ELSEVIER

Catalysis Today 58 (2000) 57–69

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Mimicking photosystem II reactions in artificial photosynthesis: Ru(II)-polypyridine photosensitisers linked to tyrosine and manganese electron donors

Leif Hammarström [a,*], Licheng Sun [b], Björn Åkermark [b], Stenbjörn Styring [c]

[a] *Department of Physical Chemistry, Uppsala University, Box 532, S-751 21 Uppsala, Sweden*
[b] *Department of Organic Chemistry, Stockholm University, S-10691 Stockholm, Sweden*
[c] *Department of Biochemistry, Centre for Chemistry and Chemical Engineering, Lund University, Box 124, S-22100 Lund, Sweden*

Abstract

The paper describes a project aiming at constructing functional mimics of the oxygen evolving complex in photosystem II, coupled to photoinduced charge separation. Biomimetic electron donors, manganese complexes and tyrosine, have been linked to a Ru(II)-polypyridine photosensitiser. Oxidation of the donors by intramolecular electron transfer from the photooxidised Ru(III) complex was demonstrated using optical flash photolysis and EPR experiments. A step-wise electron transfer Mn(III,III)→tyrosine→Ru(III) was demonstrated, in analogy to the reaction on the donor side of photosystem II. Electron transfer from the tyrosine to Ru(III) was coupled to tyrosine deprotonation. This resulted in a large reorganisation energy and thus a slow reaction rate, unless the tyrosine was hydrogen bonded or already deprotonated. A comparison with analogous reaction in photosystem II is made. Finally, light-induced oxidation of a manganese dimer linked to a Ru(II)-photosensitiser was observed. Preliminary results suggest the possibility of photooxidising manganese dimers in several steps, which is an important step towards water oxidation.

Keywords: Artificial photosynthesis; Photosystem II; Electron transfer; Manganese; Ruthenium; Photochemistry

1. Introduction

In natural photosynthesis, light is converted to chemical energy through a chain of electron transfer reactions [1,2]. As a source of electrons for the photosynthetic fixation of CO_2, higher plants, algae and cyano-bacteria are able to use water, generating molecular oxygen as a side product. Water is abundant, which gives an advantage over photosynthetic species that use other substrates. However, in order to oxidise water at reasonably low potentials, without forming high-energy intermediates, four electrons have to be taken in one step

$$2H_2O \rightarrow 4e^- + 4H^+ + O_2 \quad (E^0 = 0.82\,V \text{ vs. NHE at pH } 7) \tag{1}$$

Water oxidation is catalysed by a tetranuclear manganese complex in photosystem II (PSII). During the light-induced charge separation cycles it serves to accumulate the oxidising equivalents needed for reaction (1), but the complex structure and the reaction mechanism are not known [3–6]. The primary electron donor, the chlorophylls of P_{680}, is photooxidised by electron transfer to the quinones on the acceptor

* Corresponding author. Fax: +46-18-50-85-42.
E-mail address: leifh@fki.uu.se (L. Hammarström)

0920-5861/00/$ – see front matter
PII: S0920-5861(00)00242-X

side of the reaction centre. In a subsequent reaction, P_{680} is regenerated by electron transfer from the manganese complex on the donor side, via a tyrosine residue. After four consecutive steps of light excitation and oxidation, the manganese complex extracts four electrons from two water molecules, and releases molecular oxygen.

For more than 20 years, large efforts have been made to develop a chemical artificial photosynthetic system, based on photoinduced charge separation [7]. In terms of photosynthesis of energy rich chemicals, the success has been modest so far, but much has been learnt on the fundamental level. During the last decade, artificial photosynthesis has mainly concerned either (i) supermolecules performing photoinduced charge separation through a chain of electron transfer reactions [8–10], or (ii) mimics for the manganese complex of PSII [5]. The former systems include mimics of bacterial reaction centres [11–13], but have only rarely involved the transfer of more than one electron or been coupled to any further chemical reaction [13,14]. The artificial manganese complexes on the other hand have mainly been structural mimics, with fewer examples of multi-step oxidation or verified catalytic activity [5,15,16]. In the latter cases the oxidation has been achieved in dark reactions (chemically or electrochemically) and not with light.

In the present paper, we describe the development of a project where we try to combine these lines of artificial photosynthesis and obtain a functional mimic of the oxygen evolving complex of PSII that is coupled to photoinduced charge separation. Thus, following the strategy of nature, we initially aim at accumulating oxidative equivalents in an artificial manganese complex, using light-induced redox reactions. Ultimately, the complex should also be able to oxidise water to oxygen in a catalytic reaction. This would allow the use of water as an electron source also in artificial photosynthesis, for the reduction of, e.g., protons to generate H_2.

Adopting natural structures and principles serves as a starting point and source of inspiration for the construction of biomimetic systems, but it is wise not to be too strict on this point. Alternative, non-biological molecular components often posses favourable properties, and one may possibly even supersede nature at certain points by using solutions that have not been available to evolution. As an example of these ideas, we have chosen to use ruthenium polypyridine complexes as photosensitisers, because they have favourable photochemical and synthetic properties [17,18]. At the same time, we have used tyrosine and manganese complexes as electron donors, following nature more closely.

2. Ru–Mn complexes

Our first aim was to investigate if complexes could be made where the Ru(II) moiety is oxidised in a photoreaction, and then regenerated by electron transfer from the manganese in the same molecule. The reaction sequence is schematically described in Fig. 1, and it was indeed realised for a number of Ru(II)–Mn(II) complexes (Scheme 1), as shown in the photochemical experiments described below [19–23].

First, the redox potentials for the $Mn^{II/III}$ and $Ru^{II/III}$ couples of **1**–**6** showed that the electron transfer from Mn(II) to the oxidised Ru(III) was feasible. In cyclic voltammetry experiments, all compounds displayed reversible oxidations of both metals with $E_{1/2}$=+0.8 to +0.9 V for $Mn^{II/III}$ and +1.3 V for $Ru^{II/III}$ (vs. SCE in CH_3CN).

In the photochemical experiments, the Ru(II)–Mn(II) complexes **1**–**6** were excited by a laser flash in the visible absorption band of the Ru(II) complex moiety (band maximum around 455 nm). An electron was transferred from the Ru excited state to the external electron acceptor methylviologen (MV^{2+}), forming Ru(III) and MV^+ (Fig. 1, step 1). When manganese was not present in the complexes, the diffusion controlled recombination reaction $Ru(III)+MV^+ \rightarrow Ru(II)+MV^{2+}$ occurred (first half-life ca. 100 μs). This reaction could be followed by the recovery of the Ru(II) absorption around 455 nm and the decay of the MV^+-radical signal around 602 nm. However, for the compounds **1**–**6** with Mn(II), the Ru(II) recovery was much faster, while the MV^+ decay remained diffusion-controlled. The photooxidised Ru(III) must then have received an electron from the manganese (Fig. 1, step 2), which is the only additional electron source. The decay of the MV^+ signal was attributed to the diffusion-limited recombination with Mn(III) (Fig. 1, step 3), making the whole photoreaction sequence reversible.

