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ARTICLES

Intramolecular Electron Transfer from Manganese(II) Coordinatively Linked to a Photogenerated Ru(III)−Polypyridine Complex: A Kinetic Analysis

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For further investigations in the field of artificial photosynthesis, a model compound, **1**, has been developed to mimic the electron-transfer steps from the manganese cluster to P_{680}^{+} in photosystem II. In this model compound the photosensitizer ruthenium(II)−trisbipyridyl was linked to a manganese(II) ion through a bridging ligand. Photoexcitation of **1** in the presence of the electron acceptor methyl viologen (MV^{2+}) lead to electron transfer from the Ru moiety to MV^{2+}. Laser flash photolysis experiments at different concentrations of **1** were performed in order to follow the subsequent reduction of the photooxidized Ru(III) species. A kinetic model, taking different parallel reactions into account, could explain the experimental data. It was shown that the major part of the photooxidized Ru(III) created was reduced again by intramolecular electron transfer from the attached Mn(II), with a rate constant of $1.8 \times 10^5\ s^{-1}$. However, Mn(II) was partially dissociated from **1**, giving a fraction of Ru(III) without Mn(II) attached. In these complexes electron transfer could occur only after a rate-limiting reassociation of Mn(II), with a rate constant $2.9 \times 10^9\ M^{-1}\ s^{-1}$. In the analysis of the data, the fraction of dissociated Mn(II) could be determined independently at each concentration of **1**, utilizing the fact that bound Mn(II) quenched the excited state, probably by energy transfer.

Introduction

In natural photosynthesis light absorbed by green plants is transformed into chemical energy. This is done by a sequence of electron-transfer steps, following the initial excitation in the photosynthetic reaction centers, ultimately leading to the reduction of carbon dioxide. In plants and algae, the electrons needed for this reduction are generated in the reaction where water is oxidized to molecular oxygen.[1,2] Water oxidation occurs in the photosystem II reaction center where the electron-transfer reactions start by excitation of the primary electron donor P_{680}. An electron is then transferred from $*P_{680}$ to the acceptor pheophytin and further to two quinones, Q_A and Q_B.[1,2] For these steps to be repeatable, the oxidized form P_{680}^{+} has to be reduced. An electron is transferred to P_{680}^{+} from the donor side through the oxidation of a tetramanganese cluster. The transfer of electrons is mediated to P_{680}^{+} via the electron donor tyrosineZ, which interfaces the manganese cluster and P_{680}^{+}.[1−3] Four electron abstractions to P_{680}^{+} lead to oxidation of two water molecules releasing one molecule of oxygen. The manganese cluster has an important role in this process, coordinating water and storing four oxidizing equivalents.[1,2,4]

To mimic the natural way of converting solar energy to chemical energy and to learn more about the structure and function of the natural photosystem, several model systems have been constructed and studied. These artificial systems divide mainly into two categories: they consist either of a photosensitizer, linked to electron donors and acceptors concerning the primary charge-separation process,[5] or of manganese clusters serving as models for the oxygen evolving center in PS II. Most of these latter models have been chemically inert structural models or heterogeneous catalysts with rather ill-defined structure.[6]

As far as we know, there are no previous examples of super molecules that mimic the donor side of PSII containing both a manganese moiety and a photooxidizable sensitizer. We have now synthesized some model systems in which a ruthenium trisbipyridyl complex[7] is coordinatively linked to a manganese ion or a tyrosine derivative.[8]

The possibility of photooxidation of the Ru(II) sensitizer, followed by intramolecular, Mn(II)-to-Ru(III), electron transfer in **1** was investigated by flash photolysis experiments in the presence of methyl viologen (MV^{2+}) as external acceptor. Upon illumination the excited state of $Ru(bpy)_3^{2+}$ is oxidized by electron transfer to MV^{2+}, which results in the formation of $Ru(bpy)_3^{3+}$ and MV^{+}. In the binuclear ruthenium−manganese complex **1**, shown in Figure 1, it was found that $Ru(bpy)_3^{3+}$

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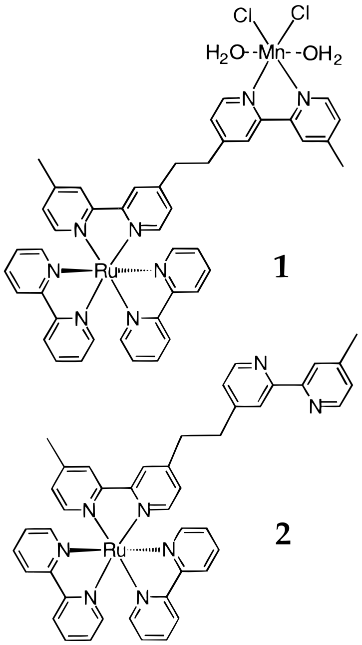

Figure 1. Model compound 1 ([Ru(bpy)$_2$Mebpy-MebpyMnCl$_2$·H$_2$O]Cl$_2$) and reference compound 2 (Ru(bpy)$_2$(Mebpy-Mebpy)Cl$_2$).

then recaptures an electron from the coordinatively bound manganese ion. A complication is the fact that manganese is partly dissociated from the complex giving two different species of Ru(bpy)$_3^{3+}$ in the photochemical reactions, one with coordinatively bound manganese, Ru^{III}LMn^{II} (oxidized **1**), and one without attached manganese, Ru(III)L (oxidized **2**).

