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Article

Ruthenium–Manganese Complexes for Artificial Photosynthesis: Factors Controlling Intramolecular Electron Transfer and Excited-State Quenching Reactions

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Continuing our work toward a system mimicking the electron-transfer steps from manganese to P_{680}^+ in photosystem II (PS II), we report a series of ruthenium(II)–manganese(II) complexes that display intramolecular electron transfer from manganese(II) to photooxidized ruthenium(III). The electron-transfer rate constant (k_{ET}) values span a large range, 1×10^5–2×10^7 s^{-1}, and we have investigated different factors that are responsible for the variation. The reorganization energies determined experimentally ($\lambda = 1.5$–2.0 eV) are larger than expected for solvent reorganization in complexes of similar size in polar solvents (typically $\lambda \approx 1.0$ eV). This result indicates that the inner reorganization energy is relatively large and, consequently, that at moderate driving force values manganese complexes are not fast donors. Both the type of manganese ligand and the link between the two metals are shown to be of great importance to the electron-transfer rate. In contrast, we show that the quenching of the excited state of the ruthenium(II) moiety by manganese(II) in this series of complexes mainly depends on the distance between the metals. However, by synthetically modifying the sensitizer so that the lowest metal-to-ligand charge transfer state was localized on the nonbridging ruthenium(II) ligands, we could reduce the quenching rate constant in one complex by a factor of 700 without changing the bridging ligand. Still, the manganese(II)–ruthenium(III) electron-transfer rate constant was not reduced. Consequently, the modification resulted in a complex with very favorable properties.

Introduction

In nature, plants efficiently convert light energy emitted from the sun into chemical energy by the process known as photosynthesis.[1,2] When energy from the sun reaches photosystem II (PS II), one of the two reaction centers in oxygen-evolving organisms, the photoactive P_{680} chlorophylls are excited. An electron is then transferred from the excited P_{680} to a primary acceptor and then to the reaction-center quinones, creating a charge-separated state, the energy of which is used in the photosynthetic reactions. The oxidized photosensitizer, P_{680}^+, is reduced to its original oxidation state through an intricate series of reactions involving the oxygen-evolving manganese cluster and a tyrosine residue, tyrosine$_Z$, a redox-active intermediate positioned between P_{680} and the manganese cluster.[3−9] The cluster stores up to four oxidizing equivalents, resulting in the catalytic oxidation of two water

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molecules. Four electrons, four protons, and one molecule of oxygen are produced in each catalytic cycle, after which the manganese cluster is restored to its most reduced state.

During the last 30 years, much effort has been devoted to the construction of an artificial system that mimics the natural way of converting solar energy to chemical energy. Several model systems have been constructed (e.g., mimics of the primary charge-separation processes [10−14] and manganese complexes serving as models for the oxygen-evolving center in PS II[6,7]). Many attempts have been made to synthesize manganese complexes capable of catalytic water oxidation, but so far the success has been modest.[7,15−17] Recently, Zouni et al.[18] presented the crystal structure of PS II at 3.8 Å resolution, including the manganese cluster. This structure is a major achievement that together with additional, more refined structures will give important information about the manganese cluster. This information will play an important role in the development of manganese complexes that mimic the oxygen-evolving reaction.

Our work has been focused on mimicking the whole donor side of PS II by synthesizing a supramolecular system containing both a manganese moiety and a ruthenium(II) tris-bipyridyl moiety as the photooxidizable sensitizer.[19−22] In this contribution, we present a series of ruthenium(II)−manganese(II) complexes with different types of manganese-binding ligands and links between the metal centers. The observed rate constants for intramolecular electron transfer from manganese(II) to photooxidized ruthenium(III) vary from $1 \times 10^5-2 \times 10^7$ s^{-1}. Because the goal is to create a system where regeneration of the primary donor ruthenium(II) is fast and efficient, it is important to understand what could cause this variation. We have therefore investigated different factors that affect the electron-transfer rate. These investigations will provide us with information to be used in the construction of more complicated systems containing several manganese ions that are capable of multielectron transfer.[23−25] We have also reported that the manganese(II) quenches the ruthenium(II) excited state in some complexes, presumably by intramolecular *energy* transfer.[21,22] In the present contribution, we discuss this reaction that competes with the desired photooxidation and present data for a larger series of complexes, showing that the quenching rate constant falls off exponentially with the metal-to-metal distance. However, by localizing the ruthenium-based metal-to-ligand charge-transfer excited state on the remote ligands, the quenching rate constant could be reduced by 2 orders of magnitude.

Experimental Section

Synthesis and Characterization. The synthesis and characterization of the mononuclear ruthenium complexes **1a**−**5a** and the binuclear ruthenium(II)−manganese(II) complexes **1b**−**5b** are described elsewhere.[19,22] All the ^{1}H NMR spectra described below were measured either on Brucker-400 MHz or Brucker-500 MHz spectrometers.

Ru(bpy)$_2$(4-CH$_3$-4′-(*N*′-CH$_3$-*N*,*N*′-Bis(2-pyridylmethyl)-1,2-ethanediamine)-(CH$_2$)$_5$-bpy)(PF$_6$)$_2$ (6a). This complex was prepared according to the literature procedure described by Sun et al.[19] 4-Methyl-4′-pentyl-(5″-*N*(*N*′-methyl-*N*,*N*′-bis(2-pyridylmethyl)-1,2-ethane-diamine))-2,2′-bipyridine (**6**, bpy-(CH$_2$)$_5$-bispicen) was synthesized by reaction of 4-methyl-4′-(5″-pentylbromo)-2,2′-bipyridine with *N*-methyl-*N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine(bispicen). The ligand was then purified by column chromatography on aluminum oxide using CH$_2$Cl$_2$ and CH$_2$Cl$_2$/MeOH (98:2) as eluents. ^{1}H NMR (400 MHz, in CDCl$_3$): δ 1.36−1.78 (m, 6H, −CH$_2$CH$_2$CH$_2$−), 2.28 (s, 3H, N−C**H**$_3$), 2.50 (s, 3H, bpy−C**H**$_3$), 2.55 (t, *J* = 5.5 Hz, 2H, −CH$_2$CH$_2$C**H**$_2$−N), 2.67 (t, *J* = 5.4 Hz, 2H, CH$_3$−N−CH$_2$C**H**$_2$−N−), 2.80 (t, *J* = 5.4 Hz, 2H, CH$_3$−N−C**H**$_2$CH$_2$−N−), 2.81−2.83 (m, 2H, bpy−C**H**$_2$CH$_2$CH$_2$−), 3.68 (s, 2H, Py−C**H**$_2$−N), 3.84 (s, 2H, Py′−C**H**$_2$−N), 7.10−7.29 (m, 4H, bpy−**H** and Py−**H**), 7.48−7.56 (m, 2H, bpy−**H** and Py−**H**), 7.65−7.78 (m, 2H, bpy−**H** and Py−**H**), 8.12 (s, 1H, bpy−**H**), 8.30−8.35 (m, 2H, bpy−**H** and Py−**H**), 8.52 (s, 1H, bpy−**H**), 8.51−8.62 (m, 2H, bpy−**H** and Py−**H**).

To obtain the ruthenium compound (**6a**), an equivalent amount of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O was added to a methanol solution of the bpy−(CH$_2$)$_5$−bispicen ligand (**6**) while stirring the solution under argon atmosphere. The brown solution obtained was then heated and refluxed for one week, resulting in a clear orange solution. After evaporation of the solvent, a red solid residue was obtained. The residue was purified by MPLC on neutral aluminum oxide, and the eluents used in the gradient were CH$_2$Cl$_2$ and CH$_2$Cl$_2$/MeOH (94:6). Dissolving the product in a minimum amount of methanol followed by addition of a concentrated NH$_4$PF$_6$ solution gave a red precipitate of **6a**. ^{1}H NMR (400 MHz, DMSO-*d$_6$*): δ 1.34−1.79 (m, 6H, −CH$_2$CH$_2$CH$_2$−), 2.14 (s, 3H, N−C**H**$_3$), 2.18 (m,

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2H, $-CH_2Cl_2CH_2-N$), 2.20 (m, 2H, bpy$-CH_2CH_2CH_2-$), 2.45 (s, 3H, bpy$-CH_3$), 2.80$-$2.90 (m, 4H, $CH_3-N-CH_2CH_2-N-$), 3.68 (s, 2H, Py$-CH_2-N$), 3.80 (s, 2H, Py′$-CH_2-N$), 7.25$-$8.86 (m, 30H, bpy$-$**H** and Py$-$**H**).