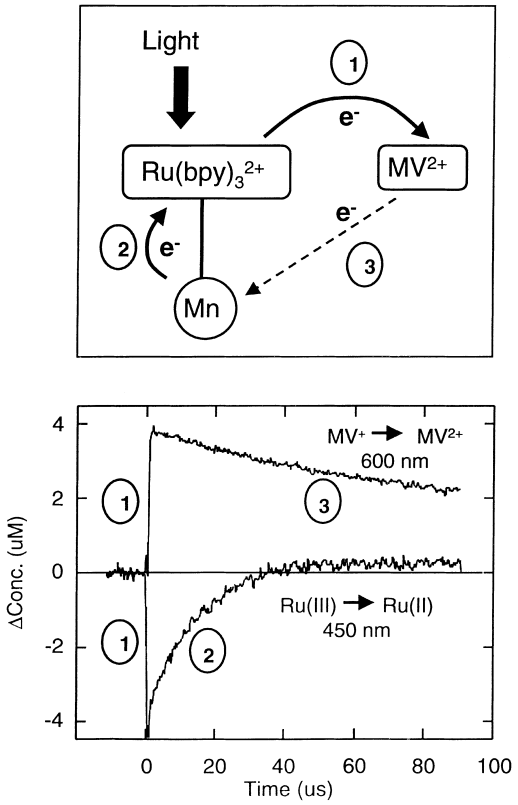


Fig. 1. Upper panel: reaction scheme for the photoinduced electron transfer reactions in the Ru–Mn complexes. In step 1 an electron is transferred from the excited Ru(II) complex to the external acceptor methylviologen (MV^{2+}). Step 2 is the intramolecular electron transfer from Mn(II) to Ru(III), regenerating the Ru(II) ground state, and step 3 is the recombination reaction $Mn(III)+MV^{+}\rightarrow Mn(II)+MV^{2+}$. Lower panel: typical transient absorbance traces after a laser flash at 460 nm. Step 1 is completed in $<1\,\mu$s. The Ru(II) recovery, followed at 450 nm (lower trace) is much faster than the decay of MV^{+} observed at 600 nm (upper trace), due to reaction step 2. The reduced MV^{+} absorbs somewhat also at 450 nm, which lifts the 450 nm signal above the base line at longer times.

Neither the Mn(II) nor the Mn(III) species absorb light in the Vis-near UV region, and formation of the Mn(III) species could consequently not be directly detected in the optical experiments. Therefore, separate experiments were performed to demonstrate the formation of Mn(III) upon oxidation by Ru(III). Equimolar amounts of a Ru(II)–Mn(II) compound and chemically oxidised $Ru(III)(bpy)_3$ were mixed. Before mixing, both the Ru(III) and the Mn(II) gave strong EPR signals. After mixing the signals disappeared, showing that the Ru(III) was reduced by Mn(II) in a 1:1 ratio, as expected, and that the EPR silent Mn(III) and Ru(II) species were formed.

2.1. The electron transfer rate

The Ru(II) recovery rate constant was independent of the concentration of the Ru(II)–Mn(II) complex, showing that the electron transfer was intramolecular, i.e. occurred between Ru(III) and Mn(II) within the same molecule. In Table 1, the Mn(II)–Ru(III) electron transfer rate constants for **1**–**6** are given [19–23]. The rate constants span more than two order of magnitude, in spite of the rather small variations in driving force ($-\Delta G^0$=0.4–0.5 eV). We are currently investigating the factors responsible for the observed variations in the rate constant, and we will use the results in the design of future complexes.

The rate constant k_{ET} for electron transfer is given by an Arrhenius-like expression [24]

$$k_{ET} = A\ \exp\left(\frac{\Delta G^{\#}}{RT}\right) \tag{2}$$

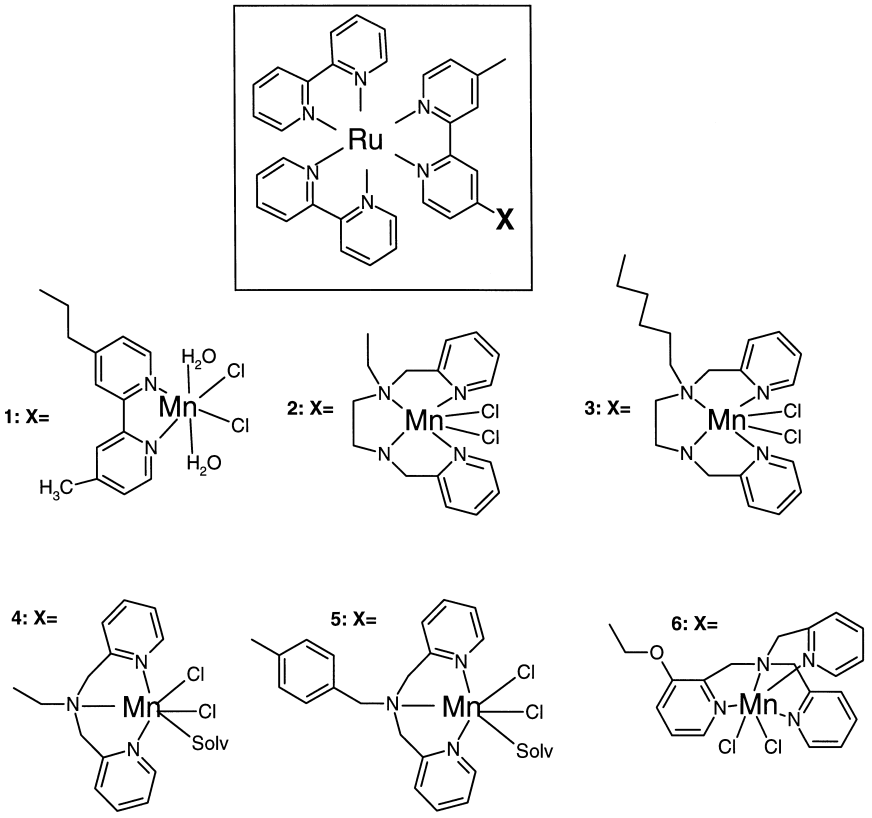
$$\Delta G^{\#} = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \tag{3}$$

$$A = \frac{2\pi^2}{h}\frac{{H_{rp}}^2}{(\pi\lambda RT)^{1/2}} \tag{4}$$

where $\Delta G^{\#}$ is the free energy of activation, determined as in Eq. (3) by the free energy change (ΔG^0) and the so-called reorganisation energy λ. The latter is (loosely) a measure of how much the positions of the reactant atoms (inner reorganisation, λ_{in}) and the polarisation of the solvent environment (outer reorganisation, λ_{out}) have to change when going to the products

$$\lambda = \lambda_{in} + \lambda_{out} \tag{5}$$

More precisely, it is the free energy that would be required to change the systems nuclear and solvent coordinates from their equilibrium position in the reactant state to that of the product state, without transferring an electron. The pre-exponential factor A depends quadratically on H_{rp}, the electronic coupling between the reactant and product states. In most cases the factor A is found to decrease exponentially with the distance between the reactants.



