Supplementary Information for

Successive Light Induced Two Electron Transfers in a Ru-Fe Supramolecular Assembly : from Ru-Fe(II)-OH_2 to Ru-Fe(IV)-Oxo.

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Experimental Section

Chemicals were purchased from Acros and used without further purification. All solvents except for dichloromethane, acetonitrile and methanol were purchased from Aldrich or VWR and were used as received. Dichloromethane and acetonitrile were distilled over CaH_2, whereas methanol was distilled over Mg. NMR spectra were taken either on a Bruker AV 300 MHz or a Bruker 600 MHz spectrometer using the residual protonated solvent as internal standard. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) are reported in hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), doublet of doublet (dd), and doublet of doublet of doublet (ddd). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were taken on a Thermo Scientific TSQ, or on a Bruker micrOTOFq in the positive mode of detection (ESI+).

Synthetic procedure

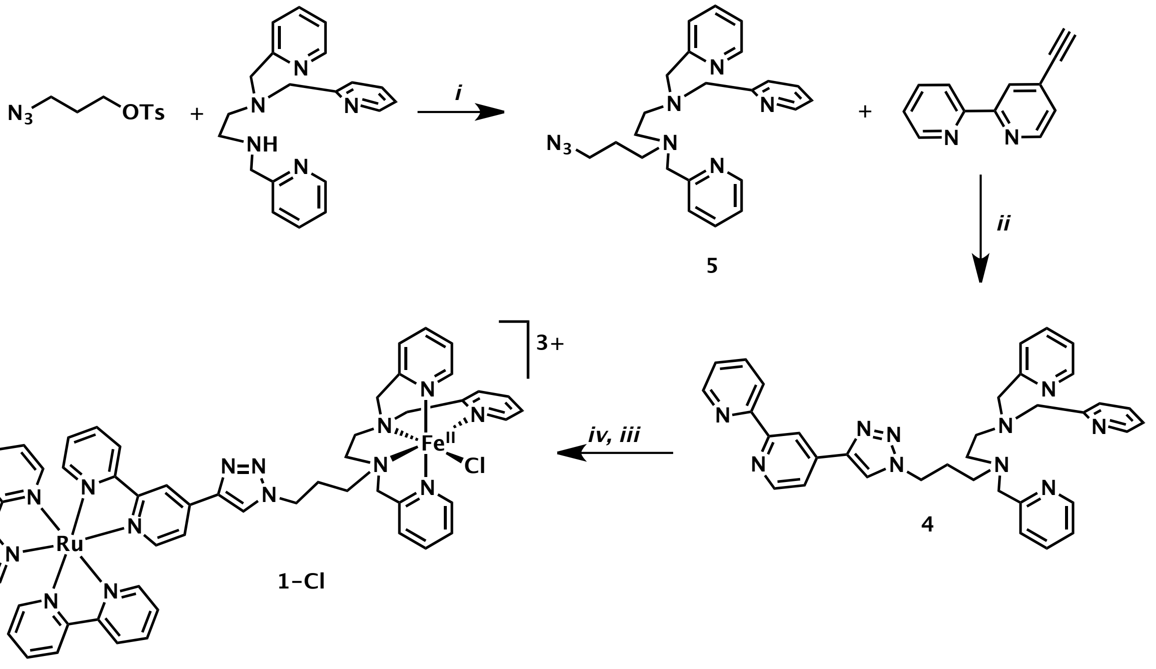

Figure SI 1: Synthetic procedure for complex Ru-FeCl **(1-Cl)**. *i)* CH_3CN, K_2CO_3, 90°C, 72 h *ii)* $CuSO_4 \cdot 5H_2O$, Na ascorbate, $CH_2Cl_2:H_2O$ *iii)* $Ru(bpy)_2Cl_2$, $AgNO_3$, MeOH, $NaPF_6$ *iv)* $FeCl_2$ $CH_3CN:MeOH$.

