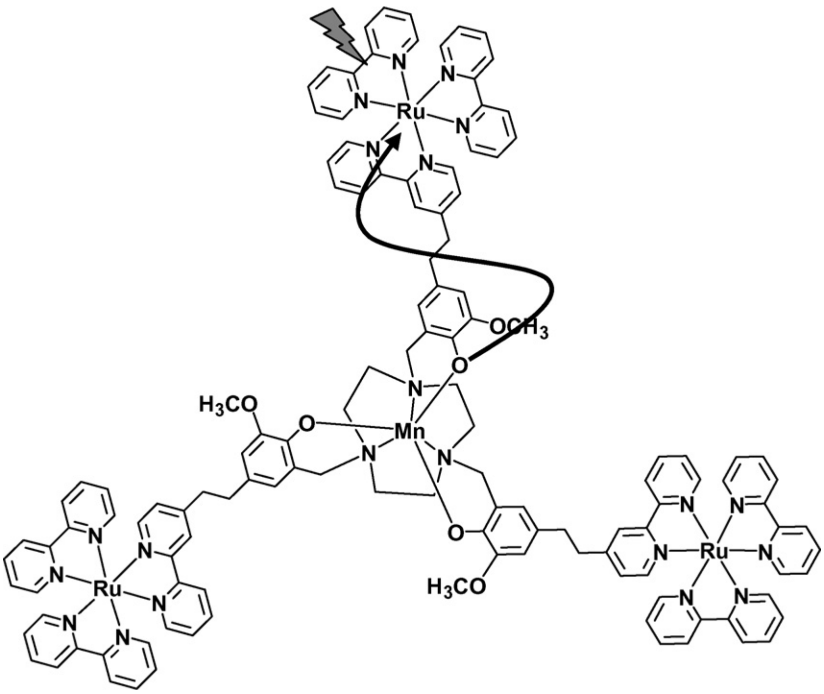

Fig. 9. Light driven oxidation of manganese bound phenolate group.

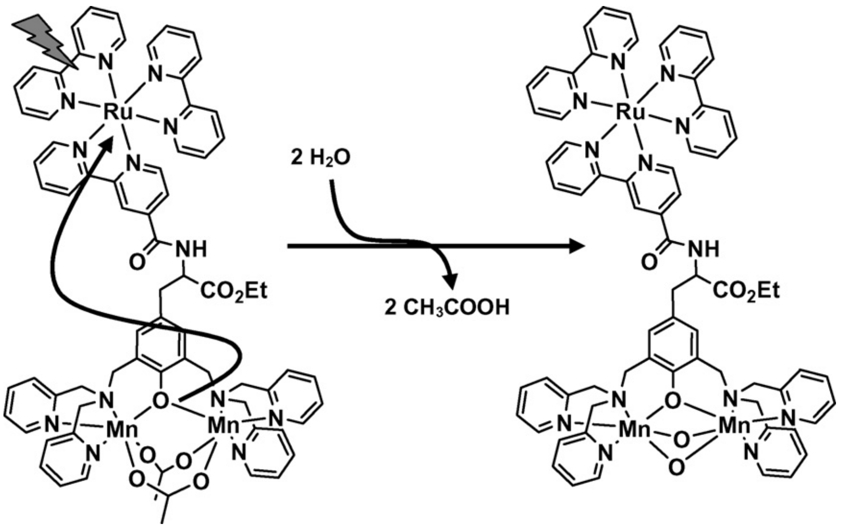

Fig. 10. Intramolecular photo-induced electron transfers from a dinuclear Mn^{II} to Mn^{II} complex, followed by ligand exchange reaction.

Phenolate-bridged bimetallic manganese complexes have yielded up to date the most promising results in the field. Huang et al. [103,112,113] showed that multi-electron transfer steps could be observed from a dimanganese complex to a $[Ru(bpy)_3]^{2+}$ unit, whether it was covalently linked or not. The intermolecular ET experiments involve the exchange of the initial acetate ligands in the manganese complexes to water molecules, which coordinate as μ-oxo bridges [112] (see Fig. 10). The exchange process was later studied itself by X-ray absorption spectroscopy on the ruthenium-free dinuclear manganese complexes [114].

