Intramolecular electron transfer from coordinated manganese(ii) to photogenerated ruthenium(iii)

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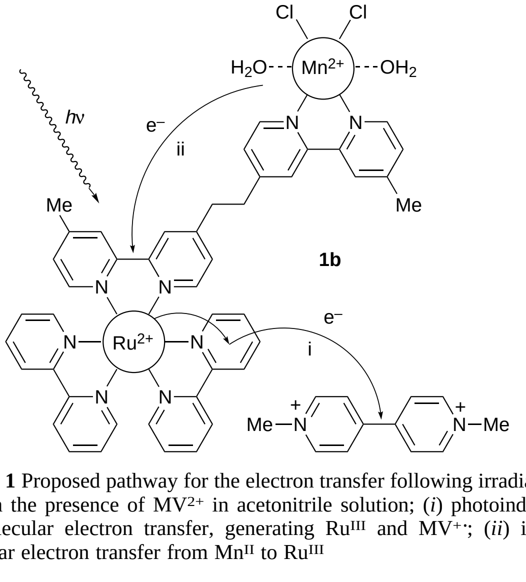
A binuclear ruthenium–manganese complex is synthesised; upon illumination the ruthenium transfers an electron to an external acceptor, then retrieves it by intramolecular electron transfer from the manganese.

A key enzyme in green plant photosynthesis is Photosystem II (PSII).[1] Upon illumination, the chlorophyll P_{680} in PSII transfers an electron to a series of acceptors, to give the $P_{680}{}^{+}$ cation which is then reduced back to P_{680} by electron transfer (ET) (mediated by tyrosine-z) from a cluster of four manganese ions. After four consecutive ET events, the cluster recovers all four electrons in one step by oxidizing two water molecules to molecular oxygen.[2] We decided to study if simple model systems could be prepared, where a ruthenium(ii) tris bipyridyl type complex on illumination transfers an electron to an external acceptor,[3,4] then recovers an electron by internal ET from a coordinated manganese ion. The bimetallic ruthenium(ii) manganese(ii) complex **1b** (Scheme 1) was found to be one model system of this type, and a suitable starting point for the development of multinuclear $RuMn_n$ complexes.

Our synthetic route started with the bridging ligand 1,2-bis[4-(4′-methyl-2,2′-bipyridyl)]ethane (Mebpy–Mebpy),[5] which was first treated with $[Ru(bpy)_2Cl_2]$[6] in refluxing methanol to give $[Ru(bpy)_2(\text{Mebpy–Mebpy})]Cl_2$ **1a**.[7] On treatment with $MnCl_2$ in acetonitrile, **1a** gave the binuclear $Mn^{II}Ru^{II}$ complex **1b**. Complex **1b** was characterized by electrospray ionization mass spectrometry (ESIMS), elemental analysis and X-band electron paramagnetic resonance (EPR) techniques. The distance between Mn^{II} and Ru^{II} in **1b** was estimated by molecular mechanics calculations to *ca.* 13 Å for the most extended conformation, which should allow efficient electron transfer.[8]



Scheme 1 Proposed pathway for the electron transfer following irradiation of **1b** in the presence of MV^{2+} in acetonitrile solution; (*i*) photoinduced intermolecular electron transfer, generating Ru^{III} and $MV^{+\cdot}$; (*ii*) intramolecular electron transfer from Mn^{II} to Ru^{III}

Comparison of the emission spectra of **1b**, **1a** and $[Ru(bpy)_3]^{2+}$[9] in acetonitrile solution showed that the wavelength of the emission maximum (*ca.* 615 nm) was essentially the same in all three cases, but the emission was considerably quenched in **1b** ($\tau \approx 260$ ns) compared to **1a** ($\tau \approx 980$ ns) and $[Ru(bpy)_3]^{2+}$. The manganese thus interacts with the excited state of ruthenium complex, but it does not quench the emission completely.

Flash photolysis experiments in the presence of 5–10 mm of an acceptor, methyl viologen (MV^{2+}), were performed in an acetonitrile solution of **1a**, **1b** and $[Ru(bpy)_3]^{2+}$, respectively. Following a laser flash ($\lambda_{ex} = 458$ nm), a rapid electron transfer from Ru^{II*} to MV^{2+} took place[4] (Scheme 1, step i) with a lifetime of *ca.* 200 ns for complex **1a**. The regeneration of Ru^{II} (monitored by the absorption at 452 nm) and the decay of the $MV^{+\cdot}$ radicals (monitored by the absorption at 600 nm) followed similar second-order kinetics with rate constants of *ca.* 5.0×10^9 dm^3 mol^{-1} s^{-1}. Thus the products of the charge separation recombine on the timescale of a few hundred μs when a few μm of the products were created. The behaviour of $[Ru(bpy)_3]^{2+}$ was identical. For the bimetallic $Mn^{II}Ru^{II}$ complex **1b**, the $MV^{+\cdot}$ radical was generated, and decayed with the same rate as in the experiments with **1a** and $[Ru(bpy)_3]^{2+}$.† In contrast, the regeneration of Ru^{II} from the photoproduced Ru^{III} was found to be one order of magnitude faster than for **1a** and $[Ru(bpy)_3]^{2+}$. This means that the photo-oxidized Ru^{III} moiety in **1b** must have received an electron from another source than $MV^{+\cdot}$, and one that is not present in **1a** and $[Ru(bpy)_3]^{2+}$.

Analysis of the transient absorbance recovery traces for **1b** over the concentration range examined {[**1b**] = $(2\text{–}10) \times 10^{-5}$ m} revealed a concentration independant first-order kinetic process with a rate constant $k = 1.5 \times 10^5$ s^{-1}. This we ascribe to the intramolecular ET from the Mn^{II} moiety to the photogenerated Ru^{III} moiety (Scheme 1, step ii). Separate experiments were performed in order to prove that the Mn^{II} moiety could be oxidized to Mn^{III} by Ru^{III}. Both managanese(ii) ($S = 5/2$) and ruthenium(iii) species give rise to distinct EPR spectra. When equimolar amounts of $[Ru(bpy)_3]^{3+}$ and complex **1b**, which contains Mn^{II}, were reacted, both EPR signals disappeared, showing that the reactants had been converted completely to the corresponding ruthenium(ii) and manganese(iii) species. The decay of $MV^{+\cdot}$ radical in the photolysis experiment with **1b** was probably due to recombination with Mn^{III}.

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Footnote

† In experiments without MV^{2+} no products of the Ru-quenching by Mn were seen. Thus, even if the quenching mechanism could be reductive, the Mn^{III}–Ru^{I} recombination would be much faster, so that the production of $MV^{+\cdot}$ *via* diffusional encounter with Ru^{I} would be negligible.

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