

# Binuclear Ruthenium–Manganese Complexes as Simple Artificial Models for Photosystem II in Green Plants

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**Abstract:** As part of a project aimed at developing models for photosystem II (PSII) in green plants, we have prepared a series of model compounds (**7**, **8**, and **13**). In these compounds, a photosensitizer, ruthenium(II) tris(bipyridyl) complex (to mimic the function of P<sub>680</sub> in PSII), was covalently linked to a manganese(II) ion through different bridging ligands. The structures of the compounds were characterized by electron paramagnetic resonance measurements and electrospray ionization mass spectrometry. The interaction between the ruthenium and manganese moieties within the complex was probed by steady-state and time-resolved emission measurements. When the binuclear complexes are exposed to flash photolysis in the presence of an electron acceptor such as methylviologen (MV<sup>2+</sup>), it could be shown that after the initial electron transfer from the excited state of Ru(II) in compound **7**, forming Ru(III) and MV<sup>•+</sup>, an intramolecular electron transfer from coordinated Mn(II) to the photogenerated Ru(III) occurred with a first-order rate constant of  $1.8 \times 10^5 \text{ s}^{-1}$ , regenerating Ru(II). This is believed to be the first supramolecular system where a manganese complex has been used as an electron donor to a photo-oxidized photosensitizer. Possible extensions to develop the manganese donor, and thus to approach the function of reaction center in PSII, are indicated.

## Introduction

The conversion of solar energy into fuel and electricity emerges as an important part of future sustainable energy systems. An attractive way to develop efficient systems for this conversion is to mimic natural photosynthesis in green plants. In this process, light energy is transformed into “fuel” by reduction of carbon dioxide. Simultaneously, water is oxidized to molecular oxygen.<sup>1</sup> This complex process starts at the reaction center of photosystem II (PSII) in green plants. The central part of this reaction center consists of a heterodimer of two proteins denoted D1 and D2 which bind most of the redox components including the primary photoelectron donor, a chlorophyll dimer P<sub>680</sub>. This dimer is surrounded by a large number (ca. 30) of protein subunits, including some chlorophyll binding proteins that absorb light.<sup>2</sup> After absorption of one quantum of light, P<sub>680</sub> is excited, and a very rapid “down hill” electron transfer (ET) chain starts, involving a primary electron acceptor pheophytin and two quinones, Q<sub>A</sub> and Q<sub>B</sub>. This is the first step of the conversion of light into chemical energy.<sup>3</sup> In green plants, a tetramanganese cluster serves as an electron donor to regenerate the photosensitizer P<sub>680</sub> by transfer of

electrons to the photo-oxidized form, P<sub>680</sub><sup>+</sup>. The ET is mediated by an tyrosyl residue, tyrosine<sub>z</sub>,<sup>4</sup> located ~5 Å away from the manganese cluster and 10–15 Å from P<sub>680</sub>.<sup>5</sup> In the unit of the oxygen evolving center (OEC), four electrons are sequentially transferred to P<sub>680</sub><sup>+</sup> and then all four electrons are recovered in a one-step, four-electron oxidation of two water molecules to molecular oxygen.

Since the crystal structure of the PSII reaction center has not been determined and the knowledge of the structure and function of the OEC is still fairly limited,<sup>6</sup> model systems<sup>7–9</sup> have been extensively studied. Such systems have in general been mainly structural models based on X-ray and EPR. Fewer examples

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exist where the OEC models have undergone some electrochemical or light-induced process.<sup>10</sup> For the primary charge separation, on the other hand, several functional models exist, with electron donor (D) and acceptor (A) assembled with a photosensitizer (S).<sup>11</sup> In some cases, detailed features of the bacterial reaction center have been mimicked in artificial D–S–A systems,<sup>12</sup> but most studies have only shown the general principle of photoinduced charge separation. Both porphyrins and ruthenium polypyridyl complexes have been widely used as photosensitizers, and their photophysical and photochemical properties have been extensively studied.<sup>13</sup> As electron acceptors, quinones and viologens have often been used,<sup>14,15</sup> and various donors, including sacrificial donors such as EDTA, have been applied to study the photoinduced ET reaction.<sup>16</sup> However, we are not aware of any studies of using manganese ions as electron donors to mimic the photoinduced ET process from OEC to P<sub>680</sub><sup>+</sup> in the reaction center of PSII. Since this appears to be a crucial step in attempts to construct a good model for PSII, we have initiated a project to mimic photoinduced ETs both from P<sub>680</sub> to Q<sub>A</sub> and from OEC to P<sub>680</sub><sup>+</sup>. We have synthesized some model systems, which contain a ruthenium tris(bipyridyl) type complex as photosensitizer, linked to a coordinated manganese ion. Here we report on the preparation and the photophysical studies of three such systems (**7**, **8**, and **13**). It was found that in the presence of an external electron acceptor such as methylviologen (MV<sup>2+</sup>) excitation of system **7** with visible light led to an intermolecular ET from the excited state of the Ru(II) moiety to MV<sup>2+</sup>, with the formation of MV<sup>•+</sup> and Ru(III). The latter is then reduced back to Ru(II) by an intramolecular ET from the manganese part of the complex. This result shows that an electron transfer from coordinated Mn(II) to a photo-oxidized photosensitizer is possible, opening the way to mimic an individual step of ET from OEC to P<sub>680</sub><sup>+</sup> in PSII.

## Experimental Section

**General Methods.** The electronic absorption spectra and steady-state emission spectra were recorded on a Varian Cary 5E UV–vis–near IR spectrophotometer and Perkin Elmer LS-5 luminescence spectrometer, respectively. <sup>1</sup>H NMR spectra were measured either on

Brucker-400 MHz or on Bruker-500 MHz spectrometers. X-Band EPR spectra were recorded on a Bruker ESP380 spectrometer equipped with an Oxford Instruments temperature controller. Infrared spectra were obtained on a Perkin Elmer FT-IR spectrometer 1725X or 1760X. Time-resolved emission measurements were conducted on single-photon-counting equipment employing a mode-locked Nd:YAG laser to pump a DCM dye laser. The output from the dye laser was frequency doubled to 327 nm and used to excite the samples and the instrumental response function (fwhm) was 200 ps. The emission was observed around 610 nm using an interference filter with 10 nm band width. All solutions used for photophysical measurements were deoxygenated by purging with nitrogen for 15 min before the measurements were taken and then kept under an atmosphere of nitrogen. The solvents used, acetonitrile (AN) and dimethyl sulfoxide (DMSO), were of spectroscopic grade. In the flash photolysis experiments, an excimer laser pumped a dye laser to produce excitation pulses of 15 ns width at λ<sub>ex</sub> = 458 nm. Transient absorption measurements were made at 452 nm (Ru(II)) and 600 nm (methylviologen radical (MV<sup>•+</sup>)), respectively. All solutions were deoxygenated. The electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a ZacSpec mass spectrometer (VG Analytical, Fisons Instrument). Electrospray conditions were the following: Needle potential, 3 kV; acceleration voltage, 4 kV; bath and nebulizing gas, nitrogen. Liquid flow was 50 μL/min using a syringe pump (Phoenix 20, Carlo Erba, Fisons instrument). Solvent compositions were the following: CH<sub>3</sub>CN/H<sub>2</sub>O 50:50 or CH<sub>3</sub>CN/MeOH 90:10. Accurate mass measurements were obtained by the use of polyethylene glycol (PEG) as an internal standard.

**Materials.** 4,4'-Dimethyl-2,2'-bipyridine, 2,2'-bipyridine (bpy), 4,4'-bipyridine, ruthenium trichloride, *n*-butyllithium in *n*-hexane, *N*-bromosuccinimide (NBS), silver triflate, triethylamine, ammonium hexafluorophosphate, potassium fluoride, and 1,2-dibromoethane were purchased from Aldrich and used as received. Silica gel 60 (230–400 mesh, Merck, Darmstadt, Germany) and aluminum oxide (Aldrich) were used for column chromatography. *cis*-Dichloro-bis(bipyridine)ruthenium (*cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O) was prepared by the method reported by Meyer et al.<sup>17</sup> Diisopropylamine was distilled from CaH<sub>2</sub>, and tetrahydrofuran was distilled from sodium benzophenone ketyl radical under nitrogen immediately prior to use. All other solvents were dried by standard methods. The precursor complex Mn(II)(bpy)Cl<sub>2</sub>·2H<sub>2</sub>O (**1**) was prepared by refluxing manganese(II) chloride tetrahydrate solution in methanol together with a molar equivalent of bpy for 3 h. After the solution was cooled to room temperature, a light yellow crystalline solid was obtained by filtration, washed with cold methanol, and dried for 4 h in vacuum at 40 °C. Similarly, the complex Mn(II)(bpy)<sub>2</sub>Cl<sub>2</sub> (**2**) was obtained as yellow crystalline solid using 2 equiv of bpy. Methylviologen dihexafluorophosphate was prepared by refluxing 4,4'-bipyridine and methyl iodide in acetonitrile solution for 10 h; the orange solid obtained was filtered, redissolved in water, and then precipitated by addition of a concentrated NH<sub>4</sub>PF<sub>6</sub> solution. White needle crystals were obtained by recrystallization twice from ethanol/water mixture (90:10, v/v).