Scheme 1.

The large variations in the observed electron transfer rate constants in Table 1 cannot be explained by the differences in Ru−Mn distance only. From the temperature dependence of the electron transfer rate constant (Eqs. (2) and (3)) we obtained significant variations in the reorganisation energy λ [23]. For both **1** and **5** the value is relatively large (1.8 and 2.0 eV, respectively), even for small reactants in a polar medium, and may

Table 1
Photochemical data for some Ru–Mn complexes in deoxygenated acetonitrile [19–23] (all values were obtained in deoxygenated acetonitrile.)

Compound	Excited state lifetime of the Ru moiety[a] (τ_{ES}, ns)	Rate constant for Mn(II)–Ru(III) electron transfer (s^{-1})	ΔG^0 for Mn(II)–Ru(III) electron transfer (eV)
1	260	1.8×10^5	−0.43
2	7	$<2\times10^7$	−0.45
3	≈300[b]	$\approx1.0\times10^{5}$[b]	−0.45[c]
4	2	1.3×10^6	−0.39[d]
5	23	1.5×10^6	−0.39
6	120	1.0×10^5	−0.49

[a] From the lifetime of the emission measured around 610 nm. The unquenched lifetimes of **1**–**4** and **6** (when manganese is removed) are all ca. 1000 ns, and for **5** equal to 1300 ns.

[b] Not a single exponential process, probably because the flexible link gives a distribution of reactant conformations.

[c] Not measured. Assumed to be the same as for **2**.

[d] Not measured. Assumed to be the same as for **5**.

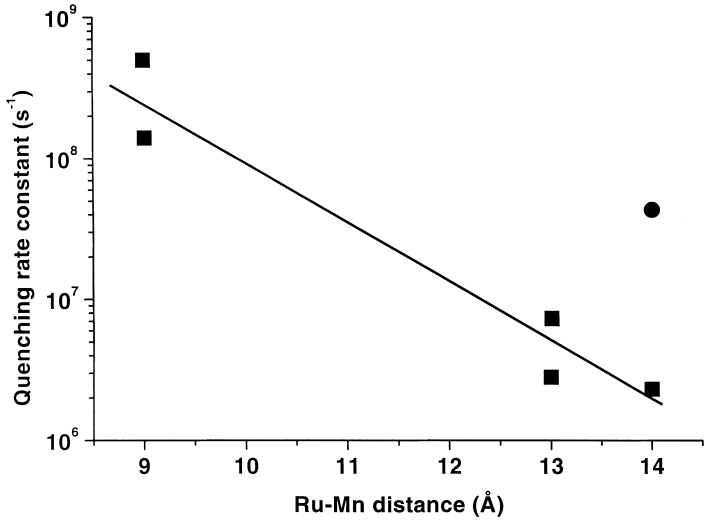


Fig. 2. The rate constant for quenching of the Ru excited state (k_q) as a function of the Ru–Mn distance for **1**–**6** [23]. Distances were estimated using molecular mechanics calculations (MM3). The rate constant is derived from the difference between the Ru emission lifetime with τ and without τ_0 manganese in the ligand cavity, $k_q=1/\tau-1/\tau_0$ (see Table 1). The line is a linear least-squares fit point to the data for **1**–**4** and **6** (squares). The value for **5** (circle) was not included in the fit because the Ru excited state is localised towards the manganese (see text).

reflect large inner reorganisations of the Mn complex, possibly due to the small ligands and the Jahn–Teller distortion of Mn(III) complexes. For **6** the value is smaller (1.4 eV) but reaction is still strongly activated. This is an important result for the development of our biomimetic systems. As seen from Eqs. (2) and (3), a low reorganisation energy is required for a fast electron transfer, if one does not want to waste too much driving force in the reaction. Also, water oxidation at a multi-nuclear Mn-complex requires large ligand rearrangements in the redox steps, and even binding of water. Thus, if large reorganisations are coupled to the electron transfer step, the manganese complex will probably never be a very fast donor. If a fast regeneration of the oxidised Ru sensitiser is wanted, another intermediate donor is required.

2.2. Mn(II) quenches the Ru excited state

A complicating factor in these complexes is that Mn(II) quenches the Ru(II) excited state. In some compounds the excited state is so short lived that the initial electron transfer to the MV^{2+} acceptor becomes too slow to compete, unless very high concentrations of MV^{2+} can be used. The quenching presumably occurs by energy transfer to the Mn(II) that has d–d excited states at appropriate energies, since we found evidence against other possible quenching mechanisms.[1] As shown in Fig. 2, the logarithm of the quenching rate constant increases linearly with decreasing Ru–Mn distance, with a slope of 1 $Å^{-1}$ [23]. This indicates that the energy of the Mn(II)-based d–d excited states is approximately constant with this type of ligands. The reason why **5** is not included in the correlation is that here the excited metal-to-ligand charge transfer (MLCT) state of the Ru moiety is delocalised over the bipyridine-phenyl ligand, and thus close to the manganese [23]. In the other complexes, the MLCT excited state is instead preferentially located on the non-substituted bipyridine ligands that point away from the manganese.

[1] Although the corresponding transitions are spin-forbidden (as shown by the negligible absorption of Mn(II) complexes in the visible region), exchange energy transfer in the reactant pair with the Ru excited triplet state can be allowed since the total spin of the pair may be conserved, see, e.g. [21].

The simple dependence on Ru–Mn distance has important predictive power for the further development of Ru–Mn compounds, where it is obviously important not to make the Ru–Mn distance too short. Also, we found that the excited singlet state of a porphyrin was quenched by a Mn(II) complex linked to the periphery [25]. These observations suggest that the quenching of the excited P_{680} chlorophylls in PSII by the manganese cluster is a potential problem that nature has solved by keeping the Mn cluster at a distance of several angstroms from P_{680}, using a tyrosine as redox intermediate [3–6,26].

A further complication in some of the Ru(II)–Mn(II) compounds is the partial dissociation of the Mn(II) ion from the complex. In the photochemical experiments, with typically 10–100 μM of the complex, 2–20% of the Mn(II) had dissociated at equilibrium, leaving some Ru moieties without a Mn donor. Here, the basically unwanted excited state quenching by the Mn(II) turned out to be a convenient tool for following the manganese binding, since the Ru complexes without Mn had a longer emission lifetime. The complexation constant depends on the nature of the ligands, and particularly **6** formed a very stable complex. The effects of dissociation were considered in the analysis of the kinetic data [21–23] and we could extract the data referring directly to the intramolecular processes in the intact Ru(II)–Mn(II) species.