In the present paper we report on a detailed kinetic analysis of these electron-transfer processes. We also report on some preliminary results concerning the mechanism of quenching of the excited state of Ru(bpy)$_3^{2+}$ by the coordinatively bound manganese.

The present study shows that intramolecular electron transfer occurs from manganese to photogenerated Ru(bpy)$_3^{3+}$. This is a first step for the development of models mimicking the donor side of PSII.

Experimental Section

Chemicals. The synthesis and characterization of the mononuclear ruthenium complex **2** and the binuclear ruthenium–manganese complex **1** is described elsewhere.[8] The emission and absorption measurements were performed at room temperature in acetonitrile of spectroscopic grade (Merck, 99.8%). The concentrations used of **1** were 14–100 μM. To quench the excited state of Ru(II), methyl viologen (Sigma) was used as received in the flash photolysis experiments. For time-resolved experiments the solution was deoxygenated with nitrogen for 15 min before the measurements.

For low-temperature measurements of the fluorescence emission, **1** and **2** were dissolved in butyronitrile (Fluka, 99%).

Instrumentation. *Time-resolved fluorescence* decay data were collected with the single-photon-counting technique. A mode-locked Nd:YAG laser was used to synchronously pump a cavity-dumped dye laser using DCM as dye. The output frequency was 80 kHz and frequency doubled to 327 nm to excite the samples. The emission around 610 nm was selected with an interference filter with a bandwidth of 10 nm and detected with a photomultiplier. The number of channels in the experiments was 512.[9] The emission data were analyzed according to a single- or double-exponential decay.

Absorption spectra were recorded on an HP 8453 diode-array spectrophotometer.

Laser flash photolysis experiments were performed with two different systems. A commercial system from Applied Photophysics used a Nd:YAG laser (Spectron Laser system, SL803G, 7 ns pulse length) for excitation at 532 nm. A pulsed xenon arc lamp was used for detection, and the different detection wavelengths were selected with a monochromator coupled to an R928 photomultiplier. The signal from the photomultiplier was transferred to a digital oscilloscope. The data were collected with an Acorn Archimedes 440/1 computer.[10] The bleaching of the Ru(bpy)$_3^{2+}$ signal was followed at 452 nm. In the other system, an ELI-94 excimer laser operating with XeCl, λ = 308 nm, was used to pump an LT-1113 dye laser (both from the Estonian Academy of Sciences) giving an excitation wavelength of 460 nm (20 ns pulse length, 1 mJ/pulse). The analyzing light was provided by a xenon arc lamp and for detection a photomultiplier coupled to a Techtronix 7912AD digitizer was used. The data were collected with a personal computer.

Stopped-flow experiments were performed on a Hi-Tech SF-51 apparatus.[11]

Results and Discussion

Emission Measurements. Before describing the electron-transfer studies, we will discuss the effect of the coordinated Mn(II) on the excited-state properties of the Ru(bpy)$_3^{2+}$ part of **1**, which was investigated by emission spectroscopy.

At room temperature the emission decay of **2** in acetonitrile was single-exponential with a lifetime of 950 ns and an emission maximum at 615 nm. For **1** a double-exponential decay was observed with $\tau_1 = 250$ ns and $\tau_2 = 980$ ns, with the same emission maximum. Mn(II) is partly dissociated from **1**, and the equilibrium Ru^{II}LMn^{II} $\leftrightarrow$ Ru^{II}L + Mn^{II} (i.e., **1** $\leftrightarrow$ **2** + Mn^{II}) is established where Mn^{II} represents all forms of manganese in the solution that is dissociated from the ruthenium complex. When MnCl$_2$ was added to **1**, the component with $\tau_1 = 250$ ns increased and there was a corresponding decrease of the component with $\tau_2 = 980$ ns. With a large excess of MnCl$_2$ the component with $\tau_2 = 980$ ns disappeared completely. Thus we attribute the slower component to the compound where Mn(II) is dissociated (**2**) and the faster to **1**, where the excited state is quenched by the attached Mn(II). The mechanism of quenching is discussed below. To determine the association constant, K_{ASS}, emission lifetime measurements were made at different concentrations of **1**, between 14 and 100 μM. The relative amounts of the different components were determined from a double-exponential fit to the curves at each concentration. The concentrations of Ru^{II}L and free Mn^{II} are equal and the association constant is given by

$$K_{ASS} = \frac{[\mathrm{Ru^{II}LMn^{II}}]}{[\mathrm{Ru^{II}L}][\mathrm{Mn^{II}}]} = \frac{[\mathrm{Ru^{II}LMn^{II}}]}{[\mathrm{Ru^{II}L}]^2} \qquad (1)$$

The total concentration of the complex is denoted C, and the fractions of the total concentration with $\tau_1 = 250$ and $\tau_2 = 980$ ns are denoted A_1 and A_2, respectively, and were determined from the fit to the emission decay curves. The values were inserted into eq 1 and plotted versus C in Figure 2 according to the modified form:

$$A_1/A_2^{\,2} = CK_{ASS} \qquad (2)$$

The association constant was obtained as $K_{ASS} = 1.3 \times 10^5$ M^{-1}.