### 1,2-Bis[4-(4'-methyl-2,2'-bipyridyl)]ethane (Mebpy-Mebpy, **5**).

This compound was prepared by a modified literature procedure.<sup>18</sup> Lithium diisopropyl amide (LDA) was prepared by dropwise addition of *n*-butyllithium solution (7.00 mL, 1.6 M solution in *n*-hexane, 11 mmol) to freshly distilled diisopropylamine (1.42 mL, 10.86 mmol) solution in freshly distilled tetrahydrofuran (THF) (25 mL) by a syringe at –20 °C under magnetic stirring and Ar atmosphere. After the solution was cooled to –78 °C by dry ice/acetone, a 4,4'-dimethylbipyridine (2.00 g, 10.86 mmol) solution in freshly distilled THF (35 mL) (the solubility of 4,4'-dimethylbipyridine in THF was relatively low) was added dropwise to the solution which became grey immediately. After another 1.5 h of stirring, 1,2-dibromoethane (2.00 mL, 22 mmol) was added rapidly to the solution; the temperature was then allowed to rise to room temperature, and water (5 mL) was added

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to quench the reaction. The resulting yellow cloudy solution was extracted with ether (3 × 50 mL), and the organic phases were combined and dried over anhydrous sodium sulfate. The crude product was obtained by evaporating the solvent in vacuum. After purification by medium pressure liquid chromatography (MPLC)<sup>19</sup> on silica gel (230–400 mesh), (eluent first CH<sub>2</sub>Cl<sub>2</sub>/acetone 90:10 to recover the starting material 4,4'-dimethylbipyridine, then a gradient of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97:3), the desired fractions (checked by TLC on silica gel, eluent CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97:3, *R<sub>f</sub>* ≈ 0.40 and <sup>1</sup>H NMR in CDCl<sub>3</sub>) were collected and further purified by recrystallization from ethyl acetate to give **5** (755 mg, 38%) as white crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.43 (s, 6H, -CH<sub>3</sub>), 3.08 (s, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 7.08–7.15 (m, 4H, 5,5'-bpy-H), 8.23 (s, 2H, 3-bpy-H), 8.31 (s, 2H, 3'-bpy-H), 8.50–8.58 (m, 4H, 6,6'-bpy-H).

**N-Methyl-N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine (Mebispicen, 9).** A solution of *N*-methyl-ethane-1,2-diamine (0.88 mL, 10 mmol) and 2 equiv of triethylamine in acetonitrile (50 mL, 99.9%) was mixed with KF/Celite (8 g, prepared by adding Celite (4 g) to a solution of KF (4 g) in 8 mL of water and then removing the water by heating at 70 °C in a rotary evaporator, followed by drying in an oven overnight at 120 °C immediately before use). A solution of 2-(chloromethyl)pyridine (3.28 g, 20 mmol) in acetonitrile (20 mL) (prepared from the hydrochloride by treatment with an equivalent amount of triethylamine and removal of triethylamine hydrochloride by filtration) was added at room temperature over a period of 30 min. The reaction mixture was then heated at reflux with magnetic stirring for 2 h under Ar atmosphere. After the solution was cooled to room temperature, additional triethylamine hydrochloride crystallized, which was filtered. The filtrate was concentrated by evaporating the solvent in vacuum and then purified by chromatography on neutral aluminum oxide (eluent in gradient, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>/MeOH 98:2), to yield compound **9** (768 mg, 30%) as a slightly yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.28 (s, 3H, N-CH<sub>3</sub>), 2.67 (t, *J* = 5.4 Hz, 2H, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N-), 2.80 (t, *J* = 5.4 Hz, 2H, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N-), 3.68 (s, 2H, PyCH<sub>2</sub>N), 3.91 (s, 2H, Py'CH<sub>2</sub>N), 7.10–7.19 (m, 2H, Py-H), 7.32 (d, *J* = 6.4 Hz, 1H, Py-H), 7.45 (d, *J* = 6.4 Hz, 1H, Py'-H), 9.60–7.69 (m, 2H, Py-H), 8.48–8.57 (m, 2H, Py-H).

**N,N'-Dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine (Me<sub>2</sub>bispicen).** This compound and its Mn(II) complex, Mn(II)Me<sub>2</sub>bispicenCl<sub>2</sub> (**3**), were prepared according to the literature procedure.<sup>20</sup>

**Ru(bpy)<sub>2</sub>(Mebpy-Mebpy)Cl<sub>2</sub> (6).** To a solution of Mebpy-Mebpy (300 mg, 0.82 mmol) in methanol (40 mL) was added *cis*-Ru(bpy)<sub>2</sub>-Cl<sub>2</sub>·2H<sub>2</sub>O (141 mg, 0.27 mmol) under magnetic stirring and Ar atmosphere. The resulting brown solution was heated, and the solution became clear orange after refluxing for 2 h. The solvent was evaporated under a vacuum, and a red solid residue was obtained. The residue was redissolved in water (20 mL), and the unreacted Mebpy-Mebpy was removed by filtration. After the residue was washed with water (5 mL), the filtrates were combined and evaporated to dryness in vacuum at 70 °C to give a red viscous oil. Purification by MPLC on neutral aluminium oxide (eluent in gradient, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>/MeOH 94:6) gave a nice separation of three bands, the first violet one was the starting material *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O and the third deep orange one was the byproduct binuclear ruthenium complex. Compound **6** (188 mg, 82%) was obtained from the second orange band as a red solid after evaporation of the solvent. Dissolution of **6** in a minimum amount of water followed by addition of a concentrated NH<sub>4</sub>PF<sub>6</sub> solution gave a red precipitate, which was recrystallized from acetone/EtOAc 1:1 to give Ru(bpy)<sub>2</sub>(Mebpy-Mebpy)(PF<sub>6</sub>)<sub>2</sub> (**6a**) in 95% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 2.41 (s, 3H, -CH<sub>3</sub>(on free ligand)), 2.52 (s, 3H, -CH<sub>3</sub>(on Ru-bound ligand)), 3.14 (unresolved t, 2H, -CH<sub>2</sub>(near free ligand)), 3.15 (unresolved t, 2H, -CH<sub>2</sub>(near Ru)), 7.29 (m, 2H, Mebpy-Mebpy-H), 7.37 (d, *J* = 5.7 Hz, 1H, Mebpy-Mebpy-H), 7.44 (dd, *J* = 5.8 Hz, *J'* = 0.7 Hz, 1H, Mebpy-Mebpy-H), 7.54–7.46 (m, 5H, Mebpy-Mebpy-H + bpy-H), 7.57 (d, *J* = 5.8 Hz, 1H, Mebpy-Mebpy-H), 7.73–7.65 (m, 4H, bpy-H), 8.15 (m, 4H, bpy-H), 8.22 (s, 1H, Mebpy-Mebpy-H), 8.32 (s, 1H, Mebpy-Mebpy-H),

8.48 (d, *J* = 4.8 Hz, 1H, Mebpy-Mebpy-H), 8.54 (d, *J* = 4.9 Hz, 1H, Mebpy-Mebpy-H), 8.79 (s, 1H, Mebpy-Mebpy-H), 8.85 (m, 4H, bpy-H), 8.88 (s, 1H, Mebpy-Mebpy-H). ESI-MS: *m/z* 925.205 (M - PF<sub>6</sub><sup>-</sup>), C<sub>44</sub>H<sub>38</sub>N<sub>8</sub>RuPF<sub>6</sub> requires 925.192. Anal. Calcd for C<sub>44</sub>H<sub>38</sub>N<sub>8</sub>RuPF<sub>6</sub>·H<sub>2</sub>O·0.25EtOAc: C, 48.70; H, 3.81; N, 10.10. Found: C, 49.00; H, 3.90; N, 9.97.