(5); step i. N,N,N'-tris(2-pyridylmethyl)-ethane-1,2-diamine **(**Trispicen) (1.36 g, 4.09 mmol) and Toluene-4-sulfonic acid 3-azido-propane (1.40 g, 4.92 mmol, 1.2 eq) were dissolved in 100 mL acetonitrile. To this mixture were added K_2CO_3 (5.7 g, 41 mmol, 10 eq) and KI (203 mg, 1.22 mmol, 0.30 eq) and the reaction was stirred at 90°C under an argon atmosphere for 72 hours. At this time the reaction mixture was allowed to cool to room temperature and filtered through a fritted filter in order to remove insoluble salts. The organic phase was removed under reduced atmosphere and the resulting solid was chromatographed using neutral alumina and CH_2Cl_2:1%MeOH as the eluent in order to collect the desired product. (437 mg, 26% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.47 (t, 3H, J = 5.6 Hz, Py-H); 7.59 (m, 3H, Py-H); 7.46 (d, 2H, J=7.7 Hz, Py-H); 7.29 (d, 1H, J=8.0 Hz, Py-H); 7.10 (m, 3H, Py-H); 3.80 (s, 4H, CH_2-Py); 3.68 (s, 2H, CH_2-Py); 3.19 (t, 2H, J = 7.0 Hz, CH_2-N_3); 2.69 (s, 4H, N-

CH_2CH_2-N); 2.49 (t, 2H, J = 7.0 Hz, CH_2-N); 1.64 (q, 2H, J = 7.0 Hz, CH_2-*CH_2*-CH_2). HRMS (ESI$^+$) $[M+H]^+$= 417.2522. Calculated for $C_{23}H_{29}N_8$ = 417.2515.

(4); step ii. 4-Ethynyl-[2,2']bipyridinyl (376 mg, 2.09 mmol, 1 eq) and **(5)** (871 mg, 2.09 mmol, 1 eq) were dissolved in 30 mL (1:1 CH_2Cl_2/H_2O). The solution was purged and degassed 3 times with argon and vacuum. To this solution were added $CuSO_4{\cdot}5H_2O$ (783 mg, 3.13 mmol, 1.50 eq) and sodium ascorbate (1.25 g, 6.27 mmol, 3 eq). The mixture was allowed to react overnight under an argon atmosphere. At this time the reaction mixture was transferred to a round bottom flask and 20 mL of a mixture containing 1M HEDTA and 3M NaOH were added followed by mixing for one hour. The solution was extracted with CH_2Cl_2 and the product was purified by column chromatography (Silica. CH_2Cl_2 to CH_2Cl_2/5% MeOH). (0.92 g, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, 1H, J = 5.0 Hz, bpy-H); 8.68 (d, 1H, J = 4.3 Hz, bpy-H); 8.61 (s, 1H, Trz-H); 8.49 (d, 3H, J = 4.6 Hz, Py-H); 8.43 (d, 1H, J = 8 Hz, bpy-H); 7.69 (dd, 1H, J = 1.5, 5.0 Hz, bpy-H); 7.84 (s, 1H, bpy-H); 7.82 (dd, 1H, J = 2.0, 7.2 Hz, bpy-H); 7.63 (q, 3H, J = 7.2 Hz, Py-H); 7.46 (s, 1H, bpy-H); 7.43 (s, 1H, bpy-H); 7.31 (m, 2H, bpy-H); 7.10 (dd, 3H, J = 5.0, 7.2 Hz, Py-H); 4.33 (t, 2H, J = 7.2 Hz, CH_2-Trz); 3.81 (s, 4H, CH_2-Py); 3.65 (s, 2H, CH_2-Py); 2.71 (s, 4H, N-C*H_2*C*H_2*-N); 2.47 (t, 2H, J = 7.0 Hz, Trz-CH_2-CH_2-C*H_2*-N); 2.02 (q, 2H, J = 7.0 Hz, Trz-CH_2-C*H_2*-CH_2-N). HRMS(ESI$^+$) $[M+H]^+$=597.3215. Calculated for $C_{35}H_{37}N_{10}$ = 597.3203.

(3); step iii. $Ru(bpy)_2Cl_2$ (170 mg, 0.352 mmol, 1 eq) and $AgNO_3$ (180 mg, 1.05 mmol, 3 eq) were dissolved in 5 mL MeOH and stirred at room temperature for one hour. The resulting solution was filtered through filter paper into a round bottom flask containing compound **4** (231 mg, 0.387 mmol, 1.1 eq) and the resulting mixture was allowed to react under an argon atmosphere at 70°C overnight. The solvent was evaporated under reduced pressure and the resulting solid was redissolved in a minimum amount of MeOH. The silver containing product **3** was precipitated by dropwise addition of a saturated aqueous solution of $NaPF_6$. (457 mg, 81% yield).