Ru(bpy)$_2$(4-CH$_3$-4′-(*N*′-CH$_3$-*N,N*′-Bis(2-pyridylmethyl)-1,2-ethanediamine)-(CH$_2$)$_5$-bpy)Mn(PF$_6$)$_2$Cl$_2$ (6b). To a methanol solution of **6a** a solution of $MnCl_2{\cdot}4H_2O$ was added while stirring at room temperature, immediately giving a red precipitate. The reaction mixture was stirred for another 20 min, and the red precipitate was filtered off and washed with a small amount of cold methanol followed by diethyl ether. The red precipitate was then dried in air to give **6b** as a red solid in 66% yield. ^{1}H NMR (400 MHz, DMSO-*d$_6$*): δ values were similar to those of **6a**, but all peaks were broadened because of the paramagnetic manganese(II).

4,4′-Bis(ethoxycarbonyl)-2,2′-bipyridine (8). 4,4′-Dicarboxy-2,2′-bipyridine[26] (2.0 g, 8.2 mmol) in 12 mL of thionyl chloride was refluxed overnight. Excess thionyl chloride was evaporated under reduced pressure. The resulting solid was suspended in 5 mL of ethanol (99.5%), and 0.5 mL of Et_3N was added. This solution was refluxed for 12 h under nitrogen. The mixture was evaporated to dryness, and the resulting solid was suspended in 20 mL of water to dissolve the $Et_3N{\cdot}HCl$ salt that formed during reaction. The diester, **8**, was then collected by suction filtration, washed well with water, and dried to yield a white powder (2.3 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, $J = 7.2$ Hz, 6H, OCH_2CH_3), 4.46 (q, $J = 7.2$ Hz, 4H, OCH_2CH_3), 7.91 (dd, $J = 5.2$ Hz, 1.6 Hz, 2H, bpy$-$**H**), 8.87 (d, $J = 5.2$ Hz, 2H, bpy$-$**H**), 8.95 (d, $J = 1.6$ Hz, 2H, bpy$-$**H**).

Ru[bpy(CO$_2$Et)$_2$]$_2$[Cl]$_2$ (9). *cis*-RuCl$_2$(DMSO)$_4$[27] (0.85 g, 1.8 mmol) was suspended in 30 mL of ethylene glycol. The suspension was heated at 150 °C for a few minutes until the solid had dissolved, and then LiCl (1.1 g, 26 mmol) was added. When all the LiCl salt had dissolved (a few minutes), the diester (**8**) (1.0 g, 3.3 mmol) was added in small portions over 1 h. The reaction mixture was heated for another 20 min and then cooled in an ice bath. Fifty milliliters of water was added, and the precipitate was collected by suction filtration and washed with water and a mixture of acetone/diethyl ether (1:2). A brown powder was obtained (0.45 g, 33%). ^{1}H NMR (400 MHz, DMSO-*d$_6$*): δ 1.29 (t, $J = 7.2$ Hz, 6H, OCH_2CH_3), 1.43 (t, $J = 7.2$ Hz, 6H, OCH_2CH_3), 4.34 (q, $J = 7.2$ Hz, 4H, OCH_2CH_3), 4.51 (q, $J = 7.2$ Hz, 4H, OCH_2CH_3), 7.48 (dd, $J = 5.6$, 1.6 Hz, 2H, bpy$-$**H**), 7.74 (d, $J = 5.6$ Hz, 2H, bpy$-$**H**), 8.24 (dd, $J = 6.0$ Hz, 1.6 Hz, 2H, bpy$-$**H**), 8.93 (d, $J = 1.6$ Hz, 2H, bpy$-$**H**), 8.11 (d, $J = 1.6$ Hz, 2H, bpy$-$**H**), 10.95 (d, $J = 6.0$ Hz, 2H, bpy$-$**H**).

Ru[bpy(CO$_2$Et)$_2$]$_2$[4′-Phenyl(4″-CH$_2$-bis(2-pyridylmethyl))-bpy][PF$_6$]$_2$ (7a). A solution of **9** (0.079 g, 0.10 mmol) and silver triflate (0.053 g, 0.20 mmol) in 10 mL of acetone was heated at 70 °C for 17 h under a nitrogen atmosphere. The solution was allowed to cool to ambient temperature and then filtered to remove the AgCl salt before 4′-(*p*-methylbromophenyl)bipyridine[22] (0.033 g, 0.10 mmol) was added. This mixture was heated for 6 h under nitrogen and then evaporated to dryness. The red-brown residue was dissolved in a minimum amount of methanol, and a saturated solution of NH_4PF_6 (10 mL) was added to precipitate the tris-bipyridyl ruthenium complex. The precipitate was collected by filtration and washed with water and Et_2O. It was then dissolved in CH_2Cl_2 (20 mL), and dipicolylamine[28] (0.020 g, 0.10 mmol) and Et_3N (0.010 g, 0.10 mmol) were added. The solution was heated at 45 °C for 13 h and then evaporated to dryness and purified by column chromatography, first using CH_3CN and then using 8:1:1 $CH_3CN/H_2O/KNO_3$(saturated) as eluents. A red fraction eluted after a brown band was collected. After evaporation of the solvent, the solid was redissolved in a minimum amount of methanol, and a solution of NH_4PF_6 was added. The red precipitate was collected by filtration, washed with water and Et_2O, and dried to give 0.066 g (46%) of the desired complex. ^{1}H NMR (400 MHz, acetone-*d$_6$*): δ 1.38 (t, $J = 7.2$ Hz, 12H, OCH_2CH_3), 3.87 (s, 6H, $PhCH_2N$ and NCH_2Py), 4.47 (q, $J = 7.2$ Hz, 8H, OCH_2CH_3), 7.26$-$7.30 (m, 2H, Py$-$**H**), 7.59$-$7.63 (m, 1H, bpy$-$**H**), 7.65 (d, $J = 7.7$ Hz, 2H, Py$-$**H**), 7.71 (d, $J = 8.1$ Hz, 2H, Ph$-$**H**), 7.78$-$7.80 (m, 2H Py$-$**H**), 7.86 (dd, $J = 5.9$ Hz, 1.8 Hz, 1H, bpy$-$**H′**), 7.93 (d, $J = 8.1$ Hz, 2H, Ph$-$**H**), 7.94$-$7.96 (m, 2H, bpy$-$ester$-$**H**), 7.99$-$8.03 (m, 2H, bpy$-$ester$-$**H**), 8.12 (d, $J = 5.9$ Hz, 1H, bpy$-$**H′**), 8.13$-$8.15 (m, 1H, bpy$-$**H**), 8.29 (dt, $J = 7.7$ Hz, 1.5 Hz, 1H, bpy$-$**H**), 8.36$-$8.43 (m, 4H, bpy$-$ester$-$**H**), 8.55$-$8.57 (m, 2H, Py$-$**H**), 9.14$-$9.17 (m, 2H, bpy$-$**H** and bpy$-$**H′**), 9.34$-$9.36 (m, 4H, bpy$-$ester$-$**H**). ESI-MS *m/z*: (M$-$PF$_6$) 1290.08, (M$-$2PF$_6$) 572.69. Anal. Calcd for $C_{61}H_{57}N_9O_8F_{12}P_2Ru{\cdot}0.5CH_2Cl_2$: C, 49.99, H, 3.96, N, 8.53. Found: C, 49.78, H, 4.02, N, 8.52.