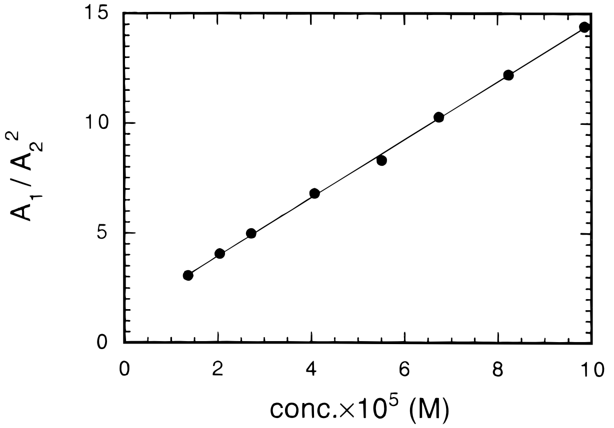

Figure 2. Fractions of **1** (A_1) and **2** (A_2) of the total concentration of the complex, *C*, versus *C*. Mn(II) is partly dissociated from **1** due to the equilibrium $Mn^{II} + Ru^{II}L \leftrightarrow Ru^{II}LMn^{II}$, the fractions A_1 and A_2 were determined from a fit to the emission decay curves at different total concentrations of the complex. The association constant K_{ASS} was given by the slope and obtained as $K_{ASS} = 1.3 \times 10^5\ M^{-1}$.

Mechanism of Quenching by Manganese. The mechanism and rate of quenching of the excited state of ruthenium by the coordinated manganese are important for the design of future Ru−Mn complexes. For example, we have previously found[8b] that in some complexes the quenching made the excited-state lifetime too short to allow the simple approach with a free viologen acceptor to photooxidize the ruthenium center in a bimolecular reaction. Some different possible quenching mechanisms have to be considered.

Paramagnetic quenching was discussed several decades ago as a general mechanism for excited-state quenching. However, detailed studies showed this mechanism to be insignificant for the quenching of excited ruthenium complexes.[12]

Another possible reason for the quenching would be that the coordination of manganese induces a change in the electronic properties of the $Ru(bpy)_3^{2+}$ part of the molecule, despite the two methylene units that separate the bipyridines of the bridging ligand. This would be expected to change the rate constants for excited-state deactivation. However, the absorption and emission spectra for **1** and **2** are identical, as well as the rate constant for radiative decay k_r (determined from the ratio of the emission quantum yield and lifetime, $k_r = \Phi_{em}/\tau_{em}$). Therefore, the excited-state energy and the electronic structure are not affected to any detectable extent by the attached manganese.

Further, we must consider energy and (reductive) electron transfer between the ruthenium and the manganese moieties. For electron transfer, an appreciable rate would require that the process is exothermic, i.e., that $E°(Ru^{I/*II}) > E°(Mn^{II/III})$. The potential for the excited-state reduction $E°(Ru^{I/*II})$ is +0.85 V (vs SCE in CH_3CN[7b]). For the $Mn^{II/III}$ potential a value of +0.90 V (vs SCE in AN) was obtained from cyclic voltammetry measurements.[13] Reductive quenching of the excited Ru moiety would thus be endothermic by ca. 0.05 eV. The reorganization energy for electron transfer between small molecules in polar solvents in typically ≥1.0 eV.[14] Reductive quenching would then be strongly activated and not likely to be responsible for the observed quenching.

Next, energy transfer quenching is considered. Mn(II) complexes are known to possess low-lying excited states, for which transitions from the ground state are spin-forbidden.[15] For example, $MnCl_2$ in a rigid matrix shows an emission maximum around 600−650 nm.[16] This suggests that energy transfer from the excited ruthenium complex, which has a 0−0 transition around 580 nm, should be slightly exoergonic. The Mn(II) transitions are not observed in our absorption spectra, due to their spin-forbidden nature. Despite this fact, exchange energy transfer[17] from the excited (triplet) $Ru(bpy)_3$ moiety can be spin-allowed, since the overall spin of the reactant pair may be conserved. Thus, energy transfer seems like a feasible quenching mechanism in **1**.