**[Ru(bpy)<sub>2</sub>Mebpy-MebpyMnCl<sub>2</sub>·H<sub>2</sub>O]Cl<sub>2</sub> (7).** To a solution of **6** (50 mg, 0.058 mmol) in methanol (10 mL) was added manganese(II) chloride tetrahydrate (12 mg, 0.060 mmol) under stirring at room temperature. The resulting red solution was heated at reflux for 2 h and then evaporated to dryness under vacuum. A red solid was obtained, which was washed with a cold mixture of EtOAc/methanol 80:20 and dried under vacuum for 5 h at 40 °C to give **7** in 90% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) signals broadened due to paramagnetic Mn(II). ESI-MS: *m/z* 940.085 (M - Cl<sup>-</sup>); C<sub>44</sub>H<sub>38</sub>N<sub>8</sub>Cl<sub>3</sub>RuMn requires 940.071. For the X-band EPR spectrum of **7** in powder, see: Figure 2a. Anal. Calcd for C<sub>44</sub>H<sub>42</sub>N<sub>8</sub>O<sub>2</sub>Cl<sub>4</sub>RuMn·2H<sub>2</sub>O: C, 50.39; H, 4.42; N, 10.68; Found: C, 49.63; H, 4.34; N, 10.44.

**[Ru(bpy)<sub>2</sub>Mebpy-MebpyMn(bpy)Cl<sub>2</sub>]Cl<sub>2</sub> (8).** To a solution of **6** (85 mg, 0.10 mmol) in methanol (10 mL) was added **1** (31 mg, 0.11 mmol). After the solution was heated at reflux for 2 h, it was concentrated to about 0.5 mL by evaporating the solvent at reduced pressure on a rotary evaporator. Addition of ethyl acetate (15 mL) gave a red precipitate which was washed with ethyl acetate and dried in vacuum for 4 h at 40 °C to give **8** in 92% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) signals broadened due to paramagnetic Mn(II). ESI-MS: *m/z* 940.046 (M - bpy-Cl<sup>-</sup>); C<sub>44</sub>H<sub>38</sub>N<sub>8</sub>Cl<sub>3</sub>RuMn requires 940.071. X-Band EPR spectrum of **8** in powder (see Figure 2b). Anal. Calcd for C<sub>54</sub>H<sub>46</sub>N<sub>10</sub>Cl<sub>4</sub>RuMn·4H<sub>2</sub>O: C, 53.83; H, 4.52; N, 11.62; Cl, 11.77; Mn, 4.56. Found: C, 53.32; H, 4.67; N, 11.34; Cl, 11.49; Mn, 4.69.

**4-Bromomethyl-4'-methylbipyridine (10).** This compound was made according to a literature procedure.<sup>21</sup> A pale yellow solid was obtained as raw product, and it was washed with ethyl acetate and *n*-hexane and then purified by column chromatography (MPLC) on silica gel (eluent in gradient, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>/acetone 98:2) to give essentially pure **10** (450 mg, 18%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.43 (s, 3H, CH<sub>3</sub>), 4.49 (s, 2H, CH<sub>2</sub>Br), 7.15 (d, *J* = 4.0 Hz, 1H, Py-H), 7.33 (dd, *J* = 3.3 Hz, *J'* = 1.3 Hz, 1H, Py'-H), 8.24 (s, 1H, Py-H), 8.42 (s, 1H, Py'-H), 8.54 (d, *J* = 5.1 Hz, 1H, Py-H), 8.65 (d, *J* = 5.1 Hz, 1H, Py'-H).

**Ru(bpy)<sub>2</sub>(4-BrCH<sub>2</sub>-4'-CH<sub>3</sub>-bpy)(PF<sub>6</sub>)<sub>2</sub> (11).** A mixture of *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (890 mg, 1.73 mmol) and silver triflate (889 mg, 3.46 mmol) in anhydrous acetone (65 mL) was stirred for 8 h at room temperature under Ar atmosphere. The solution turned gradually red, and a white precipitate of AgCl was formed. This was removed by filtration, and **10** (447 mg, 1.71 mmol) was added to the filtrate. The solution was stirred for another 2 h at room temperature and then evaporated to dryness at 40 °C in vacuum. The red viscous residue obtained in this way was redissolved in methanol (10 mL) and mixed with water (20 mL), and concentrated aqueous NH<sub>4</sub>PF<sub>6</sub> solution was added, to give a red precipitate which was isolated and washed with water and diethyl ether and then purified by column chromatography (MPLC) on neutral Al<sub>2</sub>O<sub>3</sub> (eluent toluene/CH<sub>3</sub>CN 1:1). The second orange band was collected to give the desired product **11** in 52% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 2.49 (s, 3H, CH<sub>3</sub>), 4.76 (d, *J* = 15.0 Hz, 1H, CH<sub>2</sub>Br), 4.80 (d, *J* = 15.0 Hz, 1H, CH<sub>2</sub>Br), 7.38 (d, *J* = 6.4 Hz, 1H, 4-Me-4'-BrMe-bpy(dmb)-H), 7.50–7.57 (m, 6H, bpy-4H + dmb-2H), 7.69–7.74 (m, 5H, bpy-4H + dmb-1H), 8.16 (d, *J* = 7.9 Hz, 4H, bpy-4H), 8.73 (unresolved d, 1H, dmb-H), 8.82 (d, *J* = 8.6 Hz, 4H, bpy-4H), 8.91 (d, *J* = 1.8 Hz, 1H, dmb-1H). ESI-MS: *m/z* 821.025 (M - PF<sub>6</sub><sup>-</sup>), C<sub>32</sub>H<sub>27</sub>N<sub>6</sub>BrRuPF<sub>6</sub> requires 821.017.

**Ru(bpy)<sub>2</sub>(4-CH<sub>3</sub>-4'-(N-CH<sub>3</sub>-N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine)-CH<sub>2</sub>-bpy)(PF<sub>6</sub>)<sub>2</sub> (12).** In a dry flask, **9** (80 mg, 0.31 mmol) and triethylamine (0.1 mL, 0.75 mmol) were dissolved in acetonitrile (2.0 mL, 99.9%), KF/Celite (200 mg) was added to the solution. Under stirring, a solution of **11** (200 mg, 0.20 mmol) in acetonitrile (2.0 mL) was added over a period of 5 min, and then the reaction mixture was heated at reflux for 2 h, cooled, and filtered. The filtrate was evaporated to dryness under vacuum. Repetitive column chromatography (MPLC)

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(20) Glerup, J.; Goodson, P. A.; Hazell, A.; Hazell, R.; Hodgson, D. J.; McKenzie, C. J.; Michelson, K.; Rychlewska, U.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 4105–4111.

(21) Gould, S.; Strouse, G. F.; Meyer, T. J.; Sullivan, B. P. *Inorg. Chem.* **1991**, *30*, 2942–2949.

on  $\text{Al}_2\text{O}_3$  (eluent in gradient,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  98:2) gave **12** in 70% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 2.03 (s, 3H,  $-\text{NCH}_3$ ), 2.42 (s, 3H,  $\text{dmb}-\text{CH}_3$ ), 2.62–2.70 (m, 4H,  $-\text{CH}_2\text{CH}_2-$ ), 3.52 (s, 2H,  $\text{NCH}_2-\text{dmb}$ ), 3.79 (s, 2H,  $-\text{NCH}_2-\text{py}$ ), 3.91 (s, 2H,  $\text{NCH}_2-\text{py}$ ), 7.16–7.22 (m, 2H,  $\text{py}-H$ ), 7.31 (d,  $J = 7.2$  Hz, 1H,  $\text{py}-H$ ), 7.36 (d,  $J = 6.2$  Hz, 1H,  $\text{dmb}-H$ ), 7.42 (d,  $J = 7.6$  Hz, 1H,  $\text{py}-H$ ), 7.48–7.57 (m, 8H,  $\text{bpy}-4H$ ,  $\text{dmb}-2H$ ,  $\text{py}-2H$ ), 7.65–7.74 (m, 5H,  $\text{bpy}-4H$ ,  $\text{dmb}-H$ ), 8.15 (d,  $J = 6.2$  Hz, 4H,  $\text{bpy}-4H$ ), 8.38 (d,  $J = 3.6$  Hz, 1H,  $\text{py}-H$ ), 8.44 (d,  $J = 4.4$  Hz, 1H,  $\text{py}-H$ ), 8.64 (s, 1H,  $\text{dmb}-H$ ), 8.81 (d,  $J = 7.9$  Hz, 4H,  $\text{bpy}-4H$ ). ESI-MS:  $m/z$  997.266 ( $\text{M} - \text{PF}_6^-$ ),  $\text{C}_{45}\text{H}_{46}\text{N}_{10}\text{RuPF}_6$  requires 997.261.