7b was synthesized by adding a saturated solution of $MnCl_2$ in acetonitrile to **7a** dissolved in acetonitrile. ESI-MS of **7b** (prepared as described previously) *m/z*: (M $-$ PF$_6$ $-$ solvent) 1415.18, (M $-$ 2PF$_6$ $-$ solvent) 635.14.

Luminescence Spectroscopy. The steady-state emission and absorption measurements were performed at room temperature in air-saturated acetonitrile of spectroscopic grade (Merck, 99.8%). The absorption spectra were recorded on an HP 8453 diode array spectrophotometer, and the emission spectra were recorded using a SPEX fluorolog II system. The excited-state lifetimes of all the complexes were determined in nitrogen-purged acetonitrile using a time-correlated single-photon counting setup described previously.[29] Low-temperature measurements were performed in butyronitrile (Fluka, 99%) using capillary tubes inserted into a coldfinger Dewar filled with liquid nitrogen.

Electrochemistry. The electrochemistry of **1a**$-$**3a**, **5a**, **7a**, and **1b**$-$**5b** was performed in an argon-filled glovebox. The electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile (Aldrich, 99.8%), which was used as received. The salt was dried at 140 °C for 48 h before preparing the electrolyte. For **2b**, the temperature dependence of the redox potentials was also investigated between 10 and 60 °C. A three-electrode system consisting of Ag/AgCl in LiCl-saturated acetonitrile as the reference electrode, a platinum wire or a carbon stick as a counter electrode, and a freshly polished piece of glassy carbon (diameter 3 mm) as the working electrode were used. Both the reference electrode and the counter electrode were separated from the solution by a salt bridge that was in contact with the working electrode. A potentiostat from Eco Chemie with an Autolab/GPES electrochemical interface was used.

The reported half-wave potentials, $E_{1/2}$ ($E_{1/2} = (E_{p,a} + E_{p,c})/2$), which were measured versus ferrocenium/ferrocene as an internal reference, are reported versus SCE. The conversion was made by setting the Ru$^{III/II}$ value obtained for Ru(bpy)$_3$(Cl)$_2$ equal to 1.324 V vs SCE.[30]

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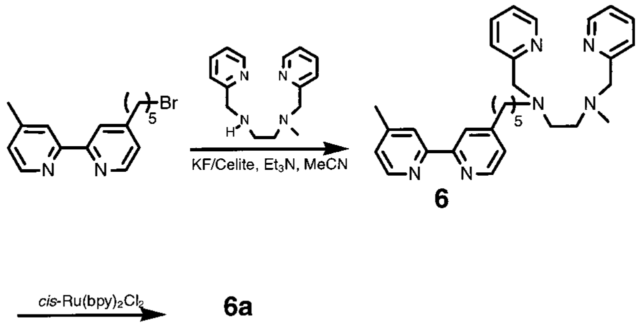
Scheme 1



Electron Transfer. Electron transfer in **1a**−**6a** and **1b**−**6b** was studied with laser flash photolysis as described elsewhere.[31] For **7a** and **7b**, the transient absorption was studied using a flash-photolysis system with a Q-switched Nd−YAG laser ($\lambda = 355$ nm) to pump an OPO delivering <10 ns flashes that were tunable between 410 and 660 nm. The analyzing light was provided by a pulsed Xe lamp in a spectrometer system from Applied Photophysics. To minimize the risk of replacement of the manganese by CO_2,[22] the acetonitrile (Merck, 99.8%) in the optical cell was purged with nitrogen directly before dissolving the complex, and purging was continued during the measurement. The samples contained ~30 μM of the complex and 30−300 mM of methyl viologen (MV-$(PF_6)_2$), which was prepared from commercial $MVCl_2$ (Sigma) by adding aqueous NH_4PF_6 to precipitate the PF_6 salt. The product was purified by recrystallization from ethanol.

For some of the complexes studied, it was shown previously that manganese(II) binding follows the equilibrium[21,22]

$$\mathrm{Ru^{II}L{-}Mn^{II}} \rightleftharpoons \mathrm{Ru^{II}L + Mn^{II}} \qquad (1)$$

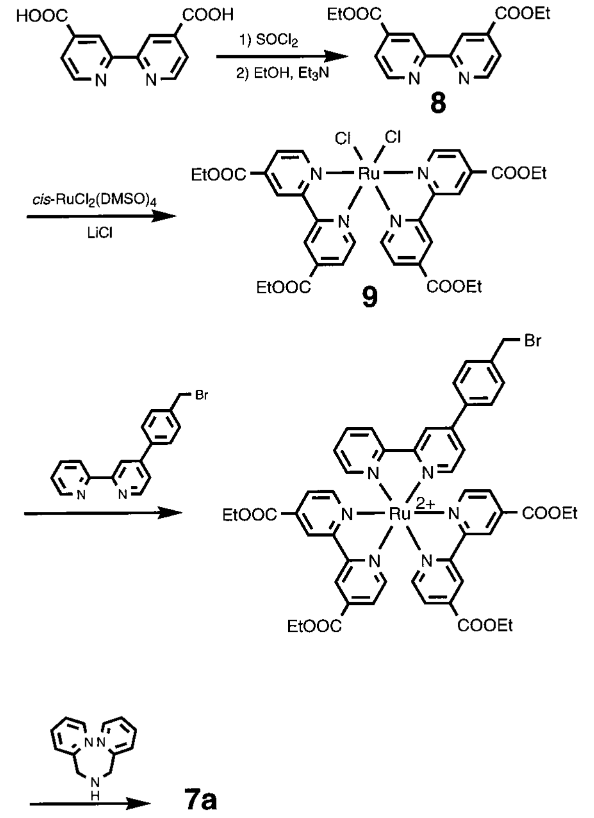
where RuL−Mn(II) are the complexes with manganese (**1b**−**7b**) and RuL are the complexes without manganese (**1a**−**7a**). To increase the fraction of ruthenium(II) complexes with manganese(II) in the electron-transfer experiments, ~100−300 μM of $MnCl_2$ was added to the sample from a saturated acetonitrile solution of $MnCl_2$. This addition shifted the equilibrium so that more than 95% of the ruthenium(II) complexes contained coordinated manganese(II). Control experiments with $Ru(bpy)_3^{2+}$ and $MnCl_2$ have shown that free $MnCl_2$ at the present concentrations does not quench the excited ruthenium(II) moiety nor does it reduce the photooxidized ruthenium(III).[21]

The temperature dependence of the electron transfer in **2b**, **3b**, and **5b** was studied from 10 to 70 °C. The experiments were done using a sealed optical cell, and to control the temperature, the cell holder was connected to a temperature bath. To minimize the concentration of O_2, the cell was degassed by four freeze−pump−thaw cycles before sealing.

Results

Synthesis. 6a was synthesized by reacting *cis*-$Ru(bpy)_2Cl_2\cdot 2H_2O$ with the bpy(CH_2)-5-bispicen ligand (**6**) (Scheme 1). This bipyridine was obtained by substituting the bromide in bromopentylbipyridine with *N*-methyl-*N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen). To promote the alkylation reaction, KF/Celite[32] was added to the reaction mixture.

Scheme 2



Because **6** contains both a bipyridine and a bispicen ligand, there is competition in binding to the ruthenium in the bis-bipyridyl complex, which lowers the yield of this reaction. The corresponding manganese(II) complex (**6b**) was obtained by treating **6a** with manganese(II) chloride.

The synthesis of **7a** is shown in Scheme 2. The carboxylic acid bipyridine was converted to the corresponding acid chloride, which reacted with ethanol to form the diester (**8**). The transformation of the diacid into the diester made the substituted bipyridine much easier to work with because the diacid is insoluble in most organic solvents. The ruthenium bis(bpyCOOEt) dichloro complex (**9**) was synthesized by reacting the diester (**8**) with the ruthenium(II)$(DMSO)_4(Cl)_2$ complex. Because of the formation of ruthenium tris(bpyCOOEt), the yield of **9** was low. The two chlorides in **9** were removed by treating the complex with silver triflate, and the bromomethylphenylbipyridine was added to form the trisbipyridyl complex, which was precipitated from the reaction mixture with ammonium hexafluorophosphate. The bromide was then substituted with dipicolylamine to give **7a**. Chart 1 shows the structure of the dinuclear ruthenium−manganese complexes **1a**−**7b**.