^{1}H NMR (600 MHz, CD_3OCD_3) δ 8.99 (s broad, 2H, Py-H & bpy-H); 8.92 (d, 1H, J = 8.1 Hz, bpy-H); 8.81 (d, 4H, J = 8.0 Hz, bpy-H); 8.52 (s broad, 3H, Py-H & Trz-H); 8.20 (m, 6H, bpy-H); 8.07 (m, 5H, bpy-H); 7.90 (dd, 1H, J = 5.9Hz & J = 1.7Hz, bpy-H); 7.82 (m, 3H, Py-H); 7.58 (m, 5H, bpy-H); 7.47 (d, 2H, J = 7.6 Hz, Py-H); 7.42 (m, 2H, Py-H); 7.32 (t, j = 7.0Hz, 2H, Py-H); 4.33 (t, 2H, J = 7.0 Hz, Trz-*CH_2*-CH2-CH_2-N)); 4.06 (s broad, 2H, CH_2-Py); 3.82 (s broad, 2H, CH_2-Py); 3.61 (s, 2H, CH_2-Py); 3.01 (s broad, 2H, N-CH_2-*CH_2*-N); 2.93 (s , 2H, N-*CH_2*-CH_2-N); 2.31 (t, 2H, J = 7.2 Hz, Trz-CH_2-CH_2-C*H_2*-N); 2.12 (m, 2H, Trz-CH_2-C*H_2*-CH_2-N).

^{13}C NMR (75.475 MHz, CD_3OCD_3) δ 158.9- 158.7 (Py-C_2); 158.6-158.2 (bpy-C_2); 153.0 (Py-C_6H); 152.9 - 152.7 (bpy-C_6H); 151.8 (Py-C_6H); 143.9 (bpy-C_4-Trz); 141.1 (Trz-C); 139.6 - 139.2 (Py-C_5H); 139.0 (bpy-C_4H); 128.8 (bpy-C_5H); 126.6 -126.11 (Py-C_3H); 125.6 - 125.4 (bpy-C_3H); 124.8 (Trz-CH); 124.5 (Py-C_4H); 123.9 (bpy-C_5H-Trz); 120.7 (bpy-C_3H-Trz); 60.1-59.6 (CH_2-Py); 52.1-51.6 (N-CH_2-CH_2-N); 51.2 (Trz-CH_2-CH_2-*CH_2*-N), 49.2 (Trz-*CH_2*-CH_2-CH_2-N), 27.3 (Trz-CH_2-*CH_2*-CH_2-N).

HRMS(ESI$^+$) $[M+PF_6]^{2+}$=632.1105. Calculated for $C_{55}H_{52}AgF_6N_{14}PRu$ = 632.1120.

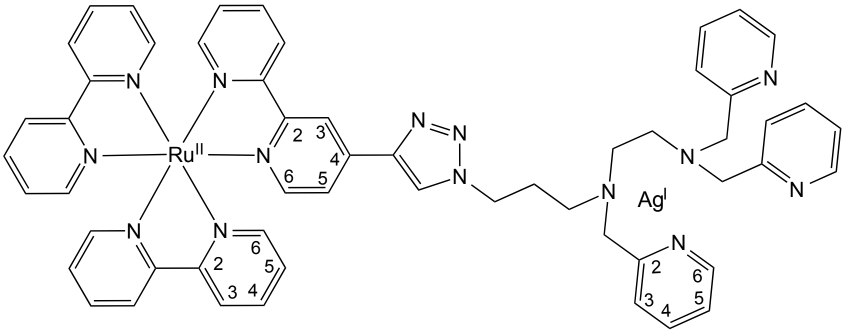

Figure SI 2. Numbering scheme of compound **3**.