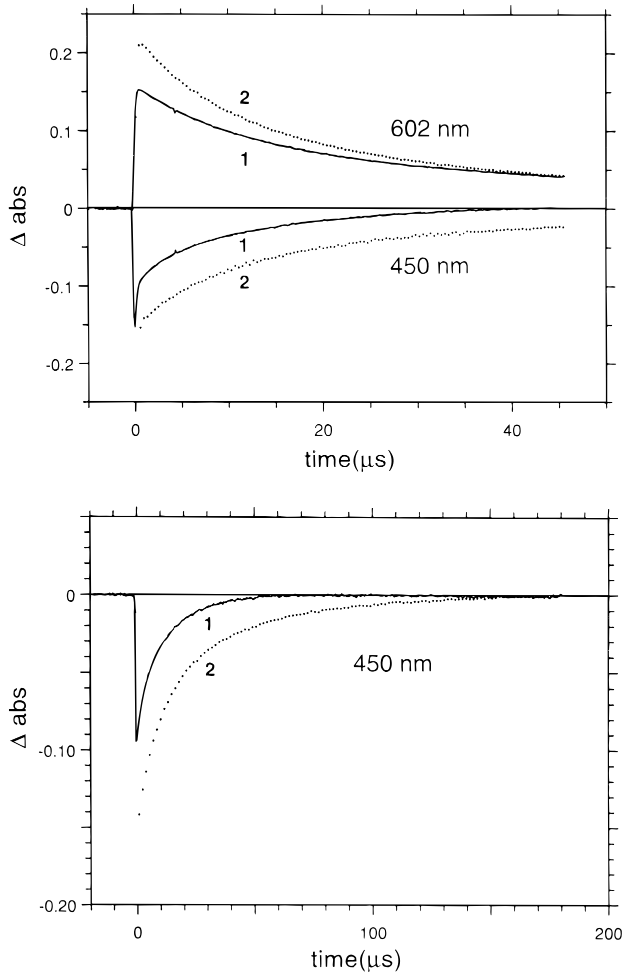

Figure 3. Transient absorption curves of **1** (60 μM) (solid line) and **2** (65 μM) (dotted line), in deoxygenated acetonitrile in the presence of MV^{2+} (20 mM), $\lambda_{ex} = 460$ nm. The kinetic traces for **1** and **2** at 602 nm shows the absorption of MV^+. The signals at 450 nm shows the bleaching and subsequent recovery of Ru(II). The recovery at 450 nm for **1** is faster than for **2** due to intramolecular electron transfer from Mn(II) to Ru(III), whereas the decay of the MV^+ signal occurs with essentially the same rate for both **1** and **2**. The Ru(II) recovery for **2** is due to the recombination with MV^+ only. The "spike" in the 450 nm curve seen for **1** originates from the excited state decay.

To discriminate between the energy- and electron-transfer mechanism, the emission lifetimes of the complexes **1** and **2** were measured in rigid butyronitrile glass at 90 K. In an ET reaction the solvent molecules around the complex need to reorganize according to a new charge distribution following the electron transfer. When the solvent is frozen, this reorganization cannot occur, and the reaction $\Delta G°$ increases by the outer reorganization energy which would be in the order of 1 eV.[18] Thus the electron-transfer process would be strongly endothermic in the present case and inhibit the quenching. On the other hand, if the quenching occurs by energy transfer, then the solvent reorganization energy is small and the effect of freezing the solvent would be much smaller.[19]

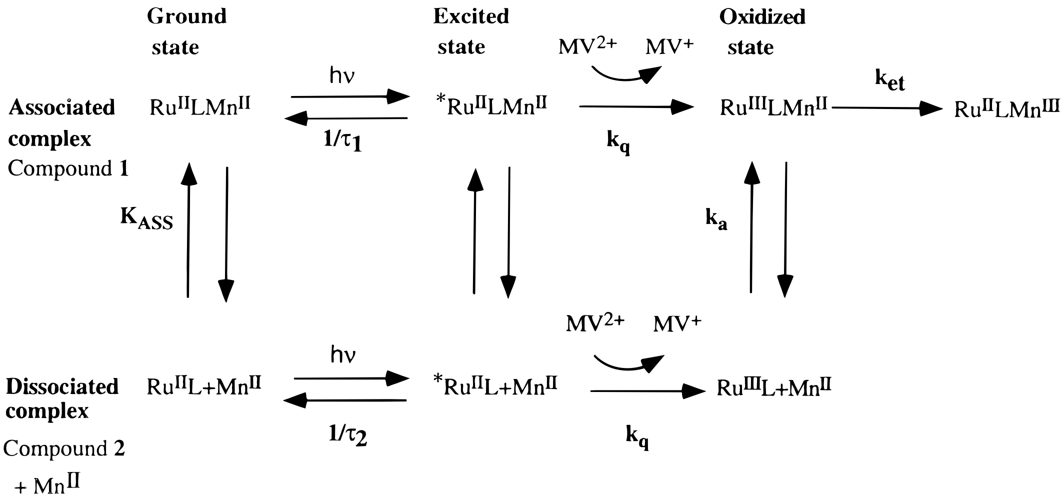

Figure 4. Reaction scheme for the electron-transfer processes that occurs in flash photolysis. The disappearance of the total concentration of Ru(III) species, after the decay of the excited state, is given by eq 10. For definitions of rate constants see the text.