Steady-State Spectroscopy. Both the absorption and emission spectra for **1a**−**6a** in acetonitrile are nearly identical to those for $Ru(bpy)_3^{2+}$, [33,34] with a strong metal-to-ligand charge transfer (MLCT) absorption band around 450 nm. The emission around 600 nm originates from the lowest

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Chart 1

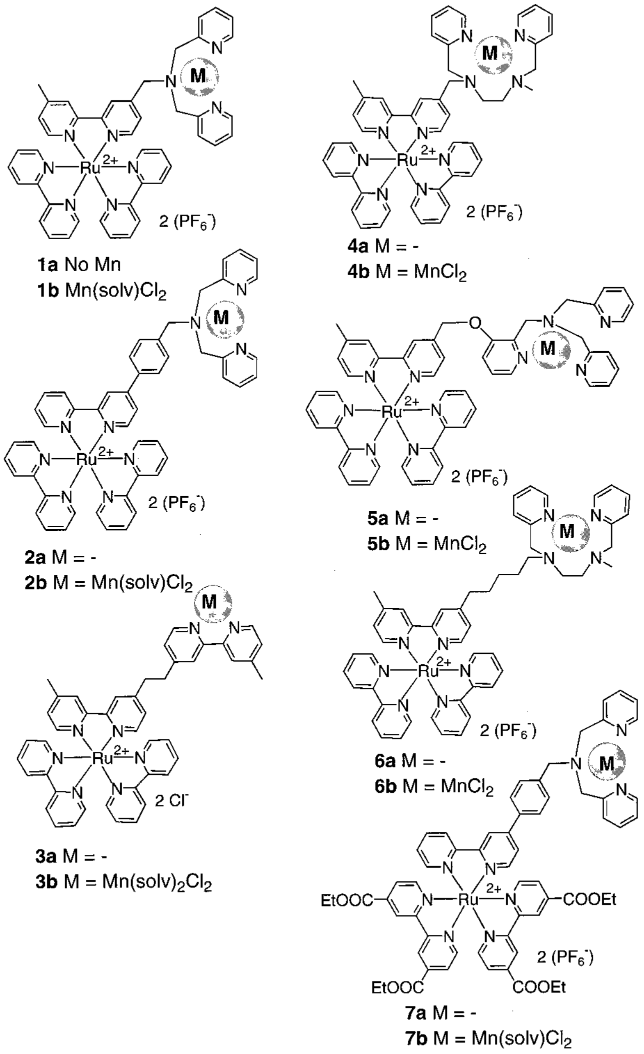

Table 1. Luminescence Data for the Mononuclear Ruthenium Complexes and Dinuclear Ruthenium−Manganese Complexes

Mononuclear Ruthenium Complexes

	293 K		77 K	
	λ_{max} (nm)	τ (ns)	λ_{max} (nm)	τ (μs)
1a	636	880[a]	585[a]	4
2a	631	1400[a]	588	
3a	631	919[a]	584	5
4a	638	1050[a]		
5a	631	900	582	4
6a	630	800		
7a	669	1300	638	

Dinuclear Ruthenium−Manganese Complexes

	293 K			77 K	
	λ_{max} (nm)	τ_1 (ns)	k_q (s^{-1})	λ_{max} (nm)	k_q (s^{-1})
1b	636	2.2[a]	4.5×10^8	584	6.4×10^6
2b	632	23[a]	4.3×10^7	588	
3b	631	255[a]	2.8×10^6		2.3×10^6
4b	639	7[a]	1.4×10^8	586	
5b	631	120[a]	7.2×10^6	582	9.7×10^5
6b		300	2.1×10^6		
7b	669	1200	6.4×10^4		

[a] From references 21 and 22.

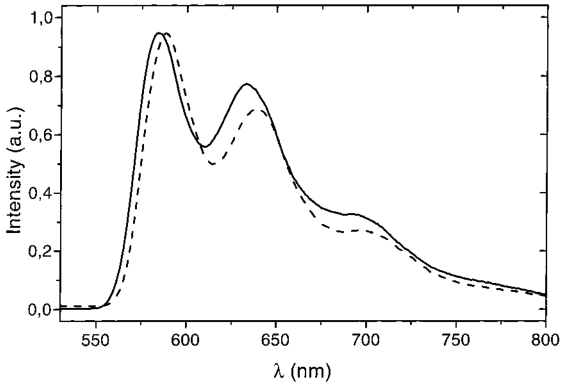

Figure 1. Luminescence spectrum for **1b** (solid line) and **2b** (dashed line) in butyronitrile at 77 K. The excitation wavelength was 450 nm.

MLCT state of predominantly triplet character that is populated with a quantum yield of 1 within less than 1 ps after excitation to the singlet MLCT states.[33,35] The wavelength maxima of the emission spectra of all the complexes are reported in Table 1. For **7a** and **7b**, the absorption spectra are red-shifted by ~20 nm compared to the spectra of **2a** and **2b**, and the emission spectra are red-shifted by ~40 nm. These shifts are due to the presence of the electron-withdrawing ester groups on the bipyridines. The presence of manganese in **1b**−**7b** gives no observable shifts of the absorption maxima and only a small red shift (<2 nm) of the emission maxima compared to the spectra of **1a**−**7a**. However, the emission intensities for **1b**−**6b** are much lower than are those for the corresponding complexes without manganese.

The emission spectra in butyronitrile at 77 K display a well-resolved vibrational progression for all complexes investigated (Table 1), as shown for **1b** and **2b** in Figure 1.

Electrochemistry. The cyclic voltammograms of all the complexes investigated show typical $Ru(bpy)_3^{2+}$ behavior, with a reversible peak at ~1.3 V versus SCE and three reversible peaks between −1.25 and −1.80 V versus SCE, corresponding to the oxidation of ruthenium(II) and the reduction of the three bipyridine ligands,[30,33,34] respectively. In the presence of manganese(II), one additional, less-reversible peak (ΔE_p < 134 mV) is observed around 0.90 V versus SCE that is assigned to the oxidation of the manganese(II).[22] The $E_{1/2}$ values obtained for the manganese(II) oxidation vary from 0.79 to 0.90 V versus SCE for the different complexes, whereas the variation in the $E_{1/2}$ values for ruthenium(II) oxidation for all the complexes, except **7a**, is less than 20 mV (Table 2). For **7a**, both the oxidation of the ruthenium(II) and the first reduction are shifted ~200 and ~360 mV, respectively, toward more positive potentials because of the presence of the electron-withdrawing ester groups. The difference in the $E_{1/2}$ values for the oxidation of the manganese(II) and ruthenium(II) gives the driving force ($\Delta G°$) for the intramolecular electron transfer in the different complexes. The temperature dependence of $\Delta G°$ was investigated for **2b** and was found to vary by less than 10 meV between 10 and 60 °C.