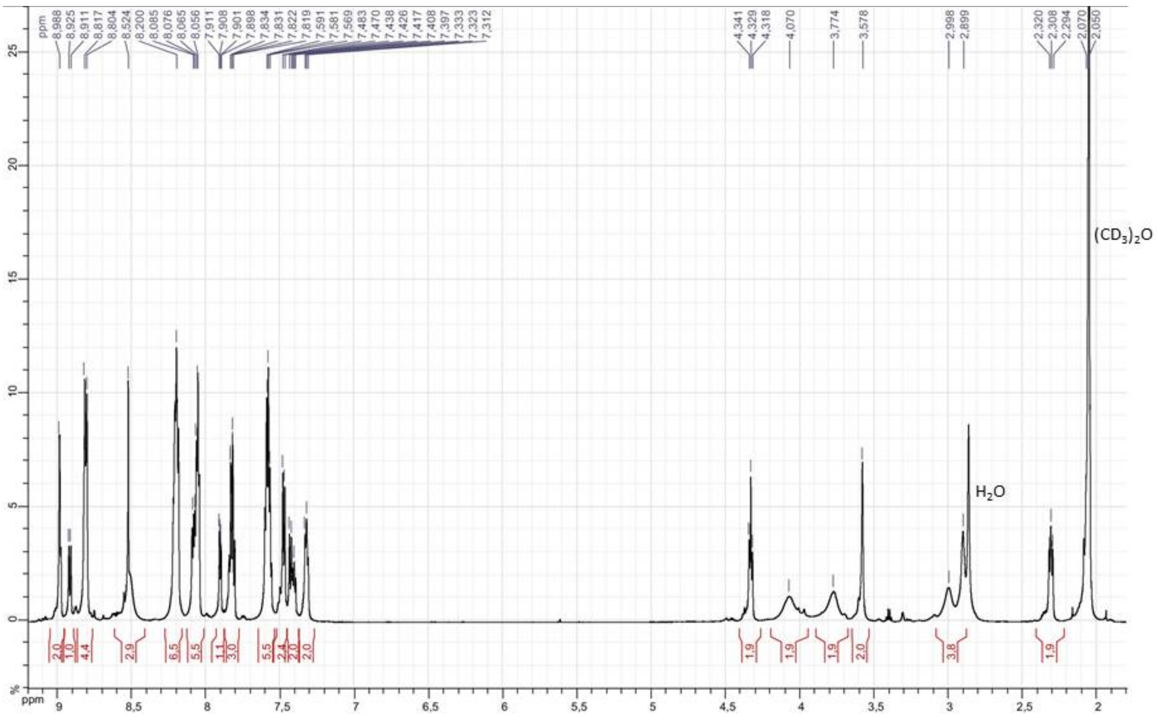

Figure SI 3. ^1H NMR of compound **3**, 600 MHz, CD_3OCD_3.