For the reference compound **2** ($Ru^{II}L$) in butyronitrile glass (90 K) the emission decay curve was a single-exponential with $\tau = 5$ μs. For **1** ($Ru^{II}LMn^{II}$) the decay traces were complex and could be fitted to a sum of three exponentials with $\tau_1 = 5$ μs, $\tau_2 = 2$ μs, and $\tau_3 = 400$ ns. The amplitude fractions were $A_1 = 0.4$, $A_2 = 0.3$, and $A_3 = 0.3$, respectively. From the similarity in value, the longer lifetime may be attributed to emission from the dissociated mononuclear species $Ru^{II}L$. The more short-lived components appear only in complex **1** and are therefore attributed to the nondissociated complex, where quenching still occurs in the rigid matrix. The reason that this contribution is not a single-exponential decay is probably that the ligand that bridges the Ru and the Mn is flexible, so that a distribution of different conformations is present. In the glass, the conformations are fixed and would be expected to display varying reactivities due to the different orientation and distance between the reactants. The rate constant for the quenching by manganese in **1** was 3×10^6 s^{-1} at 298 K and 2.3×10^6 s^{-1} at 90 K for the faster component. Thus, the quenching rate constant was almost the same at 298 and 90 K for a large fraction of the conformations. This suggests that the quenching of the excited ruthenium moiety in **1** indeed occurred by energy transfer to the manganese moiety and not by an electron-transfer mechanism.

Electron Transfer from Mn(II) to Photooxidized Ru(III). The photoinduced electron-transfer processes occurring in the complexes were studied by flash photolysis. Methyl viologen (MV^{2+}, 20 mM) was added to an acetonitrile solution of **1** or **2**. After excitation at 532 nm the excited state of ruthenium was quenched by electron transfer to MV^{2+}, forming Ru(III) and MV^+ in equal amounts in agreement with well-known ruthenium bipyridine and methyl viologen reactions.[7c,20] The subsequent regeneration of Ru(II) was followed by the bleaching at 452 nm, in the lowest metal-to-ligand charge-transfer band. The reduction of MV^{2+} to MV^+ and the following decay of MV^+ were observed at 602 nm where MV^+ has a characteristic absorption maximum.[21]

Compound **2**, which contains no attached Mn(II), was used as the reference compound. In this case the disappearance of the 602 nm signal and the recovery of the absorbance at 452 nm was solely due to recombination between MV^+ and Ru(III) and followed second-order kinetics, with a diffusion controlled rate constant, $k_{rec} = 5 \times 10^9$ M^{-1} s^{-1}.[22] For **1** the results were different: The Ru(II) recovery was much faster (Figure 3), but the decay of MV^+ showed essentially the same kinetics as for **2**. Thus the photogenerated Ru(III) in **1** must have received an electron from a source that is not present in **2** and that is not MV^+.

The most probable explanation is that the increase in the rate of Ru(II) recovery in **1** is due to electron transfer from bound Mn(II). The subsequent disappearance of the MV^+ signal can be explained by a recombination between MV^+ and the Mn(III) formed, apparently giving the same kinetics as for the recombination between Ru(III) and MV^+ observed with compound **2**. To investigate if Ru(III) is capable of oxidizing Mn(II), a control experiment was performed by EPR,[8] in which chemically produced $Ru^{III}(bpy)_3$ was mixed with an equimolar amount of **1**, which contains Mn(II). Ru(III) and Mn(II) show characteristic EPR signals whereas Ru(II) and Mn(III) are EPR-silent. After mixing, both EPR signals rapidly disappeared, showing that Ru(III) is indeed capable of oxidizing Mn(II).[8]

One important question is whether the electron transfer from Mn(II) to photogenerated Ru(III) is intra- or bimolecular, i.e., occurs between Mn(II) and Ru(III) units on the same or on different molecules. To investigate this, experiments were performed where the concentration of **1** was varied between 14 and 100 μM. The resulting kinetic traces of the Ru(II) recovery at 452 nm were not simple single exponentials and were found to depend on the concentration. They could be explained by a kinetic model where an intramolecular electron transfer occurs in the intact complex ($Ru^{III}LMn^{II}$), whereas in the dissociated complexes ($Ru^{III}L$) electron transfer can occur only after reassociation of Mn(II) (see Figure 4). The latter rate is limited by the second-order association reaction with a rate constant obtained as 2.9×10^9 M^{-1} s^{-1}. The first-order rate constant, k_{et}, for the intramolecular process was determined to be 1.8×10^5 s^{-1}.

A kinetic model for the processes is proposed below. Arguments supporting this model are presented in the following sections.

Kinetic Model. The model presented is for the reactions defined in Figure 4. Laser flash photolysis experiments in the presence of MV^{2+} result in the appearance of oxidized Ru(III) and an equimolar amount of MV^+, after 1 μs when the quenching process is completed.

The emission decay curves of **1** show that Mn(II) is partly dissociated from the complex; therefore, a mixture of $Ru^{III}LMn^{II}$ and $Ru^{III}L$ is formed:

$$^*\mathrm{Ru^{II}L} + \mathrm{MV^{2+}} \xrightarrow{k_q} \mathrm{Ru^{III}L} + \mathrm{MV^{+}} \tag{3}$$

$$^*\mathrm{Ru^{II}LMn^{II}} + \mathrm{MV^{2+}} \xrightarrow{k_q} \mathrm{Ru^{III}LMn^{II}} + \mathrm{MV^{+}} \tag{4}$$

These reactions occur in competition with emission and radiationless deactivation.