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Table 2. Electron-Transfer Data for Ruthenium(II)−Manganese(II) Complexes

	d^a (Å)	$E_{1/2}$ (Mn$^{III/II}$) (V vs SCE)	$E_{1/2}$ (Ru$^{III/II}$) (V vs SCE)	$E_{1/2}$ (first ligand) (V vs SCE)	$\Delta G°$ (eV)	k_{ET} (s^{-1})^b	$\Delta G^‡$(eV)	*λ (eV)*	H_{rp} (meV)
1b	9	(0.90)[c]	1.28	−1.31	(−0.38)[c]	1.1×10^6			
2b	14	0.90	1.29	−1.28	−0.39	1.7×10^6	0.33	2.0	12
3b	13	0.85	1.28	−1.34[d]	−0.43	1.8×10^5	0.27	1.8	1.7
4b	9	0.85	1.30	−1.30	−0.45	$>2 \times 10^7$			
5b	13	0.79	1.28	−1.31	−0.49	1.4×10^5	0.17	1.5	0.27
6b[e]	14	(0.85)[f]		(1.30)[f]	(−0.45)[f]	1×10^5			
7b	14	(0.90)[g]	1.49[h]	−0.92[h]	(−0.59)[g]	1.1×10^7			
Ru(bpy)$_3^{2+}$			1.32	−1.29					

[a] The distance between the ruthenium(II) and the coordinated manganese(II). These are the maximum distances estimated by molecular mechanics, starting from the most extended conformations using constrained metal−ligand distances. [b] Determined with an excess of $MnCl_2$ in acetonitrile to obtain a larger fraction of coordinated manganese(II) and thus a more reliable value. [c] The Mn$^{III/II}$ couple was not observed because of the instability of the complex toward dissociation of the Mn(II)[22] (see text). The redox potential for the manganese is assumed to be the same as for **2b** because the manganese ligand is the same. [d] Peak potential for the first reduction of the bipyridines. [e] Cyclic voltammetry of **6b** was not performed because of the limited availability of the complex. [f] The redox potential for the metals are assumed to be the same as that for **4b**. [g] The redox potential for the manganese is assumed to be the same as that for **2b**. [h] The redox potentials are those determined for **7a** because **7b** was prepared in situ by adding an excess of $MnCl_2$ to an acetonitrile solution of **7a**.

Excited-State Lifetimes. The emission lifetimes obtained for the ruthenium(II) complexes with and without manganese(II) have been determined in deoxygenated acetonitrile (see Table 1). The lifetimes for the mononuclear ruthenium(II) complexes (**1a**−**7a**) are all between 800 and 1300 ns. In the ruthenium(II)−manganese(II) complexes **1b**−**6b**, the lifetimes are reduced to between 2 ns and 300 ns. For **7b**, on the other hand, the lifetime is ∼1200 ns (i.e., almost the same as in the absence of manganese). These results show that coordinated manganese(II) quenches the excited state of ruthenium(II) in **1b**−**6b** in an intramolecular reaction, which is consistent with the lower emission yields obtained in these complexes. Control experiments with different concentrations of the ruthenium(II)−manganese(II) complexes and of additional $MnCl_2$ show that bimolecular quenching is not significant. The quenching rate constant k_q for each complex was calculated from

$$k_q = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad (2)$$

where τ and τ_0 are the lifetimes of the ruthenium(II)−manganese(II) complexes and the ruthenium(II) complexes, respectively. The value of k_q decreases with the metal-to-metal distance, as shown in Figure 2. A linear least-squares fit to the data of ln k_q versus distance gives a line with a slope of 1.0 Å^{-1} when the data for **2b** and **7b** are excluded. The deviating behavior for **2b** and **7b** can be explained by a different excited-state localization in these two complexes (see below).

The emission lifetimes of **1a**, **1b**, **4b**, **5a**, **5b**, and **7a** have also been measured in a rigid butyronitrile glass at 77 K (see Table 1). For the complexes without manganese, a lifetime of ∼4 μs is obtained, which is in good agreement with the value for Ru(bpy)$_3^{2+}$ under the same conditions.[33,34] In the presence of manganese(II), for **1b**, **4b**, and **5b**, the emission shows a bi- or multiexponential decay. A slow component with a lifetime similar to the one obtained for the complex without manganese is assigned to the emission from the complex in which manganese(II) has dissociated. A more short-lived component is obtained for **1b**, **4b**, and **5b** with lifetimes of 150, 200, and 820 ns, respectively. This component is assigned to the intact complex in which the coordinated manganese(II) quenches the ruthenium(II) excited state in a rigid glass at 77 K. A similar result was previously reported for **3a** and **3b**.[21]

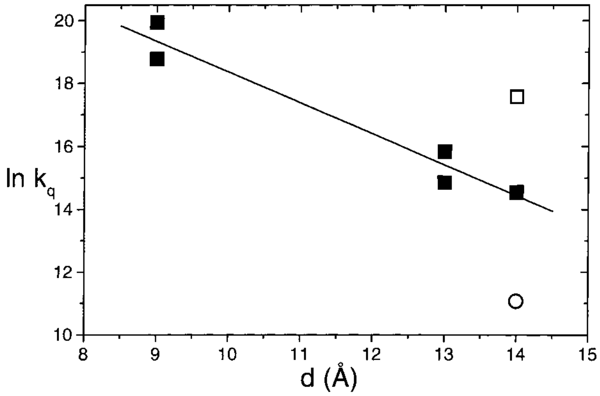

Figure 2. Distance dependence of the rate constant for quenching, k_q, of the ruthenium excited state by the manganese moiety in the ruthenium(II)−manganese(II) complexes. The unfilled square represents **2b**, and the unfilled circle represents **7b**. The distances used are the maximum distance between the ruthenium(II) and the coordinated manganese(II), estimated by molecular mechanics starting from the most extended conformations using constrained metal−ligand distances.

Electron Transfer. The ruthenium(II) moieties of the complexes have been photooxidized in the presence of methyl viologen, MV^{2+}, as the external acceptor. Excitation at 460 nm with an ∼5 ns laser flash creates the ruthenium(II) excited state, which transfers an electron to the external acceptor MV^{2+} in a bimolecular reaction, resulting in the formation of oxidized ruthenium(III) and the methyl viologen radical, MV$^{\bullet+}$. The subsequent recombination to generate the ground-state reactants has been studied by monitoring the recovery of the ruthenium(II) bleach at 450 nm and the decay of the absorption of the formed MV$^{\bullet+}$ around 600 nm.[34,36,37] For most of the mononuclear ruthenium(II) complexes **1a**−**7a**, the 450 nm recovery and the 600 nm decay curves are mirror images; these processes follow second-order kinetics with a nearly diffusion-controlled rate constant of 5×10^9 M^{-1} s^{-1}. For **1a** and **4a**, however, the recovery of ruthenium(II) at 450 nm is faster than the decay of MV$^{\bullet+}$

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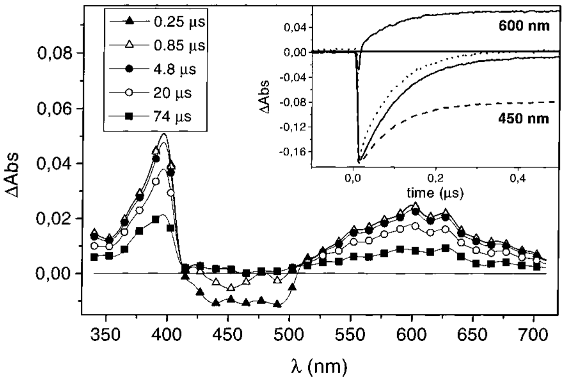

Figure 3. Transient absorption spectrum after excitation of **7b** at 478 nm in deoxygenated acetonitrile in the presence of 40 mM MV^{2+}. The bleaching of the ruthenium MLCT band around 450 nm recovers within 1 μs because of the intramolecular electron transfer from manganese(II) to the photooxidized ruthenium(III), whereas the $MV^{+\bullet}$ absorption, around 600 nm, is much more long-lived. Inset: the kinetic traces at 450 and 600 nm are shown for both **7a** (dashed) and **7b** (solid) in the presence of 0.1 M MV^{2+}. The traces at 600 nm for the two complexes overlap perfectly. The emission decay at 650 nm is also shown (dotted).

