Supporting information for

Intramolecular Light Induced Activation of a Salen-Mn^{III} Complex by a Ruthenium Photosensitizer

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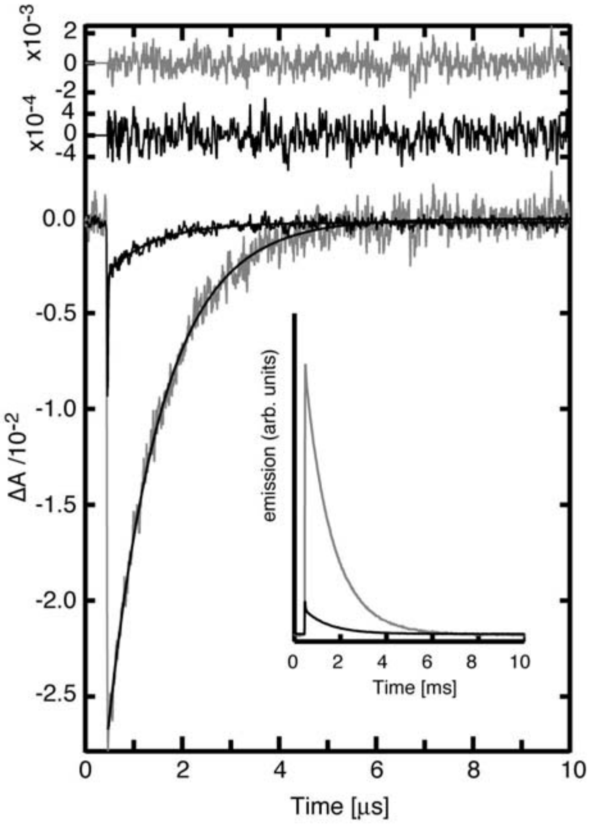
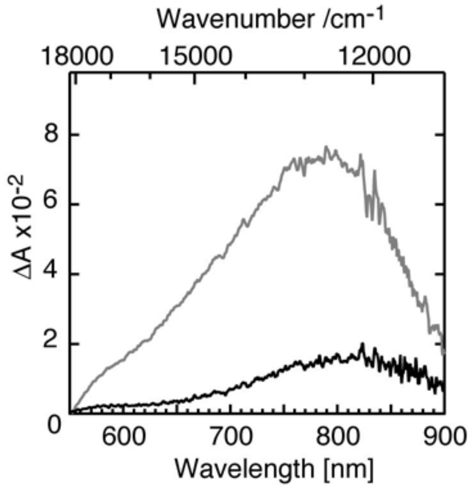
Figure S1. Transient absorption in the absence of electron acceptor



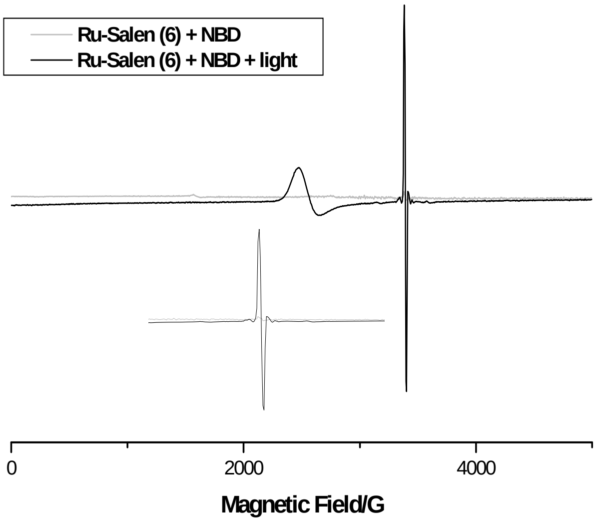
$\mathrm{Ru^{II}}$-polypyridyl ^{1}MLCT transient absorption kinetics at 20°C of absorption matched (A~0.2 at 460 nm) $\mathrm{Ru^{II}}$-Salen-$\mathrm{Mn^{III}}$ **(7)** (black traces) and $\mathrm{Ru^{II}}$-Salen **(6)** (grey traces) dissolved in acetonitrile following a ~10 mJ ~7 ns flash at 460 nm. The solid traces are single and double exponential fits to the data, for $\mathrm{Ru^{II}}$-Salen and $\mathrm{Ru^{II}}$-Salen-$\mathrm{Mn^{III}}$, respectively and the corresponding residuals are shown in the upper panel. The fits yielded values of $t_{1/2}$ = 850±50 ns for $\mathrm{Ru^{II}}$-Salen and for $\mathrm{Ru^{II}}$-Salen-$\mathrm{Mn^{III}}$ $t_{1/2}$ = 800±50 ns and $t_{1/2}$ < 50 ns (i.e. within the instrument resolution). The insert shows the ^{3}MLCT emission kinetics at 610 nm for absorption-matched acetonitrile solutions (20°C) of both complexes, and the kinetic data agree with the transient absorption. The emission yield of the $\mathrm{Ru^{II}}$-Salen-$\mathrm{Mn^{III}}$ samples was typically ~10-15% of that for $\mathrm{Ru^{II}}$-Salen. This data is interpreted to indicate that the nominally $\mathrm{Ru^{II}}$-Salen-$\mathrm{Mn^{III}}$ samples contain ~10-15% of Mn-free complexes.