The different reactions that occur after the quenching process during the time scale of interest are

$$\mathrm{Ru^{III}LMn^{II}} \xrightarrow{k_{et}} \mathrm{Ru^{II}LMn^{III}} \tag{5}$$

$$\mathrm{Ru^{III}L} + \mathrm{Mn^{II}} \xrightarrow{k_a} \mathrm{Ru^{III}LMn^{II}} \tag{6}$$

$$\left.\begin{array}{l}\mathrm{Ru^{III}LMn^{II} + MV^{+}}\\ \mathrm{Ru^{II}LMn^{III} + MV^{+}}\\ \mathrm{Ru^{III}L + MV^{+}}\end{array}\right\} \xrightarrow{k_{rec}} \mathrm{Ru^{II}LMn^{II} + MV^{2+}} \tag{7,8,9}$$

k_{et} is the first-order rate constant for the intramolecular electron-transfer process in the intact complex. k_a is the rate constant for the association of Mn(II) with the dissociated complex. The rate constant for the second-order diffusion-controlled back transfer from MV^+ to either Ru(III) or Mn(III) is assumed to be the same and is denoted k_{rec}. This assumption is supported by the observation that the recombination of Ru(III) with MV^+ occurred with essentially the same rate as the recombination of Mn(III) with MV^+, as shown by the similar decay of the MV^+ signals at 602 nm for **1** and **2**. The disappearance of Ru(III) was observed as the bleaching recovery at 452 nm. The quenching of the excited *Ru(II) was much faster than the subsequent reactions of Ru(III). Therefore the disappearance of the total concentration of Ru(III) species, after the decay of the excited state, is given by (see Appendix and Figure 4)

$$([\mathrm{Ru^{III}LMn^{II}}] + [\mathrm{Ru^{III}L}])(t) = \left([\mathrm{Ru^{III}LMn^{II}}]_0 - \frac{k_a[\mathrm{Mn^{II}}][\mathrm{Ru^{III}L}]_0}{k_{et} - k_a[\mathrm{Mn^{II}}]}\right)\frac{e^{-k_{et}t}}{k_{rec}[\mathrm{MV^+}]_0\, t + 1} + \frac{k_{et}[\mathrm{Ru^{III}L}]_0}{k_{et} - k_a[\mathrm{Mn^{II}}]}\,\frac{e^{-k_a[\mathrm{Mn^{II}}]t}}{k_{rec}[\mathrm{MV^+}]_0\, t + 1} \tag{10}$$

The parameters k_{et} and $k_a[\mathrm{Mn^{II}}]$ and the total concentration of Ru(III) ($[\mathrm{Ru^{III}}]_0\mathrm{tot} = [\mathrm{Ru^{III}LMn^{II}}]_0 + [\mathrm{Ru^{III}L}]_0$) initially formed were determined from a fit of the kinetic traces to eq 10 at each total concentration of complex **1**. The initial fractions of $[\mathrm{Ru^{III}LMn^{II}}]_0$ and $[\mathrm{Ru^{III}L}]_0$ of the total $[\mathrm{Ru^{III}}]_0^{\mathrm{tot}}$ as well as $k_{rec}[\mathrm{MV^+}]_0$ were fixed and determined independently in other experiments, as described in the Appendix.

The resulting values of k_{et} and $k_a[\mathrm{Mn^{II}}]$ from the curve fit at each total concentration of the complex are presented in Table 1 and plotted versus the concentration of free Mn(II) in Figure 5. According to the kinetic model k_{et} is constant when the concentration of Mn(II) is changed and k_a[Mn(II)] is proportional to the concentration of free Mn(II). It was found that the results are consistent with this prediction. The value, $k_{et} = 1.8 \times 10^5$ s^{-1}, is thus obtained for the intramolecular electron-transfer process from bound Mn(II) to photogenerated Ru(III), and the rate constant of association was obtained as $k_a = 2.9 \times 10^9$ $\mathrm{M^{-1}\,s^{-1}}$. The mechanistic model in Figure 4 is not unique, and to support it, control experiments described below were made.

TABLE 1: Rate Constants

total concn of complex **1** (μM)	concn of free Mn(II) (μM)[a]	$k_{et} \times 10^{-5}$ ($\mathrm{s^{-1}}$)[b]	$k_a \times [\mathrm{Mn(II)}]_{free} \times 10^{-5}$ ($\mathrm{s^{-1}}$)[c]
100	23	2.0	0.89
65	18	1.6	0.43
40	13	1.6	0.47
28	10	1.7	0.39
21	8	1.8	0.37
14	6	2.3	0.29

[a] Concentration of Mn(II) that has dissociated from **1** (see Figure 2). [b] Rate constant for intramolecular Mn(II)-to-Ru(III) electron transfer in **1**. [c] Pseudo-first-order rate constant for reassociation of dissociated Mn(II).