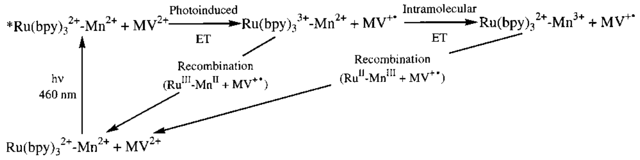

Figure 4. Reaction scheme for the electron-transfer processes between the ruthenium(II)−manganese(II) complexes and MV^{2+} in flash photolysis.

at 600 nm, which shows that the photooxidized ruthenium(III) receives an electron from a source other than $MV^{\bullet+}$. Upon repeated flashing, the concentration of $MV^{\bullet+}$ builds up and is stable on the time scale of minutes or more. This phenomenon can be explained by an irreversible oxidation of the uncoordinated amine ligand that is the only conceivable electron donor except $MV^{\bullet+}$. An irreversible oxidation at ∼1.0 V versus SCE in the cyclic voltammetry of **1a** can be assigned to the oxidation of the DPA ligand.[22,38,39]

Coordination of manganese(II) stabilizes the amine ligand against oxidation, and no build up of $MV^{\bullet+}$ is observed in any of the ruthenium(II)−manganese(II) complexes. Neverless, the recovery of the ruthenium(II) at 450 nm is much faster than the decay of the $MV^{\bullet+}$ at 600 nm; the recovery is also faster than that in the corresponding mononuclear ruthenium(II) complexes. Evidence for these differences is shown in the transient absorption spectrum and kinetic traces for **7b** in Figure 3. Manganese(II) is the only additional electron donor, which suggests that the faster recovery at 450 nm in **1b**−**7b** is due to electron transfer from the coordinated manganese(II) to the photooxidized ruthenium(III) (see reaction scheme in Figure 4). This conclusion was previously reached for **1b**−**3b**[21,22] and is now shown for four new complexes, **4b**−**7b**. The manganese(II) oxidation could not be followed optically because of the very small extinction coefficients for the manganese(II) and manganese(III) complexes. However, electron transfer is consistent with the electrochemical potentials for the ruthenium(III/II) and manganese(III/II) couples. Also, we have already shown [21] that the manganese(II) of **3b** is oxidized to manganese(III) by $Ru(bpy)_3^{3+}$, as evidenced by the disappearance of the EPR signals of manganese(II) and ruthenium(III) when the reactants were mixed in equimolar amounts. The ruthenium(II) recovery rate constant is independent of the concentrations of the ruthenium(II)−manganese(II) complexes, which shows that the reaction is intramolecular.[21,22] The k_{ET} values vary from 1×10^5 to 2×10^7 s^{-1} for **1b**−**7b**, respectively (Table 2).

In Figure 3, it is clearly shown that the recovery of ruthenium(II) at 450 nm for **7b** is completed before any significant decay of $MV^{\bullet+}$. Compared to the other ruthenium(II)−manganese(II) complexes, the bimolecular photooxidation with MV^{2+} is slow in **7a** and **7b**, which is due to a lower driving force for this reaction. To better resolve this process, a higher concentration of MV^{2+} was used (0.1 M), giving a pseudo-first-order quenching rate constant of 1.45×10^7 s^{-1}. The resulting kinetic traces are shown in the inset of Figure 3, and it is clear that the 450 nm recovery is somewhat faster then the emission decay. Because the bimolecular quenching reaction and the intramolecular electron transfer occur on the same time scale in **7b**, a consecutive first-order kinetic model (A → B → C) was used for the analysis, resulting in a value of 1.1×10^7 s^{-1} for k_{ET}. The quenching rate constant was fixed to 1.45×10^7 s^{-1} in the fit, as determined from the emission decay. The amplitude change at 450 nm corresponding to the subsequent intramolecular electron transfer was about one-third of that for the quenching process. This is expected for nearly identical differential extinction coefficients for the excited and oxidized ruthenium moiety at 450 nm and a charge-separation yield of about one-third.[34,36]

Control experiments were performed without MV^{2+} to determine if the products of the manganese-induced quenching of ruthenium(II) excited state could interfere with the analysis of the electron-transfer data. No transient absorption was observed apart from that of the excited ruthenium(II), however. In addition, with different concentrations of MV^{2+}, the ruthenium(II) excited state was quenched to varying extents by manganese and MV^{2+}, yet there was no difference in the transient absorption kinetics (rate constants) for the electron-transfer reaction.

The temperature dependence of k_{ET} for **2b**, **3b**, and **5b** has been studied between 10 and 70 °C, and in Figure 5, the values obtained are plotted as $\ln(k_{ET}T^{1/2})$ versus $1/T$. The $(n_s^{-2} - \epsilon_s^{-1})$ factor varies less than 3.5% within this temperature region. From the linear fits of the data in Figure 5, the reorganization energy (λ) was calculated from the slope according to the Marcus expression for k_{ET} (eq 3) using the $\Delta G°$ values obtained from the electrochemical measurements. The electronic coupling constant (H_{rp}) was calculated using the intercepts obtained from the linear fits in Figure 5 according to eqs 3 and 4. The temperature dependence of

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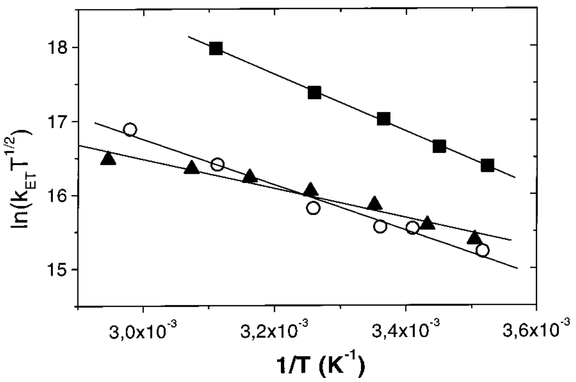

Figure 5. Temperature dependence of the electron-transfer rate constant for **2b** (■), **3b** (○), and **5b** (▲).

$\Delta G°$ was neglected, as justified by the <10 mV variation in $\Delta E°$ for the Ru(III/II) and Mn(II/II) couples of **2b** between 10 and 60 °C. The λ values calculated from the slopes are 2.0, 1.8, and 1.5 eV for **2b**, **3b**, and **5b**, respectively. The H_{rp} values calculated from the intercepts are 12, 1.7, and 0.27 meV (Table 2).

$$\ln k_{ET} = \ln A - \frac{(\Delta G° + \lambda)^2}{4\lambda k_B T} \tag{3}$$

$$A = \frac{4\pi}{h} H_{rp}^{\ 2} \frac{1}{\sqrt{4\pi\lambda k_B T}} \tag{4}$$

Discussion

Excited-State Quenching. The lifetime of the ruthenium(II) excited state is crucial to a successful electron transfer to the external acceptor MV^{2+}. A complicating factor in these complexes is that manganese(II) quenches the excited state and competes with the intermolecular electron transfer to MV^{2+}. In some of the complexes, the excited-state lifetime becomes so short that it is difficult to obtain any electron transfer, even with very high concentrations of MV^{2+}. Therefore, to control the quenching, it is of great importance to know through which mechanism it occurs.

There are several conceivable quenching mechanisms. Coordination of manganese in the complex could cause changes in the electronic properties of the $Ru(bpy)_3^{2+}$ moiety that would change the rate constants for the excited-state deactivation. However, because the absorption and emission spectra are not significantly different for the complexes with and without manganese, it seems that the effect of manganese on the electronic structure is negligible. Paramagnetic quenching has been discussed as a general mechanism for excited-state quenching, but a detailed study[40] suggested that this mechanism is insignificant in the quenching of excited ruthenium complexes. Two other plausible mechanisms that should be considered are energy transfer to manganese(II) and electron transfer from manganese(II), in the latter case generating the reduced ruthenium complex. With an excited-state reduction potential for ruthenium ($Ru^{*2+/+}$) of ca. 0.86 V versus SCE,[33] electron-transfer quenching would be nearly isoergonic in all complexes ($\Delta G° \geq -0.1$ eV, Table 2). Energy transfer is possible because manganese(II) complexes have d−d excited states that are below the energy of the ruthenium(II) excited state.[41,42] Although direct transitions from the manganese(II) ground state are spin-forbidden (and Laport-forbidden), exchange-energy transfer from the excited ruthenium(II) moiety can be spin-allowed. No transient absorption signals other than those from the ruthenium(II) excited state were observed in flash photolysis experiments with only the ruthenium(II)−manganese(II) complexes in acetonitrile. However, the products from both energy- and electron-transfer quenching are expected to be very short-lived; thus, this result does not contradict any of these mechanisms.