Figure S2. Transient absorption in the presence of electron acceptor



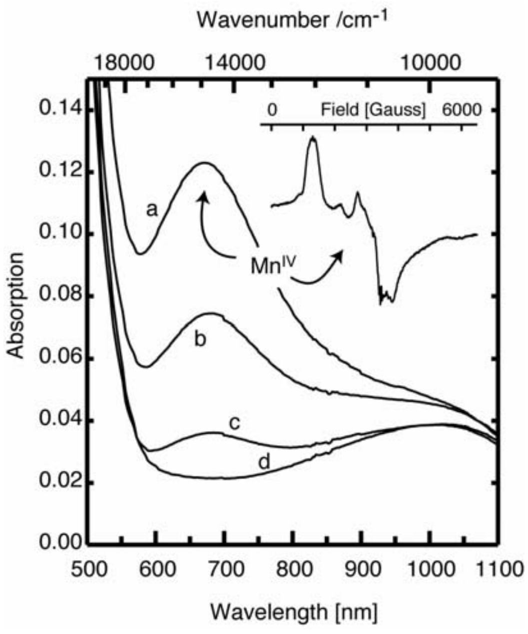
Transient absorption spectra of $\mathrm{Ru^{II}}$-Salen-$\mathrm{Mn^{III}}$ (black trace) and Ru-Salen (grey trace) in acetonitrile at 20°C in the presence of ~40 mM NBD electron acceptor taken at a delay of t = 3 µs following a ~30 mJ flash at 532 nm. The ~800 nm absorption features appear with $t_{1/2}$ < 50 ns (i.e. within instrumental resolution). The data indicate that ~10-15% of complexes in the nominally $\mathrm{Ru^{II}}$-Salen-$\mathrm{Mn^{III}}$ samples are Mn-free, in agreement with the data in the absence of electron acceptor.

Figure S3. X-band EPR spectra of light induced oxidation of Ru^{II}-Salen



EPR spectra of Ru-Salen **(6)** before (gray) and after (black) light-induced formation of organic radical species in presence of electron acceptor NBD. EPR measurement conditions: temperature 20 K, microwave frequency 9.49 GHz, microwave power 2 mW, modulation amplitude 11.37 G, modulation frequency 100 kHz, time constant 163 ms, sampling time 82 ms, gain 40 dB.

Figure S4. EPR and absorption spectra of chemically oxidized Ru^{II}-Salen-Mn^{III}.



Traces (a)-(d) correspond to addition of 2.4, 0.7, 0.35, and 0.15 equivalents of oxidant.

Inset. X-band EPR spectrum of the resulting Ru-Salen-Mn^{IV} product.

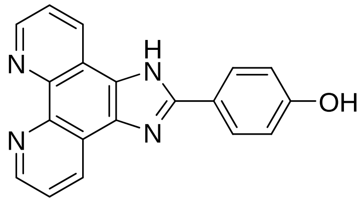
Synthesis and structural characterization

NMR studies were performed on a Bruker 400 or 300 MHz spectrometer by dissolving compounds in deuterated DMSO containing 0.03% TMS as an internal standard.

Mass Spectra were obtained on a Finnigan MAT95S by direct injection of the samples dissolved in a mixture of $CH_2Cl_2/MeOH/H_2O$ (1/1/1).

All reagents were purchased from Aldrich and used as received.