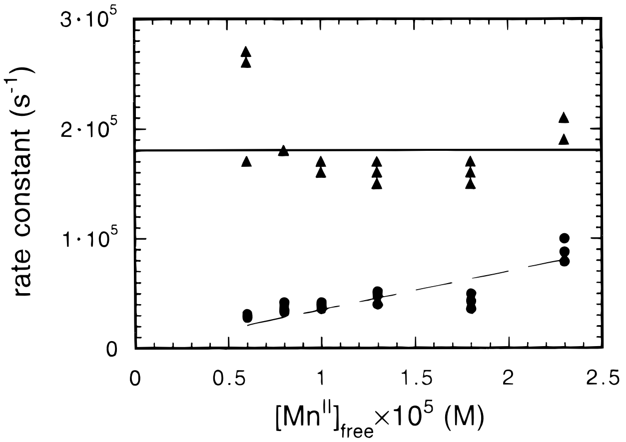

Figure 5. Rate constant for intramolecular electron transfer, k_{et}, in **1** versus the concentration of free Mn(II) (triangles). Psedo-first-order rate constant, $k_a[\mathrm{Mn^{II}}]_{free}$, versus the concentration of free Mn(II) (circles).

One alternative explanation to the results would be that the concentration-dependent process is due to an intermolecular electron transfer from Mn(II) attached to one complex molecule to a photogenerated Ru(III) of another. An experiment contradicting this explanation was performed by stopped-flow, where chemically produced Ru(III) in the form of $\mathrm{Ru^{III}(bpy)_3}$ was mixed with a solution of **1** and the disappearance of Ru(III) was monitored optically (not shown). The rate constant for this bimolecular process was obtained as about 1×10^6 $\mathrm{M^{-1}}$ $\mathrm{s^{-1}}$, which is too slow to explain the concentration dependence observed in the flash photolysis experiments.

Another conceivable electron-transfer reaction would be that free Mn(II) transferred an electron to photogenerated Ru(III). To investigate this possibility, flash photolysis experiments were performed with $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{MV^{2+}}$ and various concentrations of added $\mathrm{MnCl_2}$. However it was found that the recovery of Ru(II) was only slightly affected at the concentrations of $\mathrm{MnCl_2}$ used.

With support from the control experiments we conclude that the kinetic model gives a satisfying explanation for the electron-transfer processes that occur in complex **1** (Figure 1).

Conclusions

The most important conclusion to be drawn from this study is that intramolecular electron transfer from manganese to photooxidized ruthenium occurs in complex **1**, with a rate constant of 1.8×10^5 $\mathrm{s^{-1}}$. This is an important step for further development of artificial systems mimicking the donor side in photosystem II.

The dissociation of Mn(II) from the complex is a problem, in particular for the analysis of the photoinduced reactions. We thus try to optimize the binding conditions for the manganese ion, especially in water, using alternative ligands. On the other hand, to eventually arrive at catalytic water oxidation, the manganese complexes must not be inert cages but must allow some exchange of ligands. The distance between manganese and ruthenium is also important for effective intramolecular electron transfer. Earlier investigations have shown that if ruthenium and manganese are too close, then the quenching of the excited state of ruthenium by manganese is too rapid and will compete with the primary electron transfer to the acceptor MV^{2+}.[8b] To optimize the distance, different bridging ligands must be used. Furthermore, in the Photosystem II complex the manganese cluster contains four manganese ions. Therefore work is in progress to synthesize supramolecular complexes with two or more manganese ions coordinatively bound to ruthenium. A multinuclear manganese complex can hopefully function as a multielectron donor to one or several oxidized photosensitizers.

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Appendix

The complete derivation of eq 10 in the text can be obtained as follows: After the quenching process of $Ru^{II}LMn^{II}$ and $Ru^{II}L$ with MV^{2+} a mixture of $Ru^{III}LMn^{II}$ and $Ru^{III}L$, and an equimolar amount of MV^+ is formed.

The following relationship for the concentration of MV^+ is valid:

$$[MV^+] = [Ru^{III}L] + [Ru^{III}LMn^{II}] + [Ru^{II}LMn^{III}] \quad (A1)$$

The disappearance of MV^+ is studied at 602 nm and is given by the relation below:

$$d[MV^+]/dt = -k_{rec}\,[MV^+]^2 \quad (A2)$$

or in integrated form

$$[MV^+] = \frac{[MV^+]_0}{k_{rec}\,[MV^+]_0\,t + 1}$$

The kinetic trace at 452 nm monitors the disappearance of Ru^{III} in all forms:

$$d[Ru^{III}L]/dt = -k_a[Mn^{II}][Ru^{III}L] - k_{rec}[MV^+][Ru^{III}L] \quad (A3)$$

$$\frac{d[Ru^{III}LMn^{II}]}{dt} = k_a[Mn^{II}][Ru^{III}L] - k_{rec}[MV^+][Ru^{III}LMn^{II}] - k_{et}[Ru^{III}LMn^{II}] \quad (A4)$$

The dissociation of $Ru^{III}LMn^{II}$ is at least 1 order of magnitude slower than $k_{et}[Ru^{III}LMn^{II}]$ and therefore neglected.