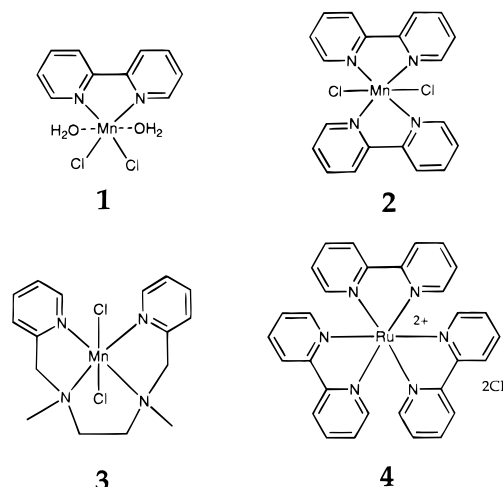
**Ru(bpy) $_2$ (4-CH $_3$ -4'-( $N'$ -CH $_3$ - $N,N'$ -bis(2-pyridylmethyl)-1,2-ethanediamine)-CH $_2$ -bpy)Mn(PF $_6$ ) $_2$ Cl $_2$  (**13**).** To a stirred solution of **12** (40 mg, 0.035 mmol) in methanol (2 mL)  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (9.7 mg, 0.048 mmol) was added at room temperature, giving immediately a red precipitate. The reaction mixture was stirred for another 20 min, and the red precipitate was filtered and washed with a small amount of cold methanol, followed by diethyl ether (20 mL), and dried in air to give **13** as a red solid in 86% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : similar to **12**, but all peaks were broadened because of the paramagnetic Mn(II). Anal. Calcd for  $\text{C}_{47}\text{H}_{46}\text{N}_{10}\text{Cl}_2\text{P}_2\text{F}_{12}\text{RuMn} \cdot 2\text{H}_2\text{O}$ : C, 43.30; H, 3.87; N, 10.74; Found: C, 43.46; H, 3.88; N, 10.43. ESI-MS:  $m/z$  1124.136 ( $\text{M} - \text{PF}_6^-$ ),  $\text{C}_{47}\text{H}_{46}\text{N}_{10}\text{Cl}_2\text{PF}_6\text{RuMn}$  requires 1124.135. For X-band EPR spectra of **13** in powder and in acetonitrile, see: Figures 3a and 4a, respectively.

## Results and Discussion

**Synthesis.** In order to link the ruthenium tris(bipyridyl) complex covalently to manganese complexes (Scheme 1), we have used two different bridging ligands, 1,2-bis[4-(4'-methyl-2,2'-bipyridyl)]ethane (Mebpy-Mebpy) and 4-methyl-4'-( $N'$ -methyl- $N,N'$ -bis(2-pyridylmethyl)-1,2-ethanediamine)methylbipyridine (bpy-bispcen). Reaction of excess Mebpy-Mebpy with *cis*-Ru(bpy) $_2$ Cl $_2$  (molar ratio 4:1) in aqueous solution at 60–90 °C gave a mononuclear ruthenium complex **6** in more than 90% yield.

Addition of excess Mebpy-Mebpy is very important to reduce formation of the binuclear byproduct, Ru(bpy) $_2$ Mebpy-Me-

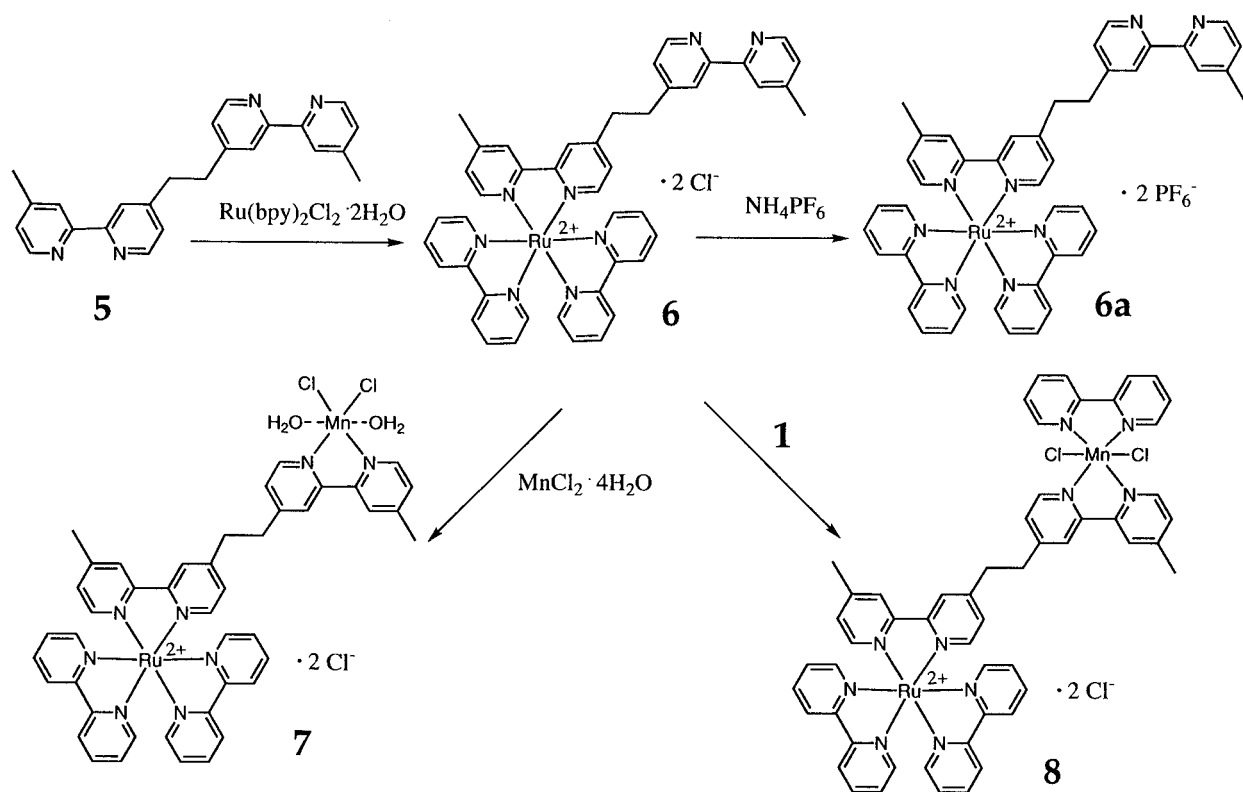
bpyRu(bpy) $_2$ . The binuclear complex can be removed from the product mixture by column chromatography. Complex **6** is soluble in water, and the counterion chloride can be changed to hexafluorophosphate by adding ammonium hexafluorophosphate to an aqueous solution of **6**, leading to precipitation of **6a**. To prepare ruthenium–manganese binuclear complexes, manganese dichloride  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  or the manganese dichloride bpy complex **1** were reacted with **6** in methanol (Scheme 1).