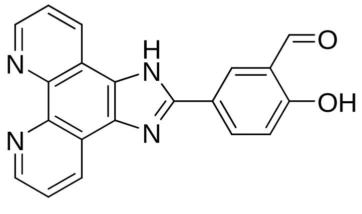
Syntheses of 1, 10 phenanthroline-5, 6-dione [17] **(1)** and $Ru(bpy)_2Cl_2$[19] were performed according to literature procedure



2

(2) Following a Steck-Day reaction procedure, 500 mg of 1, 10 phenanthroline-5, 6-dione (2.4 mmol) were dissolved together with 350 mg 4-hydroxybenzaldehyde (2.8 mmol, 1.1 eq) in 10 ml acetic acid. The mixture was heated to 80° C and stirred for 30 min. At this time 3.70 g of dry ammonium acetate (48 mmol, 20 eq) were added and the reaction was stirred at 100° C for three hours. The reaction was allowed to reach room temperature and the product was filtered through a frit funnel and washed with copious amounts of acetone and ether to yield 510 mg of the desired product (68% yield).

^1H NMR (400 MHz, DMSO): δ 9.00 (d, J=8.2 Hz, 2H, Phen-H), 8.90 (d, J=7.0 Hz, 2H, Phen-H), 8.11 (d, J=8.7 Hz, 2H, Phenol-H), 7.82 (dd, J_{A-B}=8.4 Hz, J_{B-C}=7.0 Hz, 2H, Phen-H), 6.98 (d, J=8.5 Hz, 2H, Phenol-H). ^{13}C NMR (100 MHz, DMSO): δ 159.38, 151.49, 147.82, 143.64, 143.59, 136.00, 129.85, 128.41, 123.60, 121.48, 116.27 ESI-MS *m/z* calcd. for $C_{19}H_{12}N_4O$ $[M]^+$, 312.10, obsvd. 313.2 $[M+H]^+$.

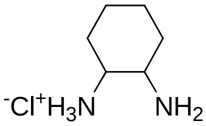


3

(3) Following a modified Duff reaction, 500 mg (1.6 mmol) of **2** and 896 mg of hexamethylene tetraamine (6.4 mmol, 4 eq) were dissolved in 10 mls trifluoroacetic acid and refluxed for three days. The mixture was allowed to cool to room temperature and 50 mls of a 4M HCl solution were added and allowed to stir for 2 hours, during which time the reaction became cloudy. The solid was collected by filtration, washed with acetone, ether and dried in vacuum to yield 452 mg of pure compound. (56% yield).

^1H NMR (400 MHz, DMSO): δ 10.32 (s, 1H, CHO-H), 9.42 (d, J=8.4 Hz, 2H, Phen-H), 9.10 (d, J=7 Hz, 2H, Phen-H), 8.51 (d, J=8.7 Hz, 1H, Sal-H), 8.46 (s, 1H, Sal-H), 8.19 (dd, J_{A-B}=8.8 Hz, J_{B-C}=8.4 Hz, 2H, Phen-H), 7.20 (d, J= 8.2 Hz, 1H, Sal-H).

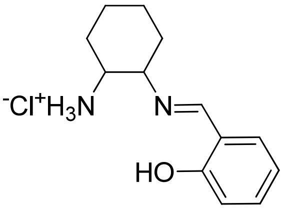
^{13}C NMR (100 MHz, DMSO): δ 190.43, 162.46, 151.34, 145.10, 135.57, 135.30, 135.02, 134.22, 126.72, 125.47, 122.72, 120.54, 118.14, 114.93. ESI-MS *m/z* calcd. for $C_{20}H_{12}N_4O_2$ $[M]^+$, 340.10, obsvd. 341.1 $[M+H]^+$.



4a

(4a) 2.00 g of the 1, 2-cyclohexanediamine (17.5 mmol) were dissolved in ether. To this solution 1.40 g of HCl dissolved in ether (36% v/v) were added in small portions over a period of 20 min. The reaction was allowed to stir for 2 hours. At this time it was filtered and washed with cold ether to yield 2.51 g (95% yield).

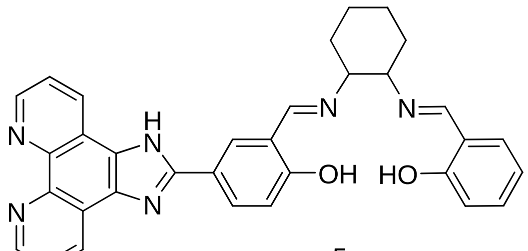
^{1}H NMR (400 MHz, D_2O): δ 2.72 (m, 2H, C*H*-NH_2), 1.91 (m, 2H, CH_2CHN^+), 1.68 (m, 2H, CH_2CHN), 1.23 (m, 4H, CH_2CH_2CHN). ^{13}C NMR (100 MHz, D_2O): δ 52.09, 29.22, 22.61. ESI-MS *m/z* calcd. for $C_6H_{15}ClN_2$ $[M]^+$ 150.09, obsvd. 115.1 $[M-Cl]^+$