These equations can be solved:

$$[Ru^{III}L] = \frac{[Ru^{III}L]_0}{k_{rec}[MV^+]_0t + 1}e^{-k_a[Mn^{II}]t} \quad (A5)$$

$$[Ru^{III}LMn^{II}] = \left([Ru^{III}LMn^{II}]_0 - \frac{k_a[Mn^{II}][Ru^{III}L]_0}{k_{et} - k_a[Mn^{II}]}\right)\frac{e^{-k_{et}t}}{k_{rec}[MV^+]_0t + 1} + \frac{k_a[Mn^{II}][Ru^{III}L]_0}{k_{et} - k_a[Mn^{II}]}\,\frac{e^{-k_a[Mn^{II}]t}}{k_{rec}[MV^+]_0t + 1} \quad (A6)$$

Equation A6 can be obtained as follows: Define y by

$$y = [Ru^{III}LMn^{II}](k_{rec}[MV^+]_0t + 1)e^{+k_{et}t} \quad (A7)$$

$$\frac{dy}{dt} = \frac{d[Ru^{III}LMn^{II}]}{dt}\,\frac{y}{[Ru^{III}LMn^{II}]} + \frac{k_{rec}[MV^+]_0y}{k_{rec}[MV^+]_0t + 1} + k_{et}y \quad (A8)$$

Introduce eqs A4 and A5:

$$\frac{dy}{dt} = k_a[Mn^{II}][Ru^{III}L]_0e^{-(k_a[Mn^{II}]-k_{et})t} \quad (A9)$$

Integrate

$$y - y_0 = \frac{k_a[Mn^{II}][Ru^{III}L]_0}{k_a[Mn^{II}] - k_{et}}(1 - e^{-(k_a[Mn^{II}]-k_{et})t}) \quad (A10)$$

Introduction of the definition of y gives eq A6, which together with eq A5 gives eq 10.

The initial fractional concentrations $[Ru^{III}LMn^{II}]_0/[Ru^{III}]_0^{tot} \equiv \alpha$ and $[Ru^{III}L]_0/[Ru^{III}]_0^{tot} \equiv \beta$ (see eq 10 and the text that follows) were calculated as described below: The concentrations $[Ru^{II}LMn^{II}]$ and $[Ru^{II}L]$, before the laser flash, at each total concentration of the complex were given by the fractional amplitudes A_1 and A_2 from the two-exponential curve fit to the emission decay without MV^{2+} (Figure 2). The shorter lifetime of $Ru^{II}LMn^{II}$, $\tau_1 = 250$ ns compared to $\tau_2 = 980$ ns for $Ru^{II}L$, was taken into account when the relative initial concentrations of Ru(III) formed in the quenching process was calculated for the two complexes. The efficiency of formation of Ru(III) in $Ru^{II}LMn^{II}$ ($\phi(Ru^{III}LMn^{II})$) compared to $Ru^{II}L$ ($\phi(Ru^{III}L)$) is equal to

$$\frac{\phi(Ru^{III}LMn^{II})}{\phi(Ru^{III}L)} = \frac{\dfrac{k_q\,[MV^{2+}]}{k_1 + k_q\,[MV^{2+}]}}{\dfrac{k_q\,[MV^{2+}]}{k_2 + k_q\,[MV^{2+}]}} = \frac{k_2 + k_q\,[MV^{2+}]}{k_1 + k_q\,[MV^{2+}]} \quad (A11)$$

k_1 ($=1/\tau_1$)and k_2 ($=1/\tau_2$) were determined to be 4×10^6 s^{-1} and 1×10^6 s^{-1}, respectively, from the emission decay curves, and the pseudo-first-order rate constant for quenching by viologen, $k_q[MV^{2+}]$, was determined to be 5.7×10^6 s^{-1} from the emission lifetime at the concentration of MV^{2+} used. These values were inserted into eq A11 above and $\phi(Ru^{III}LMn^{II})/\phi(Ru^{III}L) = 0.7$ was calculated. Thus the initial concentrations $[Ru^{III}LMn^{II}]_0$ and $[Ru^{III}L]_0$ formed in the quenching process at each total concentration of complex **1**, were given by $\alpha[Ru^{III}]_0^{tot}$ and $\beta[Ru^{III}]_0^{tot}$ respectively, with $\alpha = 0.7A_1/(0.7A_1 + A_2)$ and $\beta = A_2/(0.7A_1 + A_2)$. The values α and β entered the fitting procedure as known parameters while $[Ru^{III}]_0^{tot}$ was floating and solved by the fit.

The second-order diffusion-controlled rate constant k_{rec} was determined from the experimental curves at 602 nm and estimated to 5×10^9 M^{-1} s^{-1}, and $[MV^+]_0$ was determined for each total concentration of the complex from the initial absorption at 602 nm.

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