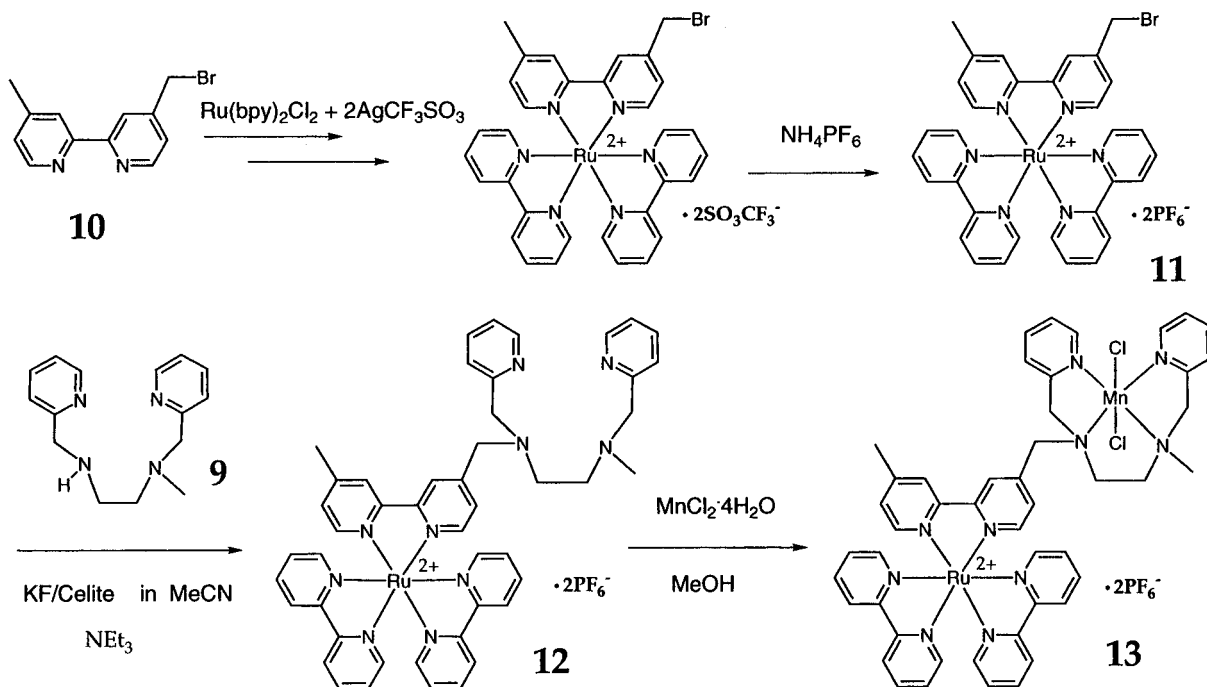
The binuclear complexes **7** and **8** were formed and characterized by elemental analysis and electrospray ionization mass spectrometry (ESI-MS) and confirmed by emission-quenching measurements. In the  $^1\text{H}$  NMR spectra of both compounds **7** and **8** in  $\text{DMSO}-d_6$ , all peaks are broadened because of the presence of paramagnetic Mn(II). ESI-MS results show that in acetonitrile/methanol (90:10) solution there is an equilibrium between **7** and **6**, which can also be monitored by emission quenching (see text below) of these complexes in solution.

To make the binuclear complex **13**, one route is to synthesize

## Scheme 1



## Scheme 2



first the bridging ligand bpy-bispicen and then introduce Ru(II) and Mn(II). However, the reaction of bpy-bispicen with *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> in aqueous solution afforded a complicated mixture, due to the poor ligand selectivity for *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>. It was very difficult to separate the desired **12** from other byproducts. Therefore, another synthetic route was designed (Scheme 2).

In this route, silver triflate in dry acetone solution was used to remove two chlorides from *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, forming intermediate *cis*-Ru(bpy)<sub>2</sub>(acetone)<sub>2</sub>. Reaction of this with ligand 4-bromomethyl-4'-methylbipyridine (**10**) at room temperature followed by addition of ammonium hexafluorophosphate gave Ru(bpy)<sub>2</sub>(4-BrCH<sub>2</sub>-4'-Me-2,2'-bpy)(PF<sub>6</sub>)<sub>2</sub> (**11**). Direct complexation of *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> with the ligand **10** in aqueous solution at 60–90 °C gave lower yield of **11**, the reason probably being self quaternization of ligand **10** with the active bromomethyl group. The nucleophilic reaction of **11** with ligand *N*-methyl-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (**9**), in refluxing dry acetonitrile solution in the presence of triethylamine and potassium fluoride on Celite as bases, gave the ruthenium complex **12**. Column chromatography on aluminum oxide provided a practical way to obtain pure **12** in about 70% yield. The ruthenium–manganese binuclear complex Ru(bpy)<sub>2</sub>(4-methyl-4'-(*N,N'*-methyl-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine)-bpy)MnCl<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (**13**) was produced quantitatively as a red precipitate by adding manganese dichloride (MnCl<sub>2</sub>·4H<sub>2</sub>O) to a solution of **12** in methanol at room temperature. The structures of compounds **11** and **12** were fully characterized by <sup>1</sup>H NMR and ESI-MS and **13** by ESI-MS and EPR spectroscopy.

**Molecular Modeling.** The distance and orientation between the electron donor and acceptor in a covalently linked system are very important for ET.<sup>11,22</sup> In order to estimate the maximum Ru–Mn distance in molecules **7** and **13**, we performed molecular mechanics calculations.<sup>23</sup> The optimiza-

tions gave geometries with distances between the Ru and Mn centers of 13 Å for **7** and 9 Å for **9** (Figure 1). These distances are reasonable for intramolecular electron transfer between the two metal centers.

**EPR Characterization of Mn(II) complexes.** Ruthenium(II) tris(bipyridine) complexes are diamagnetic, while manganese(II) complexes are EPR active, with *S* = 5/2. The spectra have line shapes and *g* values that depend strongly on the ligands. Free Mn(II) in DMSO and MeCN gives a well-resolved six-line narrow EPR signal around *g* = 2.0. The EPR spectrum of **7** in powder at low temperature (77 K) is characterized as a N<sub>2</sub>X<sub>2</sub> ligand donor set (Figure 2a) with a broad *g* ≈ 2 centered resonance without manganese hyperfine structure. A powder spectrum of manganese 4,4'-dimethylbipyridine (dmb) dichloride (Mn(II)(dmb)Cl<sub>2</sub> (not shown)) is similar to that of **7**. Dowsing et al. observed a similar *g* ≈ 2 centered resonance for the complex Mn(II)(picoline)<sub>2</sub>Cl<sub>2</sub>.<sup>24</sup> They explained these observations as resulting from a polymeric structure giving extensive intermolecular magnetic interactions. Related EPR studies in solution were difficult due to the low solubility of the compound **7** in acetonitrile, and also because it is not stable in DMSO or DMF or in MeOH at low concentration. The powder EPR spectrum of complex **8** can be characterized as an N<sub>4</sub>X<sub>2</sub> ligand donor set and displays a broad fine structure resonance without any resolved hyperfine patterns (Figure 2b). A similar X-band EPR spectrum is afforded by 1 mM Mn(bpy)<sub>2</sub>Cl<sub>2</sub> (**2**) in MeOH and in DMF (not shown) at 4 K.<sup>25</sup> Powdered Mn(*o*-phen)<sub>2</sub>Cl<sub>2</sub> also displays a similar spectrum which may be simulated using zero-field splitting parameter *D* = 0.12 cm<sup>-1</sup> and *E/D* = 0.04.<sup>24</sup>

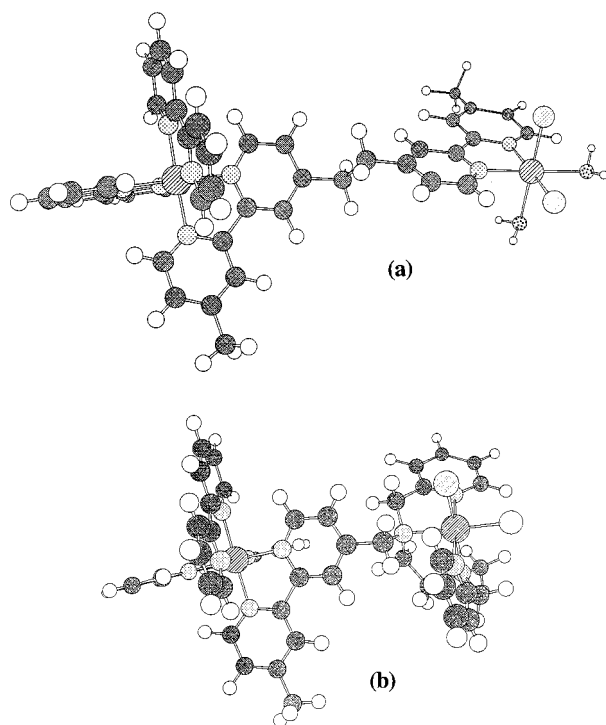
The complex **13** in powder state and in DMSO at 77 K gives rise to the rhombic EPR spectra shown in Figure 3a,c, which are similar to that of **8**. At 77 K in acetonitrile solution, the EPR spectrum of **13** (Figure 4a) is similar to that in solid **13** (Figure 3a). It is interesting to note that in acetonitrile solution

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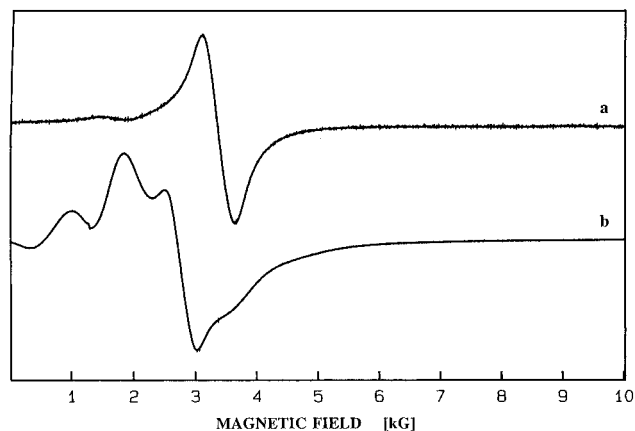
(23) The optimizations were performed starting from the most extended conformations using constrained metal–ligand distances. The Sybyl force field was used in Spartan SGI Version 4.1.1 OpenGL.