4

(4) 510 mg of 1, 2 di-amino cyclohexane (4.43 mmol) and 541 mg of salicylaldehyde (4.43 mmol, 1 eq) were mixed in 20 mls dry MeOH. To this solution 10 drops of triethyl orthoformate and some molecular sieves were added. The solution was allowed to stir for 5 hours under Ar. At this time the solid that had formed was filtered off and the remaining solution was evaporated under reduced pressure. This solid was redissolved in CH_2Cl_2: 5% MeOH and the solution was allowed to crystallize at 4°C. The product was collected by filtration to yield 592 mg of product. (61 % yield).

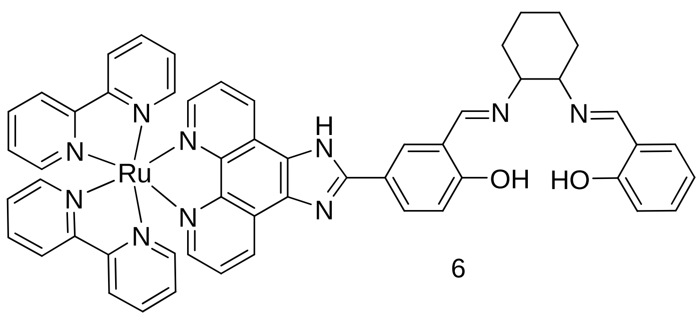
^{1}H NMR (400 MHz, DMSO): δ 8.58 (s, 1H, C=N-H), 7.42 (d, J= 7.3 Hz, 1H, Phenol-H), 7.35 (t, J= 7.5 Hz, 1 H, Phenol-H), 6.91 (t, J= 7.7 Hz, 1 H, Phenol-H), 6.90 (d, J= 7.9 Hz, 1 H, Phenol-H), 2.05-1.15 (m, 12 H, Aliph-H). ^{13}C NMR (100 MHz, DMSO): δ 167.32, 160.62, 132.87, 132.30, 119.39, 119.03, 116.68, 54.12, 51.79, 33.41, 29.25, 23.89, 23.18. ESI-MS *m/z* calcd. for $C_{13}H_{19}ClN_2O$ $[M]^+$, 254.12, obsvd. 219.10 $[M-Cl]^+$.



5

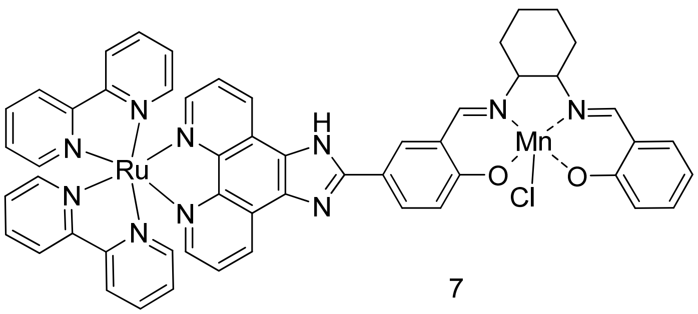
(5) Compound **3** (170 mg, .50 mmol) was dissolved in 10 mls dry MeOH to which some molecular sieves, and 100 mgs of triethyl amine (1 mmol, 2 eq) were added. To this mixture 110 mgs of half salen **4** (.50 mmol, 1 eq) were added, and the mixture was stirred under Ar for 2 days. At this time the solution was evaporated under reduced pressure and the resulting solid was washed with plenty of dichloromethane and ether in order to get rid of any symmetrical salen. Flash chromatography on silica using CH_2Cl_2:MeOH (90:10) yielded 142 mg of product (67% yield).

^{1}H NMR (400 MHz, DMSO): δ 9.00 (d, J=8.2 Hz, 2H, Phen-H), 8.86 (dd, J=9.3 Hz, 2H, Phen-H), 8.72 (s, 1H, C=N-H), 8.65 (s, 1H, C=N-H), 8.47 (s, 1H, Sal-H), 8.30 (dd, J=8.5 Hz, 1H, Sal-H), 7.74 (m, 2H, Phen-H), 7.36 (dd, J=7.9 Hz, 1H, Phenol-H), 7.26 (q, J=7.2 Hz, 1H, Phenol-H), 7.04 (dd, J=8.5 Hz, 1H, Sal-H), 6.82 (t, J=7.6 Hz, 1H, Phenol-H), 6.79 (d, J=8.1 Hz, 1H, Phenol-H), 2.20-1.27 (m, 10 H, Aliph-H). ESI-MS *m/z* calcd. for $C_{33}H_{28}N_6O_2$ $[M]^+$, 540.23, obsvd. 541.2 $[M+H]^+$.