One way to discriminate between the electron- and energy-transfer mechanisms is to measure the emission lifetimes in a low-temperature glass. In an electron-transfer reaction, the solvent molecules around the complex need to reorganize according to the new charge distribution. When the reaction occurs in a rigid medium, the reorganization cannot take place. This situation will result in a decrease of the reaction driving force by an amount equal to the outer reorganization energy,[43−45] which is ca. 1.0 eV for complexes of this size in polar solvents.[46] As a consequence, the electron transfer would be strongly endoergonic in the present complexes, and quenching would not occur. However, in an energy-transfer reaction, the effect of the frozen solution would be much smaller because the solvent reorganization in this case is relatively small.[47] We have previously reported that quenching in **3b** is rapid even in a solvent glass.[21] From the emission lifetimes at 77 K reported here, it is clear that this result is general for all complexes investigated (**1b**, **4b**−**5b**). The conclusion is that quenching of the excited state of ruthenium(II) does not occur through an electron-transfer mechanism but presumably through energy transfer to a short-lived excited state of manganese(II) with the appropriate energy.

The rate constant for an exchange-energy transfer decreases exponentially with distance.[48,49] In Figure 2, we plot the natural logarithm of the quenching rate constant versus the distance between the two metals. A linear least-squares fit to the data gives a slope of 1.0 Å^{-1} when the data for **2b** and **7b** are excluded (see explanation below), which is a reasonable value for a through-bond exchange energy transfer. Although only a limited set of data are available, this correlation indicates that even though the ligand that

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coordinates the manganese(II) is different for the complexes studied here the energy of the manganese(II)-based excited state is approximately constant. As a consequence, changing the manganese(II) ligands does not seem to be an efficient strategy to reduce the quenching. Figure 2 suggests that the only way is to increase the distance between the two metals. Manganese(II) is believed to be involved in the lowest oxidation state (S_0) of the manganese cluster in PS II.[6,50−54] Our data suggest that quenching of the excited P_{680} in PS II by the manganese cluster that involves manganese(II) in its lowest oxidation state may be a potential problem that Nature has solved by keeping these units 15−20 Å apart and using tyrosine$_Z$ as an interface between them. Thus, by increasing the distance between P_{680} and the manganese cluster, the risk of quenching P_{680}* would be minimized while electron transfer via tyrosine$_Z$ can still be efficient. It is of interest to mimic this organization in a synthetic triad including tyrosine in which the sensitizer−manganese distance is controlled.

Complexes **2b** and **7b** deviate from the trend described by the line in Figure 2. Despite the relatively long metal-to-metal distance (14 Å), the excited-state lifetime of **2b** is only 23 ns while the lifetime of **7b**, at the same metal-to-metal distance, is instead much longer. These deviations can be explained by the difference in the ligands around the ruthenium(II)−metal center. In all the ruthenium(II)−manganese(II) complexes studied, except **2b** and **7b**, the bipyridine ligand linking the manganese(II) is substituted with electron-donating groups (4,4′-dialkyl-bipyridine). This substitution will increase the energy of the MLCT state such that the lowest excited MLCT state will involve the unsubstituted bipyridines that are remote to manganese(II). In **2b**, the manganese ligand is instead linked to the ruthenium moiety via a phenyl group that is conjugated with the bipyridine. Earlier studies have shown that the electron in an excited MLCT state can be delocalized over a conjugated ligand, leading to a decrease in the excited-state energy.[55−58] Thus, the lowest MLCT state may involve the substituted, bridging bipyridine ligand rather than the unsubstituted ligands, as shown in Figure 6. The involvement of the bridging bipyridine ligand would move the MLCT state of **2b** much closer to the manganese moiety, as compared to the MLCT states of the other complexes, and could explain why the emission lifetime of **2b** is shorter than those of **3b**, **5b**, and **6b**, even though the metal-to-metal distances are the same.

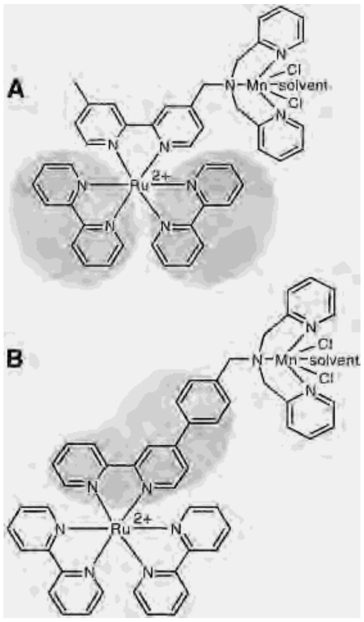

Figure 6. Schematic picture of the localization of the transferred electron on the lowest MLCT excited state for complex **1b** and **2b**, showing how the phenyl substituent moves the lowest ruthenium MLCT state closer to the manganese moiety (see text).

A higher degree of delocalization is accompanied by a smaller nuclear equilibrium displacement of the potential energy curves for the luminescent MLCT excited state with respect to the curve for the ground state.[56] This situation is directly reflected in the Franck−Condon envelope of the vibrational progression exhibited by the low-temperature luminescence spectra. The relative peak heights of the 0−1 and 0−0 transitions could therefore be used as a measure of the displacement. From the spectra in Figure 1, it is clear that the 0−1 peak height is lower for **2b** than for **1b**, showing that the displacement parameter for **2b** is smaller. The room-temperature emission spectrum of **2a** shows a smaller spectral width compared to that of **1a** (not shown), which is expected for a system with a smaller displacement parameter. These data support the assumption that the lowest MLCT state of **2b** involves the substituted bipyridine and is also delocalized over the phenyl group.[55,58,59] Also, from the electrochemical data, it is clearly easier to reduce the first ligand in **2b** than it is to reduce the first ligand in **1b** (Table 2). Finally, the emission maximum of **2b** is red-shifted compared to that of **1b**. All these results suggest that the lowest MLCT state in **2b** involves the substituted ligand that bridges ruthenium(II) and manganese(II).

One way to counteract the effect of delocalization in **2b** and increase the excited-state lifetime would be to introduce strong electron-withdrawing groups on the unsubstituted bipyridines. The lowest MLCT state would then be localized on these ligands that are easier to reduce instead of on the phenyl-substituted bipyridine. The distance from the units involved in the lowest MLCT state to the manganese moiety

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would then be increased. To investigate this possibility, complex **7a** was synthesized. This complex has the same structure as **2a** except that four ester groups have been introduced in the previously unsubstituted bipyridine ligands. The emission maximum of **7a** at 293 K is red-shifted by ~40 nm compared to the emission maximum of **2a**, and the first ligand reduction occurs at a 360 mV-less-negative potential, which is consistent with the localization of the MLCT on the ester-substituted bipyridines in **7a**. The emission lifetime of **7a**, without manganese(II), is 1300 ns, which is similar to the value for that of **2a**. In contrast, the lifetimes for the complexes with manganese(II) are very different: ~1200 ns for **7b** but 23 ns for **2b**. Thus, it is clear that the ester groups move the excited state away from manganese(II), thereby increasing the excited-state lifetime from 23 to ~1200 ns. This dramatic improvement shows that it is possible to control the quenching without changing the metal-to-metal distance or the bridging ligand.