(24) (a) Dowsing, R. D.; Gibson, J. F.; Hayward, P. J. *J. Chem. Soc. A* **1969**, 187–193. (b) Dowsing, R. D.; Gibson, J. F.; Goodgame, D. M. L.; Goodgame, M.; Hayward, P. J. *Nature* **1968**, *219*, 1037–1038.

(25) (a) Policar, C.; Artaud, I.; Mansuy, D. *Inorg. Chem.* **1996**, *35*, 210–216. (b) Lynch, W. B.; Boorse, R. S.; Freed, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 10909–10915. (c) Mabad, B.; Cassoux, P.; Tuchagues, J.-P.; Hendrickson, D. N. *Inorg. Chem.* **1986**, *25*, 1420–1431.



**Figure 1.** Computational representations of the binuclear compound **7** (a) and **13** (b) obtained by force field calculation. The parameters for ruthenium are based on the crystal structure geometry of complex **4**.



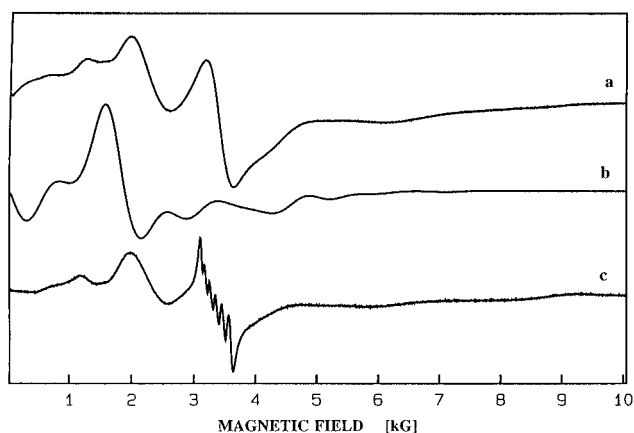
**Figure 2.** X-Band EPR spectra of microcrystalline **7** (a) and **8** (b) at 77 K. Instrumental parameters: modulation frequency, 100 kHz; modulation amplitude, 10 G; microwave power, 10 mW; microwave frequency, 9.47 GHz.

**13** appears to be EPR invisible at room temperature, while under the same condition in DMSO, **13** displays an EPR spectrum which has typical Mn(II) ( $S = 5/2$ ) line shape.

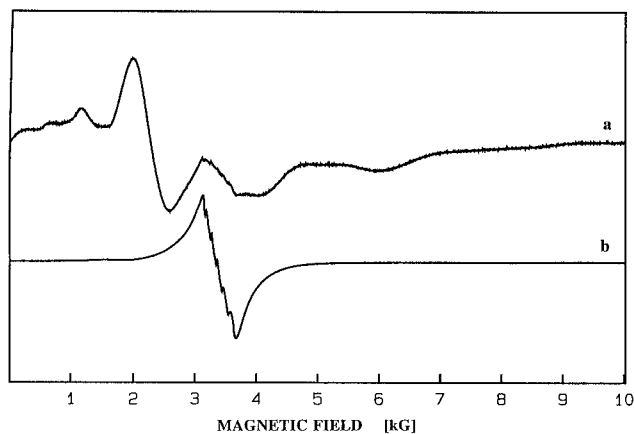
A comparison of the powder spectra of **13** (Figure 3a) and the related manganese complex **3** (Figure 3b) indicates that ruthenium(II) tris(bipyridyl) complex in **13** has some effect on the structure of Mn(II) center within the molecule. The spectrum in Figure 3b is characteristic of a mononuclear Mn(II)N<sub>4</sub>X<sub>2</sub> complex and may be simulated using the parameters  $0.1 \text{ cm}^{-1}$  for  $D$  and  $\leq 0.1$  for  $E/D$ .<sup>24</sup>

#### Chemical Oxidation of Manganese(II) by Ruthenium(III).

In the anticipated photochemical reaction of the binuclear complexes **7**, **8**, and **13**, the excited state of Ru(II) is expected to deliver an electron to the added electron acceptor to yield Ru(III). Ru(II) would then be regenerated by intramolecular ET from the coordinated Mn(II) to the photogenerated Ru(III). In order to determine if such a process is reasonable, some



**Figure 3.** X-Band EPR spectra of microcrystalline **13** (a) and **3** (b) as well as 3 mM of **13** in DMSO (c) at 77 K. Instrumental parameters are the same as in Figure 2.

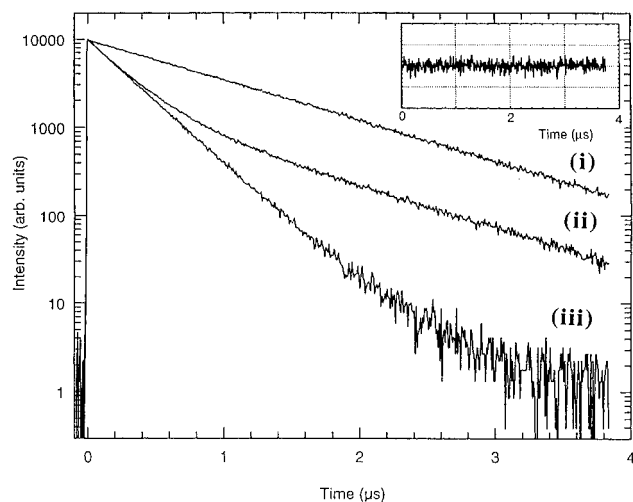


**Figure 4.** X-Band EPR spectra of **13** in acetonitrile at 77 K (a) and in a mixture of **13** with Ru(III)(bpy)<sub>3</sub> (molar ratio 1:7) in acetonitrile at 77 K (b). Instrumental parameters are the same as in Figure 2.

control experiments were performed where chemically produced Ru(III) in the form of Ru(III)(bpy)<sub>3</sub> was added to the complexes containing Mn(II). Since both Ru(III)(bpy)<sub>3</sub> and the manganese(II) in complexes **7**, **8**, and **13** have characteristic EPR spectra while Ru(II) and Mn(III) species are EPR-silent,<sup>26</sup> oxidation of Mn(II) by Ru(III) should be readily monitored by EPR. This is observed in the case when complex **7** was mixed with a molar equivalent amount of Ru(III)(bpy)<sub>3</sub> in acetonitrile. The signals from Ru(III) and Mn(II) rapidly disappeared, showing that Ru(III) can indeed oxidize Mn(II) in complex **7** (not shown). From a measurement using the stopped-flow technique, monitoring the disappearance of Ru(III) optically, a second-order rate constant for the reaction of ca.  $1 \times 10^7 \text{ s}^{-1} \text{ M}^{-1}$  was obtained. In a similar experiment with compound **13**, the EPR signal from Ru(III) rapidly disappeared as expected, but an EPR signal from a Mn(II) species with a modified EPR pattern was still observable at room temperature. We suspect that the result is due to oxidation of the bispicen ligand. Addition of Ru(bpy)<sub>3</sub><sup>3+</sup> to this solution at a molar ratio 7:1 did not result in oxidation of Mn(II) into Mn(III), but resulted in a dramatic modification of the EPR pattern (see Figure 4b). These experiments indicate that in acetonitrile solution Ru(bpy)<sub>3</sub><sup>3+</sup> modifies the ligand of the manganese in complex **13** rather than oxidizing Mn(II).

**Photophysical and Photochemical Studies.** The absorption spectra of the compounds **6**, **6a**, **7**, **8**, **12**, and **13** in acetonitrile

(26) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Dover: New York, 1986.