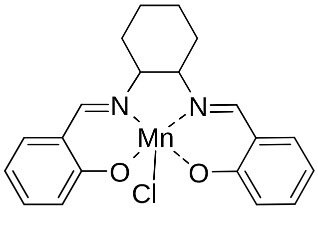
6

(6) $Ru(bpy)_2Cl_2$ (237 mg, .491 mmol) and $AgNO_3$ (165 mg, .982 mmol, 2 eq) were dissolved in 10 mls methanol and stirred for one hour at room temperature. The resulting AgCl precipitate was filtered off and the resulting methanolic solution was reacted with asymmetric salen **5** (291 mg, 540 mmol, 1.1 eq) overnight at 55°C under Ar. At this time the solution was allowed to reach room temperature. The solvent was removed by reduced pressure and the resulting product was dissolved in a minimum amount of methanol to which a couple drops of a saturated aqueous solution of NH_4PF_6 were added. The precipitate was filtered off and collected to yield 367 mg (60% yield).
ESI-MS *m/z* calcd. for $C_{53}H_{44}N_{10}O_2Ru$ $[M]^+$, 954.27, obsvd. 477.1 $[M]^{2+}$.



7

(7) 300 mg of compound **6** (.31 mmol) dissolved in 20 mls AcN and 227 mg Mn(II)OAc (.93 mmol, 3 eq) dissolved in 5 mls MeOH were mixed in a three neck flask and heated to 70°C for three hours under Ar. While keeping the reaction at this temperature air was bubbled in the solution for 2.5 hours. At this time, the solution was allowed to go back to room temperatue and 10 mls of a saturated aqueous solution of NaCl were added to the solution while stirring for an additional hour. The mixture was extracted carefully by adding additional AcN and water and the organic phase was dried over anhydrous sodium sulfate. The solution was filtered and the solvent was evaporated under reduced pressure and redissolved in a minimum amount of methanol. The product was precipitated by addition of several drops of a saturated NH_4PF_6 aqueous solution to yield 235 mgs. (57% yield)
ESI-MS *m/z* calcd. for $C_{53}H_{42}ClMnN_{10}O_2Ru$ $[M]^+$, 1042.16, obsvd. 1041.2 $[M - H]^+$, calcd. for $C_{53}H_{42}MnN_{10}O_2Ru$ $[M - Cl]^{3+}$, 335.73, obsvd. 335.85 $[M - Cl]^{3+}$.



8

(8). Model compound **8** was synthesized according to literature procedures[3]

Laser Flash Photolysis

Flash illumination

For transient absorption spectral and kinetic measurements in the time range 10 ns to 100 ms we used an Edinburgh Instruments LP920 Flash Photolysis Spectrometer system that incorporated a Continuum Surelite OPO for sample excitation (~7 ns pulse duration). The OPO was pumped by a Continuum Q-switched Nd:YAG laser operating at 355 nm. For some experiments the Nd:YAG second harmonic was used to provide excitation at 532 nm. The LP920 system uses a 450 W Xenon arc lamp as the probe for the transient absorption kinetic measurements. For the measurements where an irreversible electron acceptor was employed, the Xenon arc lamp was operated in continuous mode to minimize actinic effects at the sample. In the absence of electron acceptor, the Xenon arc lamp was pulsed. The presented transient absorption spectra were typically the average of 20-50 measurements. A 435 nm pass filter was positioned between the arc lamp and the sample ensuring second order light has negligible effect on the presented spectra.

To use the irreversible electron acceptor (4-nitrobenzenediazonium tetrafluoroborate, NBD), we employed a flow system incorporating a peristaltic pump and sealed tubing connected to a 1 cm path length quartz cuvette. The flow rate ensured the measured sample volume was refreshed before each measurement. Acetonitrile solutions of the Ru-Salen-Mn complex and the NBD irreversible acceptor were added under dim light, and the flow tubing was light-shielded during the experiment. The final concentration of the acceptor was ~40-45 mM, and the Ru-Salen-Mn complex typically ~0.02-0.08 mM. The sample vessel was sealed and then purged with Ar for 20 minutes before the flow was started. The Ar purge was kept on during the data collection period.