Although the data point for **2b** in Figure 2 is above the line, the energy of the lowest ^{3}MLCT state is nearly identical to those of the other complexes that follow the line. It seems clear that the reason for the unusually rapid quenching in **2b** is the localization of the MLCT state closer to manganese. In contrast, the data point for **7b** is well below the line. There are at least two possible explanations for this situation. First, the excitation in the ^{3}MLCT state of $Ru(bpy)_3^{2+}$ hops rapidly between the ligands.[60] In studies of electron-transfer quenching by acceptors linked to a $Ru(bpy)_3^{2+}$ complex, it was concluded that quenching occurred predominantly when excitation involved the bridging ligand.[60,61] Thus, when the MLCT state involving the remote ligands was lower in energy, quenching occurred via transient hopping to the higher MLCT state on the bridging ligand. This situation may also be true in this case; therefore, the slow quenching in **7b** could be ascribed to the much larger energy difference between the different MLCT states; this energy difference is much larger than those for the other complexes. Alternatively, if direct quenching from the remote ^{3}MLCT state dominates, the energy of this state is about 0.17 eV lower than that of the other complexes, which may give rise to a slower energy-transfer reaction. The activation energy for the different quenching routes will be different, but because the quenching is so slow in **7b** compared to the intrinsic decay of the MLCT state already at room temperature, it is not possible to extract reliable activation energies to distinguish between the two alternatives.

To conclude, we have investigated the excited-state quenching in the series of ruthenium(II)−manganese(II) complexes. The correlation between the quenching rate constant and the metal-to-metal distance (Figure 2), together with the substantial increase in the excited-state lifetime for **7b** as compared to that of the similar complex **2b**, shows that we can design complexes in which the quenching is controlled.

Electron Transfer. The flash photolysis experiments showed that intramolecular electron transfer occurs from the coordinated manganese(II) to the photooxidized ruthenium(III). The rate constants obtained for this reaction vary from 1×10^5 to 2×10^7 s^{-1} for **1b**−**7b**, respectively. To make a complex where intramolecular electron transfer is fast and efficient, it is of interest to investigate the factors responsible for this large variation in rates. In contrast to the excited-state quenching discussed above, the electron-transfer rate does not have a simple dependence on the metal-to-metal distance. For example, the rate constants for **1b** and **4b** are 1.1×10^6 s^{-1} and $>2 \times 10^7$ s^{-1}, respectively, although the metal-to-metal distance is 9 Å in both complexes.

According to the Marcus expression for k_{ET} (eqs 3 and 4), there are three factors that alter k_{ET}: variations in the reaction driving force ($\Delta G°$), the electronic coupling constant between the reactant and the product state (H_{rp}), and the reorganization energy (λ). The variation in $\Delta G°$ lies within 0.1 eV for **1b**−**6b** and is hence too small to explain the large variation in k_{ET}. The reorganization energies obtained from the temperature dependence of eqs 3 and 4 for **2b**, **3b**, and **5b** are 2.0, 1.8, and 1.5 eV, respectively; these values are larger than the 1.0 eV that one would expect for the outer reorganization energy in a polar solvent.[46] We believe that these large values are due to internal rearrangements of the manganese complex moiety as the labile manganese(II) complex is oxidized to the relatively stable manganese(III) complex. The Jahn−Teller distortion of manganese(III) complexes may also contribute to the reorganization energy. The reason for the variation in the reorganization energy (1.5−2.0 eV) may be the difference in the coordination stabilities of the manganese(II) complexes. Note that the complex that is most stable toward the dissociation in the manganese(II) state is **5b**, which also displays the lowest λ value. Taken together, these results indicate that similar ruthenium(II)−manganese(II) complexes will always have large reorganization energies. They will therefore not be rapid electron donors unless the driving force is high.

Although **2b** has the largest λ value (2.0 eV), its k_{ET} is larger than the k_{ET} values obtained for **3b** and **5b**. This result can be explained by the relatively large H_{rp} value of 12 meV that was calculated for **2b**, which is probably due to the extended conjugated π-system of the bridging bipyridine ligand between the two metals. The H_{rp} value for **5b**, on the other hand, is much smaller, only 1.7 meV. The small value may partly be due to the presence of the oxygen in the link between the two metal ligands, an effect that has not been reported in the literature. Another possible explanation is that the ruthenium(II) moiety is linked to the meta position of the pyridine ligand in relation to the manganese. The pyridine HOMO has a significant contribution from the atomic orbitals on both the nitrogen and C4 but a small contribution from C3. Thus, the coupling to the manganese ion via the pyridine would probably be stronger through the para position.

The variation in electronic coupling between the complexes causes a great difference in the preexponential factors of the electron-transfer rate constants (A in eqs 3 and 4). The prefactor ratio is 1800:36:1 for **2b**/**3b**/**5b**. For **2b**, it is

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as high as $A = 6 \times 10^{11}$ s^{-1}, which emphasizes that it is really the high activation energy that makes the electron transfer relatively slow. Another important result that also should be noted is that the observed k_{ET} for **7b** is much higher than that for **2b**. This result shows that our modification of the ruthenium(II) moiety in **7b** not only reduces the excited-state quenching to a minimum but also improves the electron-transfer properties, thus making this compound the best in the series. The 10-fold increase in the electron-transfer rate constant of **7b** compared to that of **2b** (see Table 2) can be explained by the larger driving force. If all other parameters are the same, a change in $\Delta G°$ from −0.39 to −0.59 eV would increase the rate constant by a factor of 20, which is within the experimental uncertainty equal to the observed increase.

Manganese(II) complexes may never be able to act as fast electron donors in an artificial photosynthetic system because of the large reorganization energy involved. A rapid regeneration of the photooxidized sensitizer is usually important to avoid deleterious recombination reactions. This problem could be solved by mimicking PS II, where tyrosine$_Z$ is the primary electron donor to P_{680}^{+}. In addition, a redox intermediate would increase the distance between the metals, which would also reduce the excited-state quenching. Some progress along these lines has been reported.[23−25,38]

Conclusions

We have shown that intramolecular electron transfer from manganese(II) to photooxidized ruthenium(III) occurs in a series of ruthenium(II)−manganese(II) complexes. The rate constants for this process lie in the range $1 \times 10^5 - 2 \times 10^7$ s^{-1}. This variation cannot be explained only by the difference in the metal-to-metal distance and the small variation in the driving force ($\Delta G°$ ranges between −0.39 and −0.49 eV for **1b**−**6b**). Instead, variations in reorganization energy and electronic coupling are important. The relative coupling strength is not related to the reactant distance in a simple way, thus showing the importance of specific through-bond effects. The reorganization energy is 1.5−2.0 eV for the complexes examined, which is higher than expected for outer (solvent) reorganization. Instead, internal reorganization of the manganese−ligand bonds may contribute to explain the data. Our results suggest that manganese complexes may never be fast electron donors and that the introduction of other redox intermediates may be necessary for rapid regeneration of the photooxidized sensitizer.

The ruthenium(II) excited MLCT state is quenched by the appended manganese(II). In some cases, the excited-state lifetime is only a few nanoseconds, which made photooxidation by the external acceptor difficult. We demonstrated that for complexes with similar ligands around ruthenium(II) the quenching rate constant decreases exponentially with the metal-to-metal distance, being independent of the type of manganese ligands involved. This result implies that efficient photooxidation requires a long metal-to-metal distance, but this distance would reduce the rate of subsequent electron transfer from manganese(II) to ruthenium(III) if other factors remain constant. However, by a manipulation of the MLCT-state energy involving the different ligands around ruthenium, the excitation could be distributed mainly on the ligand bridging the manganese or on the remote ligands. In this way, we could reduce the quenching rate constant in **7b** by 2−3 orders of magnitude compared to the quenching rate constant in the similar complex **2b**. Furthermore, subsequent electron transfer from the manganese was even somewhat faster in **7b** than it was in **2b**.

The purpose of the present study was to investigate the importance of the different parameters that affect the efficiency and rates of excited-state quenching and intramolecular electron transfer between manganese(II) and photooxidized ruthenium(III). With our results, we can understand the variation of these parameters within the series of complexes studied, and we can design complexes, such as **7b**, with improved properties. These results are also very important to the design of more complicated systems containing manganese complexes of higher nuclearity.

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