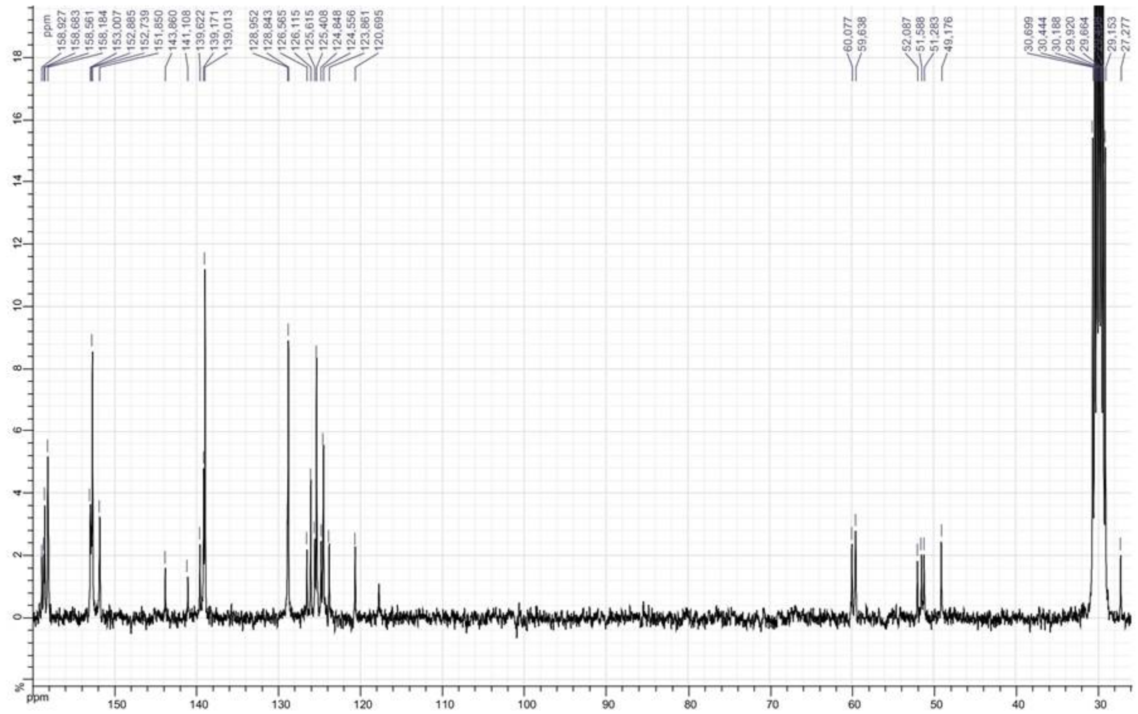

Figure SI 4. ^{13}C NMR of compound **3**, 75.475 MHz, CD_3OCD_3.

***(1-Cl); step iv*.** Compound **3** (200 mg, 0.13 mmol, 1 eq) was dissolved in 10 mL CH_3CN and placed in a Schlenk tube which was degassed with argon. In a different Schlenk tube $FeCl_2 \cdot 2H_2O$ (100 mg, 0.65 mmol, 5 eq) was dissolved in 10 mL MeOH and degassed with argon. The Fe-containing solution was transferred via cannula and the mixture was allowed to react overnight under an argon atmosphere. The content of the Schlenk tube was transferred to a round bottom flask where the solvents were removed under reduced pressure. The resulting solid was redissolved in a minimal amount of MeOH and the desired compound **1-Cl** was obtained as a red precipitate by the dropwise addition of a saturated aqueous solution of $NaPF_6$. (120 mg, 60% yield). HRMS(ESI$^+$) $[M+PF_6]^{2+}$= 623.1112. Calculated for $C_{55}H_{52}ClF_6FeN_{14}PRu$ = 623.1112. Elemental analysis calculated for $C_{55}H_{52}ClF_6FeN_{14}PRu$; 7 H_2O : C 39.74, H 4.00, N 11.80; found: C 39.62, H 3.31, N 12.06.

(1-CH$_3$CN). *(Method A).* Compound **1-Cl** was dissolved in acetonitrile and 1.5 eq. Silver trifluoromethanesulfonate dissolved in acetonitrile was added to the solution. *(Method B)* Compound **1-Cl** was dissolved in acetone and 1.5 eq. Silver trifluoromethanesulfonate dissolved in acetonitrile (33% v/v) was added.

(1–OH$_2$). Compound **1-Cl** was dissolved in acetone and 1.5 eq. silver trifluoromethanesulfonate dissolved in water (33% v/v) was added.

(2-Cl). $[L_5^2Fe^{II}Cl](PF_6)$ reference complex was prepared as previously described.[1] Ligand exchange in order to obtain **(2-CH$_3$CN)** and **(2-OH$_2$)** was performed following the same procedures as described above.

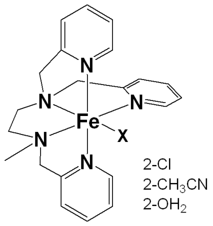

Figure SI 5. Structure of reference compound **2** with different ligand substitutions (X=Cl, CH_3CN, H_2O).

EPR. 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. The complex was dissolved in a 4:1 (v/v) mix of water/acetonitrile, transferred to an EPR tube and frozen to 77 K. Sample concentrations were typically 1-2 mM in Ru-Fe complex and 16-20 mM in $[Co^{III}(NH_3)_5Cl]^{2+}$. We prepared the samples for EPR 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 Thorlabs high power LED operating at 455 nm. Illuminations were performed with the sample in the EPR tube (prepared as described above). 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.