At this point, one must remember that water most probably has to bind reversibly to the manganese cluster in PSII [3–6]. For the construction of artificial manganese complexes performing catalytic water oxidation, some lability in the coordination of manganese is therefore not necessarily unfavourable.

2.3. Summary

To summarise this section, we have made and studied a number of Ru(II)–Mn(II) complexes that feature electron transfer from the Mn(II) to the photogenerated Ru(III), and we have learned to handle some of the complications in their synthesis and function. Thus, our main concept at this initial stage, i.e. to oxidise a Mn moiety by a photogenerated Ru(III) complex by intramolecular electron transfer, has proven feasible. In order to achieve multiple oxidation, and also oxidise water, we must turn to larger Mn complexes. The manganese cluster in PSII is comprised of four manganese ions in higher valence states, predominantly Mn(III) and Mn(IV) in the lower oxidation states of the cluster [3–6]. The experiments described in this section has laid a good ground for the development of larger and more complicated Ru–$(Mn)_n$ complexes.

3. Introduction of a tyrosine as redox intermediate

With an intermediate electron transfer component between ruthenium and manganese, the distance between the metal centres can be increased. Still it may be possible to obtain a rapid and efficient electron transfer in two short-range steps via the intermediate (X)

$$\mathrm{Ru(III)–X_{red}–Mn_{red}} \rightarrow \mathrm{Ru(II)–X_{ox}–Mn_{red}} \rightarrow \mathrm{Ru(II)–X_{red}–Mn_{ox}} \quad (6)$$

The increased Ru–Mn distance serves two purposes. First, the unwanted quenching of the excited state discussed above is diminished at larger distance. Second, a problem with back-reactions in multi-step oxidation of manganese complexes can be avoided. For water oxidation to occur, several oxidising equivalents must be accumulated on the manganese complex, one equivalent for each photon that is absorbed by the system. In order to be of interest for water oxidation, the Mn potential in the single oxidation steps must be at least around +0.8 V vs. NHE. However, the excited Ru-complex is a strong reductant, $E_{1/2}=-0.8$ V [17,18], that may reduce any redox couple with a potential more positive than −0.8 V. Therefore, when the next photon is captured by the Ru complex, there is a strong driving force for the *reduction* of the oxidised manganese complex. With an intermediate X (Eq. (6)) this energy-wasting back-reaction can be avoided, since the manganese is kept further away, and the intermediate X will always be in its reduced form when the Ru-complex is excited.

Another possible advantage with an intermediate electron donor is that a faster reduction of the oxidised Ru(III) may be achieved than with the manganese complexes, and this will better compete with a possible back electron transfer from the reduced acceptors.

3.1. Ru-tyrosine–Mn systems mimicking the donor triad of PSII

In natural photosystem II (PSII), a tyrosine residue (denoted $tyrosine_Z$) is a redox intermediate between the manganese cluster and the oxidised photosensitiser P_{680}^+ [3–6,26]. The $tyrosine_Z$ transfers an electron to the oxidised P_{680}^+, and a deprotonated tyrosine radical is formed. This radical then oxidises the manganese cluster. In a recent model for water oxidation the $tyrosine_Z$ is even suggested to be directly involved in the catalytic water oxidation through a hydrogen atom transfer from manganese-bound water to the deprotonated tyrosine radical ([27] and references therein).

Following the principles for PSII, a Ru(II) complex linked to a tyrosyl residue was made (Fig. 3). Electron transfer from the tyrosine to the photooxidised Ru(III) was demonstrated in the same way as for the Ru(II)–Mn(II) complexes [28], using methylviologen or the irreversible acceptor $Co(NH_3)_5Cl^{2+}$ to photoox-

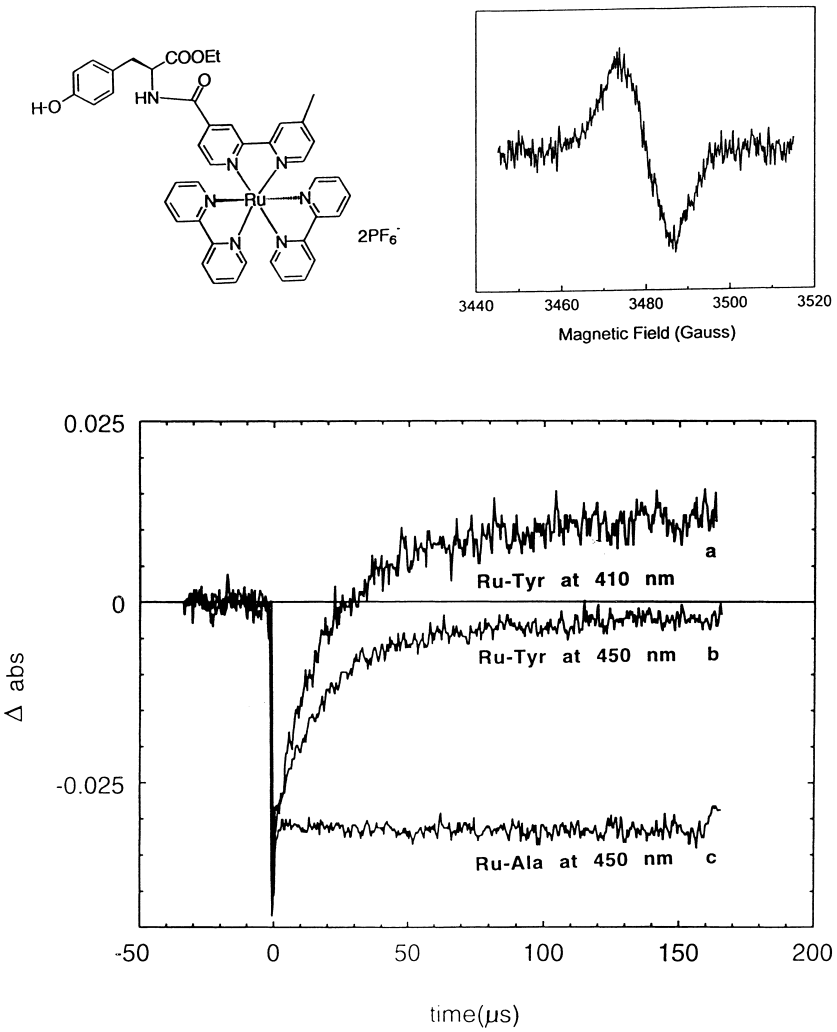


Fig. 3. Lower panel: Ru(II) recovery traces after a laser flash given to the Ru-tyrosine compound in the presence of the irreversible acceptor $Co(NH_3)_5Cl^{2+}$ (in water, pH 7). Trace **a** shows a positive absorption at the end, compared to trace **b**, due to the generation of a tyrosyl radical that absorbs at 410 nm. No Ru(II) recovery occurs in the Ru-alanine reference compound, trace **c**. Upper right panel: An EPR spectrum recorded under illumination at 20°C, attributed to the tyrosyl radical (g=2.0045, peak–trough width ≈14 G) [28].

idise the Ru(II). The subsequent electron transfer from the tyrosine to Ru(III) was monitored using the recovery of the Ru(II) ground state absorption at 450 nm. A rate constant of $4\times10^4\,s^{-1}$ was obtained in water at pH 7. With the same kinetics a positive absorption from the oxidised tyrosine radical grew in at 410 nm ($\varepsilon_{410\,nm}$=3000 $M^{-1}\,cm^{-1}$ [29]). The light-generated tyrosine radical could also be observed by EPR spectroscopy [28].