To conclude, no example has been reported where oxidation of water is driven by a photosensitiser covalently linked to a catalyst. Manganese(II) has shown to be reluctant to ET, mainly because of high reorganization energy on going from Mn^{II} to Mn^{III} [107,108]. Phenolate containing ligands have shown to be efficient electron relays [104,111]. It is to be noted that out of all the artificial OEC systems that have been reported to undergo oxidation of water, there have been no attempts to link them to photoactive centres.

5. Discussion

Of all the components required for a molecular artificial photosynthesis device described above, the catalytic part is the most elusive. As already mentioned, the lack of efficient water oxidizing catalysts is an obstacle to the design of an all-in-one system. However, lessons can already be drawn from the examples shown above, concerning the issues that overlap water oxidizing/reducing catalysts and charge separating units.

Attempts to tackle the subject of charge build-up and compensation are closer to serendipity than design. Ligand exchange reactions have been observed, where bridging acetates are replaced by μ-oxo bridges [112]. These oxo-bridged adducts of manganese complexes are thermodynamically stable and are very unlikely to perform O–O bond formation. The PSII machinery keeps the oxidation potential of the OEC to a reasonable level thanks to CPET, and produces highly reactive oxo ligands (bridging or not), most likely stabilized by secondary sphere interactions. In order to reproduce these features, catalysts with a scaffold providing basic groups in the secondary sphere should be developed [115–117]. They should also be capable of holding the metal ions at such a distance [118] that collapse into oxo-bridged unreactive polynuclear complexes is not possible.

The electronic coupling between the sensitiser and the donor side (manganese catalyst) has been nicely laid out by the use of different phenol groups. Intermolecular ET from $Mn_2^{II,II}$ [112] and $Mn_2^{III,III}$ [111,112] complex has been shown to be possible. However, there is no example of a ruthenium–manganese system with a non-coordinated Tyr_Z equivalent. Such a compound would be of great help for confirming or discarding the H atom abstraction mechanism proposed for water oxidation in the natural system.

Another point of crucial importance, which has not been given sufficient attention, is the conditions under which the catalytic reactions occur most efficiently. First, this has to be taken into account in the tuning of the electronic properties of the catalysts themselves and second, the groups and linkages used should be chosen among those which do not suffer damage under such particular conditions. Therefore, basic principles for designing robust and efficient catalysts [119] should also be applied to the whole architecture of a molecular artificial photosynthesis device, in order to prevent the molecule from auto-oxidation phenomena [120].

6. Conclusion

Work in the field of artificial photosynthesis is still in its infancy. While there have been vast improvements in the knowledge of the structure [18,19,24] and functioning of the natural system [121], there is still no definite answer to these issues. On the chemistry side, individual problems have been thoroughly studied and the basic science seems to be understood (except for water oxidation). Problems arise when trying to combine all these aspects into a functioning system. Efficient light absorption, generation of a charge-separated state both sufficiently long-lived to allow subsequent reactions, and energetic enough to make them happen, sequential multiple electron transfer, substrate binding to catalytic centres, and catalysis must be all harnessed in one complex in order for this to work. As in any multi-step process, the loss of efficiency at any given step constitutes a burden to the rest of the process. On top of these requirements, there are additional demands placed on the synthetic process of the system. Besides the perennial needs of stability and high yield synthesis, one must take in consideration the ability to have/use different templates for the catalytic centres, the different substitution patterns for the optimization of the system and the different linkages between these modules. To date, complexes that try to encompass all these processes are few. Whether for reduction or oxidation models, ruthenium bispyridine complexes are the main candidates for sensitization. On the reduction side, catalytic production of H_2 has been reported but with limited turnovers [8,9]. On the oxidation part, no successful complex has been found, and none of the structures that have shown activity by chemical or electrochemical means [10–17] have been tried in a light powered complex [122]. A new approach seems to have emerged with the use of surfaces, which allows to short-cut many complications. Photochemical cells have been set up and showed good results [30], but the case was only applied to the oxidation of sugar. Again, the rate-limiting step to the achievement of artificial photosynthesis seems to be the finding of an efficient water oxidizing complex.

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