Electrochemistry. All electrochemical experiments were run under an argon atmosphere. Cyclic voltammetry measurements were recorded using an Autolab potentiostat controlled with a Nova 1.10 software package. The counter electrode used was a Pt wire and the working electrode was a glassy carbon disk carefully polished before each voltammogram with 1 µm diamond paste, sonicated in an ethanol bath, and washed with ethanol. The reference electrode used was a SCE electrode isolated from the rest of the solution by a fritted bridge. Experiments were run with 1 mM solutions of complex in acetonitrile or acetone using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

Steady-state absorption and emission

Ground state absorption spectra were measured in a Specord spectrophotometer (Analytic Jena) with 1 cm quartz cells. Steady state emission spectra were recorded in a Varian Eclipse Spectrofluorimeter. Samples were excited at 460 nm with absorbances optically matched at 0.1. $[Ru(bpy)_3]^{2+}$ was used as reference for emission quantum yield (φ_{em}) calculation in acetonitrile (φ_{em} = 0.059).[2] A cut-off filter at 475 nm was put in front of the emission monochromator to avoid excitation light. Samples were purged for 10 min with argon prior to each experiment.

Nanosecond Laser Flash Photolysis.

Transient absorption spectral and kinetic measurements were performed on an Edinburgh Instruments LP920 Laser Flash Photolysis Spectrometer system that incorporated a Continuum OPO for sample excitation (~7 ns pulse duration). The OPO, was pumped by a Continuum Surelite Q-switched Nd:YAG laser operating at 355 nm. Samples were excited by 460 nm wavelength pulses at ~10 mJ laser energy. The LP920 system uses a 450 W Xenon arc lamp as source for the probe light for the transient absorption measurements. For kinetic measurements in the time range 10 ns to 100 µs, the Xenon arc lamp was pulsed. Detection is performed either via a Czerny-Turner blazed 500 nm monochromator (bandwidth: 1-5 nm) coupled with a Hamamatsu R928 photomultiplier tube (kinetic mode), or via a 500 nm blazed spectrograph (bandwidth: 5 nm) coupled with a water-cooled ICCD nanosecond Andor DH720 camera (spectral mode). Samples, purged with argon for 10 minutes prior to each experiment, had an absorbance of ~0.40 at excitation wavelength. The presented transient absorption spectra were typically the average of 20-50 measurements. Experiments in the presence of electron acceptors were performed using either 20 mM of MV^{2+} or $[Ru^{III}(NH_3)_6]^{3+}$. A circulating system, equipped with a 2 mm path length cuvette was employed to study the second photoinduced electron transfer.

Catalysis. In a typical catalytic experiment Ru-Fe complex **1-Cl** dissolved in acetonitrile (200 µL), $[Co^{III}(NH_3)_5Cl]^{2+}$ dissolved in 50 mM acetate buffer pH 5 (800 µL), and triphenyl phosphine dissolved in methylene chloride (180 µL) were mixed in a 2 mL vial equipped with a magnetic stirrer and a septum cap. The final concentrations of each species were 0.5 mM complex, 14 mM acceptor and 83 mM substrate in a 4:1 water:acetonitrile mixture. The solution was purged with argon for 5 min and then subjected to illumination for the determined amount of time. The solutions were extracted with 2 mL CH_2Cl_2 and dried with sodium sulfate before being injected in the GC for analysis. ^{18}O insertion in triphenyl phosphine was done by adding 200 µL 95.4% $H_2{}^{18}O$ to the solution described above. This results in 16 % ^{18}O in the final solution.

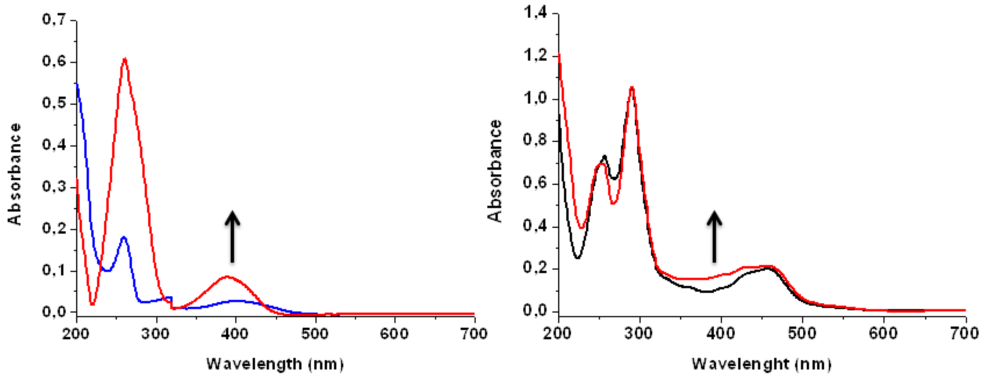

Figure SI 6. Left: UV/Vis absorption spectra of reference complex **2-Cl** in acetonitrile (blue) and in a 4:1 water:acetonitrile mixture (red). Right: UV/Vis absorption spectra of complex **1-Cl** in acetonitrile (black) and in a 4:1 water:acetonitrile mixture (red).