The redox potential of the tyrosine radical (the TyrOH/TyrO$^\bullet$ couple) at pH 7 is +0.98 V vs. NHE, and the lifetime of the radical is quite long (ca. 100 ms) [28]. We used the high potential of this long-lived radical to oxidise a manganese complex in a photochemical reaction. A dinuclear Mn(III,III) complex that displayed a reversible (III,III) to (III,IV) oxidation around +0.6 V was available through a collaboration with the group of Prof. Jean-Jaques Girerd (Orsay) [30]. Using the Ru-tyrosine compound together with the Mn(III,III) complex, the light-induced electron transfer sequence in Fig. 4 was demonstrated [31], in which the tyrosine has the function of a redox intermediate.

Light excitation of the Ru(II) moiety generated Ru(III) (Fig. 4, step 1), that is reduced again by the tyrosine (step 2). In step 3, the Mn(III,III) complex was oxidised in a bimolecular reaction with the tyrosyl radical, that reverted to tyrosine. The main evidence for the occurrence of step 3 was obtained from product EPR spectra showing Mn(III,IV), and the increased decay rate of the tyrosyl radical EPR signal with increasing concentration of the Mn(III,III) complex. The oxidation of the manganese was very slow: it occurred on the timescale of tens of milliseconds with 0.1–1 mM Mn(III,III). As required for the redox intermediate (Eq. (6)) the reduced tyrosine did not quench the Ru excited state; only the oxidised state (Ru(III)) has a redox potential high enough to take an electron from the tyrosine at neutral pH.

The redox potentials for the molecular components are shown in Fig. 4, and compared to those of PSII, together with the schematic representation of the pho-

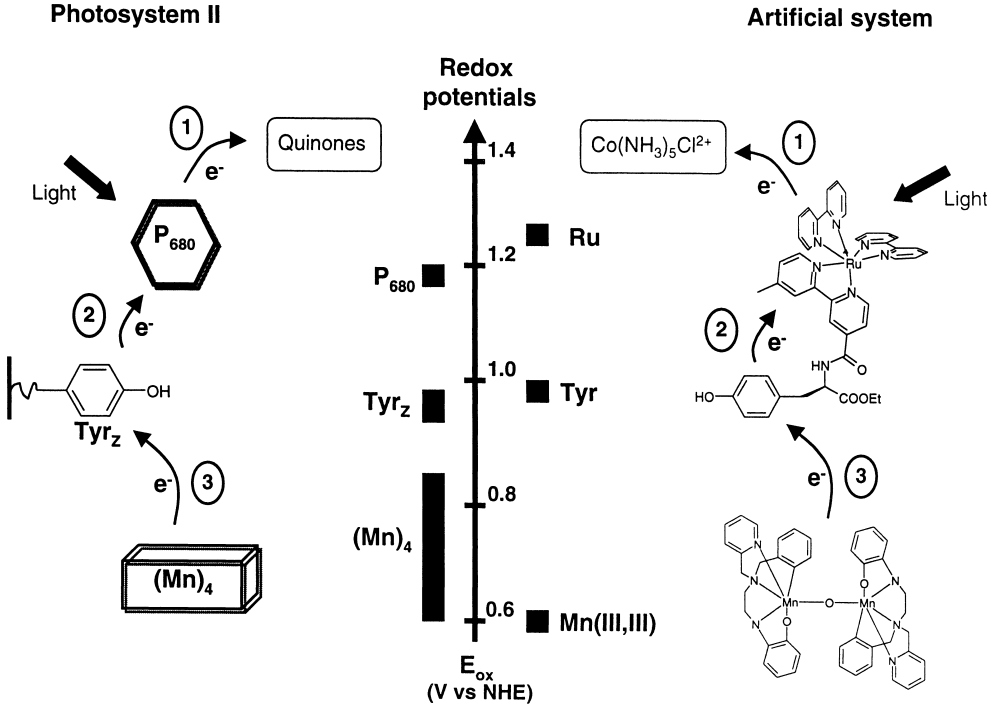


Fig. 4. Reaction scheme for photosystem II (left) and the artificial system (right), with a comparison of the redox potentials (middle). The schematic figures are not drawn to scale.

toinduced electron transfer reactions. Both the reaction scheme for this single-electron transfer sequence and the redox potentials correspond closely to the donor side reactions of PSII. Although one must appreciate the large structural differences, the comparisons made in Fig. 4 show that this artificial system represents a promising step towards a mimic of the donor side reactions in PSII.

A further biomimetic feature of the system is that the Mn(III,III) complex protects the tyrosine against photodegradation, which in fact also gives further evidence for the occurrence of reaction step 3. The tyrosine radical undergo irreversible degradation reactions, if it is not reduced rapidly enough. When the irreversible acceptor $Co(NH_3)_5Cl^{2+}$ was used in our experiments, the tyrosine moieties that were reduced in a laser flash experiment were degraded, if no Mn(III,III) was present to reduce the tyrosine radicals [31]. Therefore the initial tyrosine EPR signal decreased in magnitude with increasing number of flashes given to the same sample. However, when the Mn(III,III) was added, a tyrosine radical signal of the same magnitude was observed after every flash, until the Mn(III,III) had been consumed. An analogous protective behaviour is observed in natural reaction centres, where the $tyrosine_Z$ is photodegraded in manganese-depleted PSII [32]. However, when Mn(II) is added to the system the photodegradation is prevented.

3.2. Proton coupled electron transfer from the tyrosine

The pK_a value of tyrosine changes from 10 to −2 upon oxidation [33] which causes the redox potential of the TyrOH/TyrO$^\bullet$ couple to decrease with 59 mV per pH unit up to pH 10 [31]. In Fig. 5 the pH dependence of the electron transfer rate constant in the Ru-tyrosine compound is shown (upper panel) [34]. The results of Ahlbrink et al. [35] (lower panel) for the electron transfer from the $tyrosine_Z$ to the oxidised chlorophylls of $P_{680}{}^+$ in manganese-depleted PSII are also shown. There is a remarkable similarity between the two sets of data. In the following paragraphs our results for the Ru-tyrosine compound will be discussed, and it will be shown that the conclusions have relevance for the understanding of tyrosine electron transfer also in the natural system.