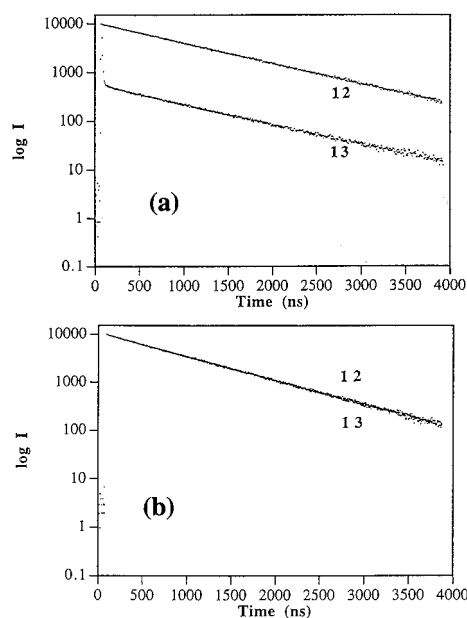
**Figure 5.** Time-resolved emission spectra of compound **6a** (i), compound **7** (ii) and compound **7** + excess  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (iii) in  $\text{N}_2$ -purged acetonitrile at room temperature:  $\lambda_{\text{ex}} = 327$  nm,  $\lambda_{\text{em}} = 610$  nm, and the concentration of the complex,  $5.0 \times 10^{-5}$  M,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $1.0 \times 10^{-3}$  M.

**Table 1.** Emission Life-Time Data at Room Temperature

cmpd	solvent <sup>a</sup>	$\tau$ /ns	fraction	concn ( $\mu\text{M}$ )
<b>6a</b>	AN	$\tau$	950	41
<b>7</b>	AN	$\tau_1$	906	0.20
		$\tau_2$	255	0.80
<b>7</b>	AN	$\tau_1$	956	0.16
		$\tau_2$	258	0.84
<b>7</b>	AN	$\tau_1$	1015	0.25
		$\tau_2$	259	0.75
<b>8</b>	AN	$\tau_1$	982	0.31
		$\tau_2$	240	0.69
<b>8</b>	AN	$\tau_1$	1009	0.49
		$\tau_2$	240	0.51
<b>12</b>	AN	$\tau$	1037	64
<b>13</b>	AN	$\tau_1$	1046	0.07
		$\tau_2$	7	0.93
<b>12</b>	DMSO	$\tau$	874	69
<b>13</b>	DMSO	$\tau$	866	69

<sup>a</sup> AN = acetonitrile, DMSO = dimethylsulfoxide, and  $\tau$  and fraction are given by the curve fit program.

are quite similar, all with a ruthenium metal to ligand charge transfer (MLCT) band at ca. 452 nm and with similar extinction coefficients. Also, the shapes and positions of the emission spectra are similar, but the coordination of manganese(II) has a profound influence on the emission intensity and decay rate. The emission decay of **6a** and **7** in acetonitrile are shown in Figure 5. In this solution, compound **6a** has a single exponential decay with a lifetime ( $\tau$ ) of 950 ns, whereas a double exponential decay was observed for compound **7**, having one component with  $\tau_1 = 980$  ns (20%) and another with  $\tau_2 = 260$  ns (80%). Addition of  $\text{Mn(II)}$  lead to a relative increase of the component with short lifetime and a decrease in the one with long lifetime (Figure 5, iii). This suggests that the long-lived species is the mononuclear compound **6** and the shorter-lived species the binuclear compound **7**. In the very dilute solutions used, partial dissociation occurs and an equilibrium between **6** and **7** is established. The fractions of the rapid and slow components were found to vary with the concentration of complex according to a simple dissociation equilibrium (Table 1). The equilibrium was also studied by observing the decrease in steady-state emission intensity of an acetonitrile solution of **6** which was titrated with a solution of manganese(II) chloride. After 1.2 equiv of  $\text{Mn(II)}$  was added, the emission of **6** became constant. By a determination of the stability constant from the titration



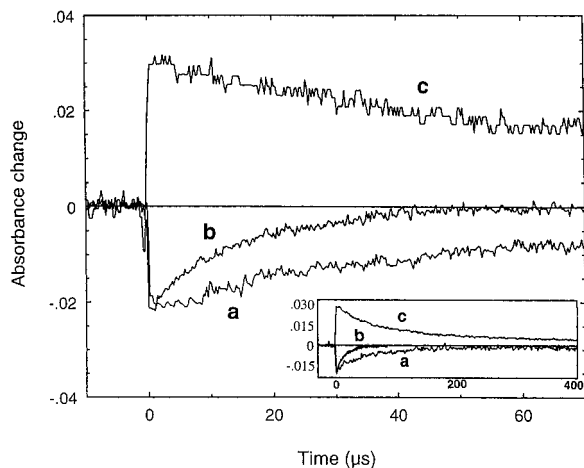
**Figure 6.** Time-resolved emission spectra of compound **12** and **13** in acetonitrile solution (a) and in DMSO solution (b), at room temperature,  $\lambda_{\text{ex}} = 327$  nm,  $\lambda_{\text{em}} = 610$  nm, and the concentration of the complex,  $5.0 \times 10^{-5}$  M.

curve, it was found to be  $6 \times 10^5 \text{ M}^{-1}$  for complex **7** in acetonitrile solution.

The behavior of **8** is similar with a double exponential emission decay with lifetime of  $\tau_1 = 980$  ns and  $\tau_2 = 240$  ns, showing that also **8** dissociates to form **6**. As judged from the relative intensities of these two emission components, compound **8** is more dissociated than **7** at equal concentrations. As for **7**, addition of  $\text{Mn(II)}$  increased the relative contribution of the species with  $\tau = 240$  ns. The differences between compounds **7** and **8** may be fortuitous, however, since there is strong evidence from ESI-MS that the bipyridyl ligand of  $\text{Mn(II)}$  in **8** is dissociated in fluid solution. The fraction of nondissociated **8** was probably small, and the behavior of compound **8** was therefore not further investigated. The compound **12** appears to have a lifetime slightly longer ( $\tau = 1040$  ns in acetonitrile) than that of compound **6a**. When  $\text{Mn(II)}$  was added, the concentration of this species was decreased and a new species with lifetime of 7 ns appeared, which was identified as compound **13** (Figure 6a). In comparison with **7** and **8**, **13** was less dissociated in acetonitrile, proving that bispicen is a stronger ligand for  $\text{Mn(II)}$  than bpy. In DMSO, the lifetime of **13** was increased to 870 ns, the same as the mononuclear complex **12** (Figure 6b), suggesting that complete dissociation takes place in this solvent at the low concentrations used in the photo-physical measurements.

Addition of small amounts of DMSO to the acetonitrile solution of **13** also leads to a relative decrease of the fast decay component, showing that the presence of DMSO induces dissociation of manganese from the complex **13** in acetonitrile solution.

**Electron Transfer from Manganese(II) to Photogenerated Ruthenium(III).** In the attempts to observe photoinduced intramolecular ET from manganese(II) to photogenerated ruthenium(III), the compounds **6a**, **7**, and **13** were dissolved in acetonitrile and methylviologen ( $\text{MV}^{2+}$ ) was added as external electron acceptor. When the deoxygenated solution was excited with a laser flash (15 ns) at 458 nm, an electron was transferred from the excited state of  $\text{Ru(II)}$  to  $\text{MV}^{2+}$ , to give  $\text{Ru(III)}$  and  $\text{MV}^{\bullet+}$  at a concentration of about  $2 \mu\text{M}$  each. The recovery of  $\text{Ru(II)}$  and the disappearance of  $\text{MV}^{\bullet+}$  were then monitored at



**Figure 7.** Transient absorption curves of deoxygenated acetonitrile solutions of **6a** and **7** ( $7.0 \times 10^{-5}$  M) in the presence of  $MV^{2+}$  ( $1.0 \times 10^{-2}$  M) at room temperature, laser pulse 15 ns,  $\lambda_{ex} = 458$  nm. The Ru(II) complex absorption recovery is monitored at 452 nm for **6a** (a) and **7** (b); (c) shows the decay of the  $MV^{+•}$  to  $MV^{2+}$  as measured by the decrease in absorption at 600 nm.