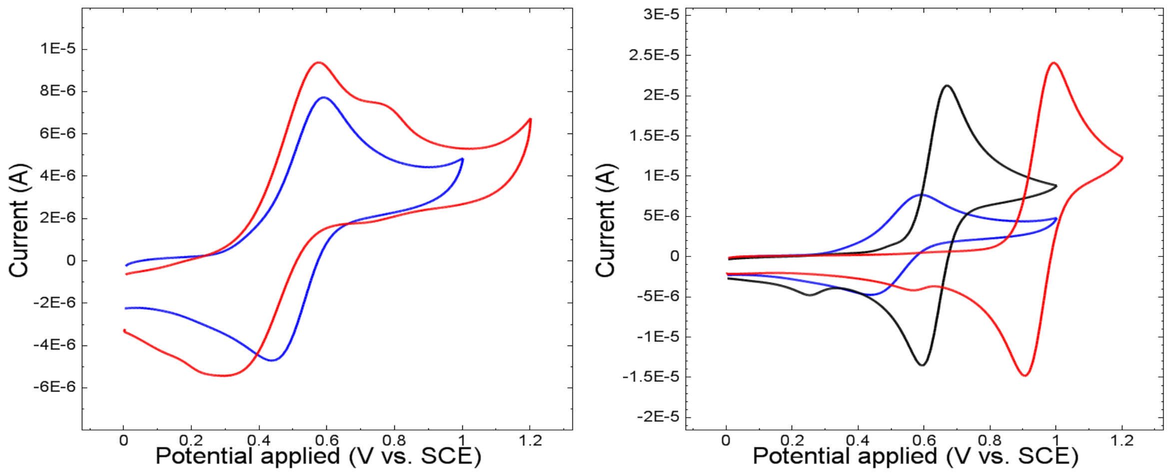

Figure SI 7. Left: Cyclic voltammetry of compounds **2-OH$_2$** (blue) in acetone and **2-Cl** (red) in a 4:1 H_2O:CH_3CN solution. Scan speed 100 mV.sec^{-1}. Right: Cyclic voltammetry of compounds **2-Cl** (black), **2-CH$_3$CN** (red), and **2-OH$_2$** (blue) in acetone. Compound **2-CH$_3$CN** was obtained by addition of 1.5 eq. silver triflate in acetonitrile to a solution of **2-Cl** in acetone. **2-OH$_2$** was obtained by addition of 1.5 eq. silver triflate in water to a solution of **2-Cl** in acetone. Scan speed 100 mV.sec^{-1}.