From the fit to Eqs. (2) and (3) in Fig. 5 (upper panel) it can be seen that the rate constant in the Ru-tyrosine compound follows the expected dependence on driving force for an electron transfer reaction, although the data span only a small part of the parabolic curve [24]. The reorganisation energy (that gives the position of the maximum in the parabola) was determined independently from temperature-dependent measurements, according to Eq. (2), so that only the pre-exponential factor was allowed to vary in the fit. Note that the change in driving force with pH is caused by the tyrosine deprotonation, that is not necessarily a part of the rate-determining reaction step. In fact, electron transfer followed by deprotonation of $TyrOH^+$ is not expected to give a pH-dependent rate, since the individual steps are not pH-dependent. Neither can deprotonation followed by electron transfer from $TyrO^-$ explain the data since deprotonation of the reduced tyrosine is too slow. Even with a diffusion-controlled protonation rate constant $k_p = 1\times10^{11}\,M^{-1}s^{-1}$, the p$K_a$ value=10 shows that the deprotonation rate constant cannot be larger than $k_d = 1\times10^{1}\,s^{-1}$ ($k_d/k_p = K_a = 1\times10^{-10}\,M^{-1}$). In contrast, we observe much higher values. Also, a deprotonation followed by electron transfer would not give the observed discontinuous change of the rate constant value around the pK_a. Therefore, the pH-dependence of the rate implies that deprotonation and electron transfer is one concerted reaction step. The pH-dependent rate can now be understood, since the products (Ru(II)–TyrO$^\bullet$+H$^+$) are stabilised as the pH increases. Thus, the product curve of free energy vs. reaction coordinate is lowered (ΔG^0 decreases) and the activation free energy decreases (Eqs. (2) and (3)). From the data it seems that this deprotonation-coupled reaction on a simple level can be described with the same formalism as a pure electron transfer. However, for a more correct description, one has to take into account the entropy changes in the reaction and the fact that the product-free energy curve is dissociative in the OH-bond coordinate [24,34]. This modifies somewhat the reorganisation energy value obtained from the experimental activation energy [34]. However, it does so in the same way for the natural and artificial systems, which allows us to use the simplified formalism for the comparisons made here.

An activation energy of 0.32 eV was obtained for the tyrosine to Ru(III) electron transfer at neutral pH.

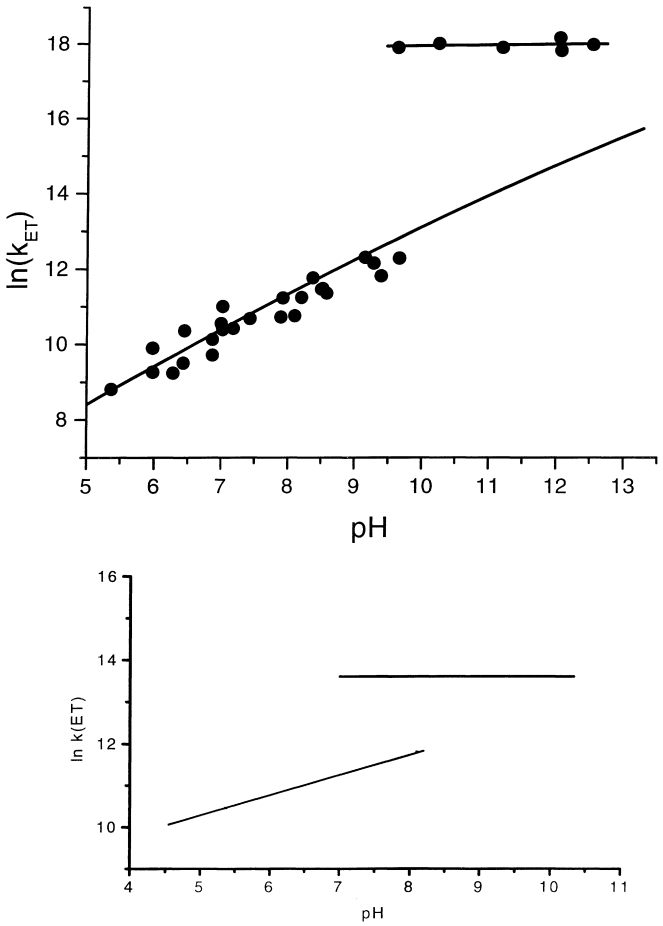


Fig. 5. Upper panel: the rate constant for electron transfer from the tyrosine to Ru(III) in the Ru-tyrosine compound (Fig. 3) as a function of pH [34]. Each point is an average from several individual measurements. Lower panel: the rate constant for electron transfer from $tyrosine_Z$ to P_{680}^+ in manganese depleted PSII, adapted from Ahlbrink et al. [35]. Only the fit to their data is reproduced. For both sets of data biexponential kinetics was observed near the apparent pK_a value, due to the presence of both protonated and unprotonated species. This is represented by two rate constants in the pK_a region.

From Eqs. (2) and (3) a large value of the reorganisation energy, λ=1.8 eV was obtained [34], presumably reflecting the stretch of the tyrosine OH-bond as the system goes to the transition state. Above pH 10 instead, when the tyrosine is already deprotonated, the electron transfer was nearly activation less. Consequently, the reorganisation energy was much smaller, λ=0.9 eV, which is more typical for a pure electron transfer reaction in polar media [24]. This is presumably because the reorganisation related to the OH-bond was no longer present.

It is interesting to compare our activation energy values with those of Ahlbrink et al. [35] (Fig. 5, lower panel). They obtained E_a=0.30 eV at pH 6.5 with a driving force similar to ours. Thus, the observed rate, the activation energy and the reorganisation energy around pH 6.5 are all nearly identical in the manganese-depleted PSII and our Ru-tyrosine model. At higher pH, both systems display a higher rate, that is also pH-independent. However, for PSII the activation energy is higher (0.15 eV compared to 0.05 eV) and the rate constant is lower than in the Ru-tyrosine

system. Also, the pH value where the rate constant becomes faster and pH-independent is different, around 7.6 for PSII and 10 for the Ru-tyrosine compound. The reason for these differences can be explained in the model below.