EPR spectroscopy and Sample Illuminations

For X-band EPR measurements, we used a Bruker Elexsys E 500 EPR spectrometer with an Oxford ESR9 liquid helium flow cryostat using a gold-chromel thermocouple directly below the sample position. A dual mode cavity ER 4116DM was used with resonance frequency 9.6 GHz (perpendicular mode) and 9.4 GHz (parallel mode). Ru^{II}-Salen-Mn^{III} and Salen-Mn^{III} complexes were dissolved in a 4:5 (v/v) mix of propionitrile/butyronitrile, transferred to an EPR tube and frozen to 77 K. Sample concentrations were typically 20-40 mM.

We prepared the samples for EPR under dim light in an ethanol/ice bath, and then transferred ~100 µL into an EPR tube that was pre-cooled in an ethanol/ice bath. The EPR tube was then rapidly transferred to an ethanol bath at ~ -100°C (ethanol cooled with liquid nitrogen). The EPR tube was then pumped to vacuum 4-5 times to purge oxygen from the sample, and finally transferred into liquid nitrogen for cooling to 77 K before being entered into the EPR spectrometer.

For sample illumination with monochromatic light, we used a Coherent® Innova® Sabre™ Ar^+ laser operating at the 514.5 nm line. We used neutral density filters to reduce the power as required, ensuring the laser was operated with a sufficiently high current to maintain good lasing output stability. We used a divergent lens to expand the beam to uniformly illuminate the sample. Illuminations were performed with the sample in the EPR tube (prepared as described above). The end of the EPR tube containing the sample was submerged in an ethanol/ice bath at -12±2°C in a glass vessel. After illumination, the sample was rapidly transferred to a ~ -100°C ethanol bath for ~1-2 minutes, and then into liquid nitrogen before being transferred to the EPR spectrometer.

Chemical oxidations

For chemical oxidation, 10-20 μL of 0.6 M m-chloroperoxybenzoic acid (*m*-CPBA), dissolved in the same 4:5 propionitrile/butyronitrile mix, was added directly to sample (~200 μL) in the EPR tube at –40°C. The sample was then taken from the CO_2/ethanol bath and allowed to warm. The sample was shaken until the solution changed color (brown to green). The sample was then rapidly re-frozen to 77 K. The whole procedure, from addition of the oxidant to re-freezing the sample to 77 K, took ~30 s. The final concentration of the oxidant was 30-60 mM. The poor solubility of Ce^{IV} (used for the optical measurements, see below) in 4:5 (v/v) propionitrile/butyronitrile limited the EPR studies to the use of *m*-CPBA in acetonitrile solutions. The lack of well-resolved Mn^{III} parallel mode X-band EPR signals for the Ru^{II}-Salen-Mn^{III} complex in acetonitrile solution limited quantitative EPR studies to the propionitrile/butyronitrile solvent mix.

Steady state absorption

We recorded the steady state absorption spectrum with an Analytikjena SPECORD® 210 dual-beam absorption spectrometer.

Electrochemistry

Cyclic voltammetry was performed at room temperatue in a potentiostat-galvanostat using a 3 mm^2 surface glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and a Ag/$AgClO_4$ (0.01 M) electrode in acetonitrile as the reference electrode (+.292 vs. SCE). Acetonitrile was distilled prior to each experiment and the solution (1 mM for the complexes, 0.10 M of tetrabutylammonium hexaflurophosphate introduced in an Argon purged electrochemical cell.

Compound	**$E_{1/2}$ Ru^{III}/Ru^{II}**	**$E_{1/2}$ Mn^{IV}/Mn^{III}**	**ΔG^0**
Salen-Mn (**8**)		0.79 (160)	
Ru-Salen-Mn (**7**)	1.39 (189)	0.86 (85)	0.53

Table 1: Electrochemical data for complexes **7** and **8** (1mM) in acetonitrile with 0.10 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Potentials vs SCE. Scan speed = 100 mVs^{-1}. For reversible or quasi-reversible processes peak to peak distances are reported in parenthesis.

17. C. Hiort, P. Lincoln, B. Norden, *J. Am. Chem. Soc.* 1993, **115**, 3448.
19. G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, D. G. Whitten, *J. Am. Chem. Soc.* 1997, **99**, 4947.
3. M. J. Sabater, M. Alvaro, H. Garcia, E. Palomares, J. C. Scaiano, *J. Am. Chem. Soc.* 2001, **123**, 7074.