452 and 600 nm,<sup>27</sup> respectively. With the compound **6a**, this process occurred by a second-order, diffusion-controlled (rate constant  $5 \times 10^9$  s<sup>-1</sup> M<sup>-1</sup>) recombination of Ru(III) and  $MV^{+•}$  (i.e., with a first half-life of about 0.1 ms at the concentrations produced). This is essentially the same rate constant as observed for the electron transfer between Ru(III)(bpy)<sub>3</sub> and  $MV^{+•}$ .<sup>28</sup>

Interestingly, with **7**, a different behavior was observed. The production of  $MV^{+•}$  and its decay were similar to those observed for **6a**. In contrast, the recovery of Ru(II) was 1 order of magnitude faster ( $t_{1/2} = ca. 10 \mu s$ ) (Figure 7).

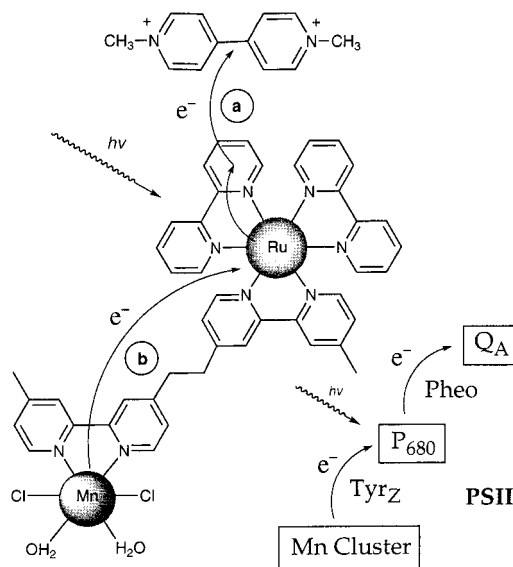
This means that the photogenerated Ru(III) in the bimetallic complex **7** must have received an electron from a source not present in complex **6a** and which is not  $MV^{+•}$ . We propose that this is the Mn(II) which is coordinatively bound ca. 13 Å from the Ru center in complex **7**. In this case, the rate of recovery of Ru(II) would be independent of the concentration of **7**. This hypothesis was tested in an experiment where the concentration of **7** was varied from  $1.5 \times 10^{-5}$  M to  $1.0 \times 10^{-4}$  M. The results of this experiment (not shown) revealed that more than one process occurred in parallel. The recovery of Ru(II) was found to be concentration dependent and nonexponential. However, the results could be satisfactorily described by a mechanism (Scheme 3) involving one concentration independent reaction path, involving the major part of the Ru(III), and one minor path that was concentration dependent.

The concentration independent reduction of Ru(III) in the photo-oxidized compound **7** occurs with a rate constant of ca.  $1.8 \times 10^5$  s<sup>-1</sup>, in competition with back electron transfer from  $MV^{+•}$ . We assign this process to intramolecular electron transfer from coordinated Mn(II) to the photogenerated Ru(III).<sup>29</sup> The concentration dependence is more difficult to explain, but careful analysis of the data (a detailed description of these experiments and our kinetic analysis will be published elsewhere<sup>30</sup>) reveals that it stems from those complex molecules in

(27) (a) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617. (b) Yoshimura, A.; Hoffman, M. Z.; Sun, H. *J. Photochem. Photobiol. A* **1993**, *70*, 29.

(28) (a) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic: London, 1992. (b) Kelly, L. A.; Rodgers, M. A. *J. Phys. Chem.* **1995**, *99*, 13132–13140.

(29) In the experiments with chemical oxidation of **7** by Ru(III)(bpy)<sub>3</sub>, a second-order rate constant of ca.  $1 \times 10^7$  s<sup>-1</sup> M<sup>-1</sup> was determined for intermolecular ET from Mn(II) in **7**. Such an intermolecular ET would not show up in the flash photolysis, where the concentration of complex **7** was less than  $1 \times 10^{-4}$  M, and the rate would be about  $1 \times 10^3$  s<sup>-1</sup>.



**Figure 8.** Photoinduced electron transfer pathway of compound **7** in the presence of  $MV^{2+}$  in acetonitrile: (a) transfer of an electron from excited state of Ru(II) complex to  $MV^{2+}$ ; (b) intramolecular electron transfer from coordinated Mn(II) to photogenerated Ru(III).

which the Mn(II) is dissociated (see above), and this fraction was determined independently from the emission decay curves (compare Figure 5). The recovery of Ru(II) in these complexes only occurs after a rate-determining reassociation of Mn(II) (Scheme 3) and has a bimolecular rate constant of  $2.9 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. Since the concentration of nonbound Mn(II) was below  $10 \mu M$ , the pseudo-first-order rate constant for this path was always lower than  $3 \times 10^4$  s<sup>-1</sup>.

The first-order process, with rate constant of about  $1.8 \times 10^5$  s<sup>-1</sup>, is thus assigned to intramolecular electron transfer from coordinated Mn(II) to photogenerated Ru(III). The demonstration of this reaction is important as it shows that the concept of intramolecular electron transfer from coordinated Mn to the photo-oxidized Ru center is viable and this process is illustrated in Figure 8.

The photoinduced ET of compound **13** could not be studied conclusively. This was mainly due to the rapid intramolecular quenching of the excited Ru(II) state (7 ns, Table 1), and because of this, very high concentrations of  $MV^{2+}$  were needed to intercept an electron from the excited species before deactivation. It was also confirmed by EPR experiments (see above) that chemical oxidation of **13** by Ru(III)(bpy)<sub>3</sub> is rapid but does not produce Mn(III); instead it appears that the ligand is oxidized.

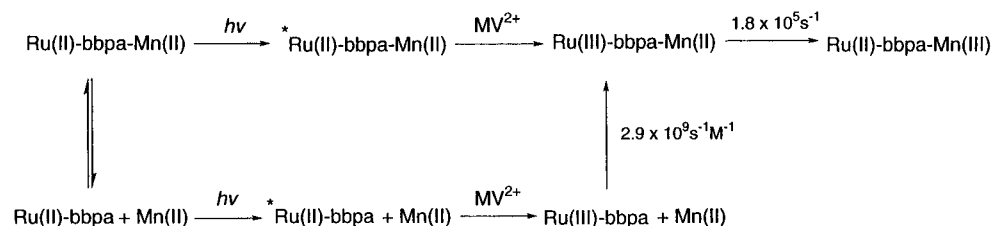
## Conclusions

Several conclusions pertaining to the development of an artificial model for mimicking an individual step of electron transfer from the oxygen-evolving complex to  $P_{680}^{+}$  in PSII can be drawn from the present study. The most important is that a coordinated manganese ion can restore the activity of a photo-oxidized photosensitizer by intramolecular electron transfer. This is a crucial event in PSII and clearly not a trivial act. A second conclusion is that the distance between the photosensitizer and the manganese is important. If the distance is short, which would promote efficiency of electron transfer, efficient quenching of the excited state of the photosensitizer may inhibit the primary electron transfer to an acceptor system. This is clearly a problem with the system **13**, which has a very short-lived

(30) Berglund, H.; Sun, L.; Hammarström, L.; Styring, S.; Åkermark, B.; Almgren, M. Manuscript in preparation.



## Scheme 3



excited state compared to **7** (ca. 2 orders of magnitude shorter). The quenching effect is observed even for **7** which has a lifetime ( $\tau$ ) ca. 250 ns as compared to 950 ns for **6a**, which lacks the manganese.

The slow electron transfer from coordinated manganese in **7** suggests that a distance of ca. 13 Å may be somewhat too long for efficient electron transfer. However, already at 9 Å, the undesirable quenching of the excited photosensitizer by the manganese complex is very fast. Although the rate of this quenching may be adjusted somewhat by changing the ligand environment of Mn(II), it will probably be favorable to insert an intermediate, an electron donor, between the ruthenium and manganese parts of the molecule. This donor should be chosen so that its quenching of the excited state of the photosensitizer is small. Also, the reorganization energy for electron transfer to Ru(III) should preferably be lower than for the Mn complex, which would allow a faster donor reaction. In PSII, a tyrosine moiety is present between P<sub>680</sub> and the manganese cluster, and

its function is probably more sophisticated than just working as an electron donor to P<sub>680</sub><sup>+</sup>. Nevertheless, an obvious extension of the present work is to continue to seek inspiration from PSII and thus insert a tyrosine or an analogous phenol group between the ruthenium and the manganese ion(s) in systems related to **7** and **13**. Also, multielectron transfer from manganese(s) is necessary for oxidation of water to oxygen at a reasonable potential. Work is therefore in progress to synthesize supramolecular complexes, where more than one manganese ion is coordinated together with ruthenium.

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