Presently, there is much research activity concerning the tyrosine$_Z$ in PSII [35–38], and it is discussed whether electron transfer to P_{680}^+ is followed by deprotonation or vice versa. Our results strongly suggest that these steps are instead concerted, occurring with a common transition state. Also, the large reorganisation energy in PSII at low pH is similar to our results, and is therefore probably not only due to the tyrosine deprotonation. Instead, this suggests that the tyrosine$_Z$ environment has a polarity close to that of neat water when the manganese cluster is not present. Furthermore, our results support one of the models discussed for PSII [35] in which the tyrosine is hydrogen-bonded to a histidine above pH 7.6. At lower pH the histidine is protonated, and the tyrosine is then not hydrogen bonded at all. Instead it releases the protons to the bulk upon oxidation, as suggested by the similarities with the simpler Ru-tyrosine system. In this model the pK_a value around 7.6 is for the histidine that forms the hydrogen bond to the tyrosine. Only at higher pH may the tyrosine$_Z$ itself be deprotonated, as is the case for the Ru-tyrosine compound at pH>10. In PSII, the tyrosine$_Z$–histidine hydrogen bond results in a reduction of the reorganisation energy at pH>7.6. The reaction rate is higher, and also pH-independent, since the proton is transferred within the hydrogen bond. In the Ru-tyrosine compound, the observed pK_a value (Fig. 5) is higher (pK_a=10) because it reflects the reaction of an already deprotonated of tyrosine. Obviously, the contribution of the OH-bond to the reorganisation energy is then absent, so that the activation energy is very low, and the rate constant becomes larger than in PSII. This model explains both the similarity at low pH between the two systems and the differences observed at higher pH values. In Mn-depleted PSII mutants where the histidine has been replaced [38], one may find a closer similarity at high pH with the Ru-tyrosine system and we suggest measurements of the electron transfer rate and activation energy in these mutants. We propose that the reorganisation energy value can be used to show whether the tyrosine is hydrogen bonded or not by other bases when the histidine is not present. Note that the reorganisation energy may report hydrogen bonds to the reduced tyrosine, while EPR experiments report the situation of the oxidised tyrosine radical [26,27,36].

The effect of a hydrogen bond to tyrosine was demonstrated in an another, similar Ru-tyrosine compound. The NMR spectra revealed the presence of an intramolecular hydrogen bond to the tyrosine, and the electron transfer rate constant was much faster than for the compound above [39].

3.3. Summary

To summarise, we have introduced tyrosine as a redox intermediate, and demonstrated the electron transfer sequence Mn(III,III)→tyrosine→Ru(III) in analogy with the donor side reactions of PSII. The electron transfer from the tyrosine is coupled to deprotonation, and we have investigated the effects of tyrosine deprotonation and hydrogen bonding on the electron transfer rate. The relative simplicity of the Ru-tyrosine system compared to PSII makes it possible to draw more certain conclusions from experiments. These conclusions can then be used to interpret experiments on manganese depleted PSII.

4. A Ru–$(Mn)_2$ complex

In order to increase the control over the reaction paths and recombination reactions, it is desirable to increase the degree of reactant organisation. Thus, the compound shown in Fig. 6 was made, where a dinuclear Mn(II)–Mn(II) complex is covalently linked to the ruthenium complex, in contrast to the free manganese complex described above. A deprotonated tyrosine derivative serves as a bridging ligand for the manganese ions. Light excitation in the presence of the methylviologen acceptor lead to oxidation and subsequent, very rapid (k>1×10^7 s^{-1}), regeneration of the Ru(II). By EPR spectroscopy, we found that the light reaction generated the oxidised Mn(II)–Mn(III) [40]. This was the first example of electron transfer from a dinuclear manganese complex to a photogenerated Ru(III) within the same supermolecule. Molecular mechanics calculations and the emission lifetime suggested that the Ru–Mn distance was ca. 16 Å, so that the link was not folded. The deprotonated tyrosine derivative binds as a ligand directly to

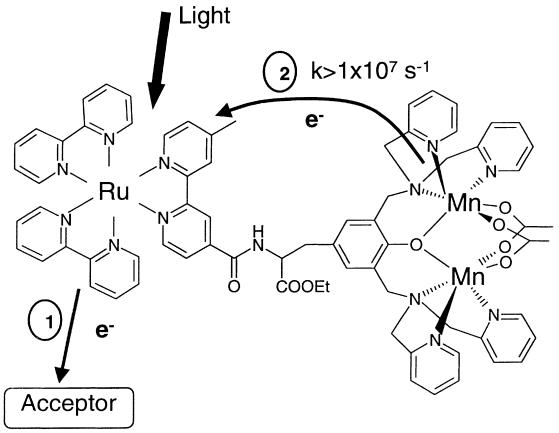


Fig. 6. Structure and light-induced electron transfer reactions in the Ru–$(Mn)_2$ complex in CH_3CN solution.

the Mn(II) ions, and although it is probably not an independent redox intermediate, the link between the Ru and the Mn-dimer seems to provide an efficient pathway for rapid electron transfer over 16 Å.

Work now in progress indicates that the manganese moiety in Ru–$(Mn)_2$ compounds similar to that shown in Fig. 6 can be photooxidised in several steps. This would be a very important result, since it would suggest the possibility to accumulate oxidative equivalents on a manganese dimer in a $Ru(bpy)_3^{2+}$-sensitised light-induced reaction. Much work remains to verify the reaction steps, and to identify the resulting manganese complex. It is quite probable that some ligand exchange has occurred, such as the replacement of the acetates with H_2O or OH^-. This type of exchange is probably necessary in order to achieve several oxidation steps in a reasonably narrow range of potentials. For example, the replacement of one bridging acetate with two OH^- or one μ-oxo-bridge upon oxidation of the manganese would compensate the increasing positive charge on the complex. Also, the binding of water ligands is of course crucial for water oxidation.

5. Conclusions

Experiments on several compounds have shown that it is possible to construct artificial systems where manganese and tyrosine act as electron donors to regenerate a Ru(II)-polypyridine photosensitiser. We have learnt about problems and possibilities concerning the construction and function of Ru–Mn compounds. The oxidation of a manganese dimer in several steps in a Ru-sensitised light reaction seems to be possible, which is an important step towards catalytic water oxidation. Furthermore, we have studied the electron transfer from tyrosine to the oxidised sensitiser. The effects of coupling to deprotonation of the tyrosine was evident in the large reorganisation energy for the reaction, and hence a low rate, unless the tyrosine was hydrogen bonded or already deprotonated. The results are relevant for the interpretation of recent results for electron transfer from tyrosine to P_{680}^+ in manganese depleted photosystem II. With a tyrosine as redox intermediate, we also demonstrated the electron transfer from a manganese dimer to the photooxidised Ru(III)-sensitiser: Mn(III,III)→tyrosine→Ru(III). This is analogous to the electron transfer $(Mn)_4 \rightarrow \text{tyrosine}_Z \rightarrow P_{680}^+$ on the donor side of photosystem II, where $(Mn)_4$ represents the manganese cluster of the oxygen evolving complex. We now try to elaborate the artificial systems, particularly to verify and improve the multi-step oxidation of the manganese complexes, that is necessary in order to oxidise water.

Acknowledgements

We acknowledge the many past and present co-workers in our groups. Some of the compounds of Scheme 1 were prepared in collaboration with the group of Prof. Hans Toftlund (Odense). We also wish to acknowledge the fruitful collaboration with Prof. Jean-Jaques Girerd and his group in Orsay, France. This work was supported by the Knut and Alice Wallenberg Foundation, the European TMR program (TMR Network CT96-0031), The Nordic Energy Research Council, and the Swedish Research Councils for Engineering Sciences (TFR) and Natural Science (NFR).

References

[1] J. Deisenhofer, J.R. Norris (Eds.), The Photosynthetic Reaction Center, Vol. 1–2, Academic Press, San Diego, 1993.
[2] J. Barber, B. Andersson, Nature 370 (1994) 31.

[3] R.J. Debus, Biochem. Biophys. Acta 1102 (1992) 269.
[4] V.K. Yachandra, K. Sauer, M.P. Klein, Chem. Rev. 96 (1996) 2927.
[5] W. Rüttinger, G.C. Dismukes, Chem. Rev. 97 (1997) 1.
[6] R.D. Britt, in: D. Ort, C. Yocum (Eds.), Oxygenic Photosynthesis: The Light Reactions, Kluwer Academic Publishers, Dortrecht, 1996, p. 137.
[7] E. Amouyal, Sol. Energy Mater. Sol. Cells 38 (1995) 249.
[8] H. Kurreck, M. Huber, Angew. Chem. Int. Ed. Engl. 34 (1995) 849.
[9] M.R. Wasielewski, Chem. Rev. 92 (1992) 435.
[10] V. Balzani, F. Scandola, Supramolecular Photochemistry, Ellis Horwood, Chichester, UK, 1991.
[11] A. Osuka, S. Nakajima, T. Okada, S. Taniguchi, K. Nozaki, T. Ohno, I. Yamazaki, Y. Nishimura, N. Mataga, Angew. Chem. Int. Ed. Engl. 35 (1996) 92.
[12] K. Hasharoni, H. Levanon, S.R. Greenfield, D.J. Gosztola, W.A. Svec, M.R. Wasielewski, J. Am. Chem. Soc. 117 (1992) 8055.
[13] G. Steinberg-Yfrach, J.-L. Rigaud, E.N. Durantini, A.L. Moore, D. Gust, T.A. Moore, Nature 392 (1998) 479.
[14] S.M. Molnar, G. Nallas, J.S. Bridgewater, K.J. Brewer, J. Am. Chem. Soc. 116 (1994) 5206.
[15] J. Limburg, J.S. Vrettos, L.M. Liable-Sands, A.L. Rheingold, R.H. Crabtree, G.W. Brudwig, Science 283 (1999) 1524.
[16] Y. Naruta, M. Sasayama, T. Sasaki, Angew. Chem. Int. Ed. Engl. 33 (1994) 1839.
[17] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[18] K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrine Complexes, Academic Press, London, 1992 (Chapter 6).
[19] L. Sun, L. Hammarström, T. Norrby, H. Berglund, R. Davydov, M. Andersson, A. Börje, P. Korall, C. Philouze, M. Almgren, S. Styring, B. Åkermark, J. Chem. Soc., Chem. Commun. (1997) 607.
[20] L. Sun, H. Berglund, R. Davydov, T. Norrby, L. Hammarström, P. Korall, A. Börje, C. Philouze, K. Berg, A. Tran, M. Andersson, G. Stenhagen, J. Mårtensson, M. Almgren, S. Styring, B. Åkermark, J. Am. Chem. Soc. 119 (1997) 6996.
[21] H. Berglund-Baudin, L. Sun, R. Davydov, M. Sundahl, S. Styring, B. Åkermark, M. Almgren, L. Hammarström, J. Phys. Chem. 102 (1998) 2512.
[22] K. Berg, A. Tran, M.K. Raymond, J. Wolny, S. Redon, M. Abrahamsson, M. Andersson, L. Sun, L. Hammarström, H. Toftlund, B. Åkermark, submitted to Eur. J. Inorg. Chem.
[23] M. Abrahamsson, et al., in preparation.
[24] R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.
[25] L. Sun, L. Hammarström, in preparation.
[26] B.A. Diner, G.T. Babcock, in: D. Ort, C. Yocum (Eds.), Oxygenic Photosynthesis: The light reactions, Kluwer Academic Publishers, Dortrecht, 1996, p. 213.
[27] C.W. Hoganson, G.T. Babcock, Science 277 (1997) 1953.
[28] A. Magnusson, H. Berglund, P. Korall, L. Hammarström, B. Åkermark, S. Styring, L. Sun, J. Am. Chem. Soc. 119 (1997) 10720.
[29] E.J. Land, W.A. Prütz, Int. J. Radiat. Biol. 36 (1979) 75.
[30] O. Horner, E. Anxolabéhère-Mallart, M.-F. Charlot, L. Tchertanov, J. Guilhem, T. Mattioli, A. Boussac, J.-J. Girerd, Inorg. Chem. 38 (1999) 1222.
[31] A. Magnuson, Y. Frapart, M. Abrahamsson, O. Horner, B. Åkermark, L. Sun, J.-J. Girerd, L. Hammarström, S. Styring, J. Am. Chem. Soc. 121 (1999) 89.
[32] C. Jegerschöld, S. Styring, Biochemistry 35 (1996) 7794.
[33] E.J. Land, G. Porter, E. Strachan, Trans. Faraday Soc. 57 (1961) 1885.
[34] M. Sjödin, S. Styring, L. Sun, B. Åkermark, L. Hammarström, Am. Chem. Soc., in press.
[35] R. Ahlbrink, M. Haumann, D. Cherepanov, O. Börgershausen, A. Mulkidjanian, W. Junge, Biochemistry 37 (1998) 1131.
[36] B.A. Diner, D.A. Force, D.W. Randall, R.D. Britt, Biochemistry 37 (1998) 17931.
[37] A.-M.A. Hays, I.R. Vassiliev, J.H. Goldbeck, R.J. Debus, Biochemistry 37 (1998) 11352.
[38] F. Mamedov, R.T. Sayre, S. Styring, Biochemistry 37 (1998) 14245.
[39] L. Sun, M. Burkitt, M. Tamm, M.K. Raymond, M. Abrahamsson, D. LeGourriérec, Y. Frapart, A. Magnusson, P.H. Kenez, P. Brandt, A. Tran, L. Hammarström, S. Styring, B. Åkermark, J. Am. Chem. Soc. 121 (1999) 6834.
[40] L. Sun, M.K. Raymond, A. Magnusson, D. Le Gourriérec, M. Tamm, M. Abrahamsson, L. Hammarström, S. Styring, B. Åkermark, J. Inorg. Biochem. (2000), in press.