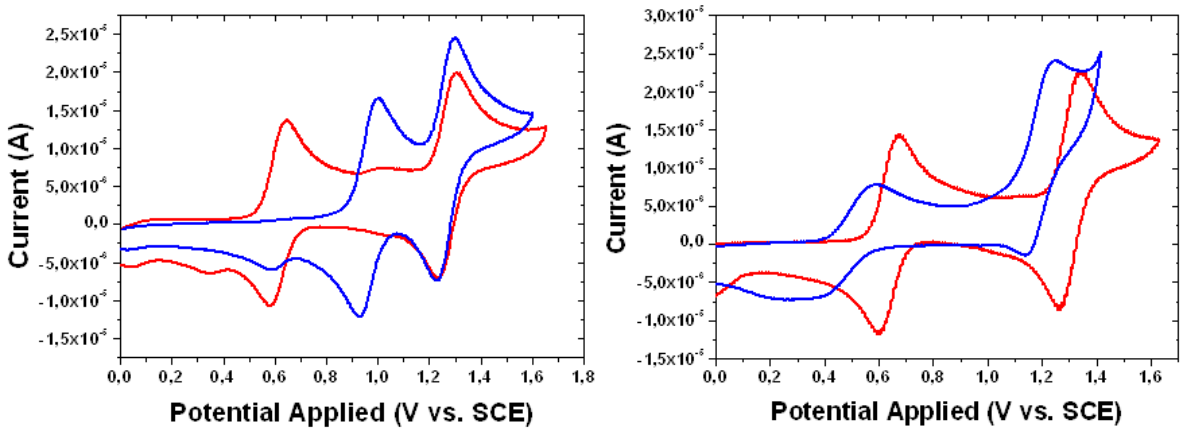

Figure SI 8. Left: Cyclic voltammetry of compounds **1-Cl** (red) and **1-CH$_3$CN** (blue) in acetonitrile. Scan speed 100 mV.sec^{-1}. Right: Cyclic voltammetry of compounds **1-Cl** (red) in acetonitrile and **1-OH$_2$** (blue) in 3:1 acetone:water. Scan speed 100 mV.sec^{-1}.

Table SI 1. Electrochemical data (V *vs.* SCE) for complexes **1** and **2**. Experimental conditions as described in Figure SI 8.

	Fe^{III}/Fe^{II}			Ru^{III}/Ru^{II}
	1-Cl	**1-CH_3CN**	**1-OH_2**	**1-X**
$E_{1/2}$	0.60 (0.63)[a]	0.97 (0.97)[a]	0.50 (0.51)[a]	1.26[b]

*a) Values given in bracket are those for **2-X**. b) The potential of the Ru^{III}/Ru^{II} wave for **1-OH_2** is slightly modified in 3:1 acetone/ water. The shape is modified as well due to the onset of the oxidation of the solvent mixture in this case.*

Based on these electrochemical values of complexes **1**, oxidation of the Fe^{II} unit by the photogenerated Ru^{III} center is exergonic by either 290, 660, or 750 mV depending on whether the exogenous ligand is acetonitrile, chloride or water, respectively. Furthermore, this observation rules out the possibility of an electron transfer mechanism from the catalyst to the excited state of the chromophore being responsible for the quenching of the ruthenium excited state ($*Ru^{II}$), which was identical for **1-Cl**, **1-CH_3CN**, and **1-OH_2**. Indeed, the oxidation potential of the chromophore excited state $E_{1/2}$ ($*Ru^{II}/Ru^{I}$) = 0.80 V *vs* SCE[1] should be able to oxidize the $Fe^{II}(Cl)$ and $Fe^{II}(OH_2)$ units (ΔE = +200 and +300 mV) but not its acetonitrile counterpart (ΔE = -170 mV).

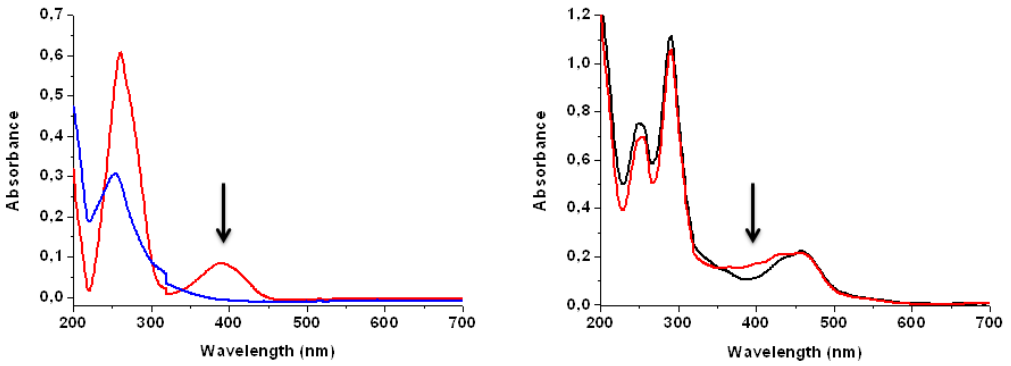

Figure SI 9. Left: UV/Vis absorption spectra of reference complex **2-OH_2** in a 4:1 water:acetonitrile mixture before (red) and after (blue) addition of 2 eq. H_2O_2. Right: UV/Vis absorption spectra of complex **1-OH_2** in a 4:1 water:acetonitrile mixture before (red) and after (black) addition of 2 eq. H_2O_2.

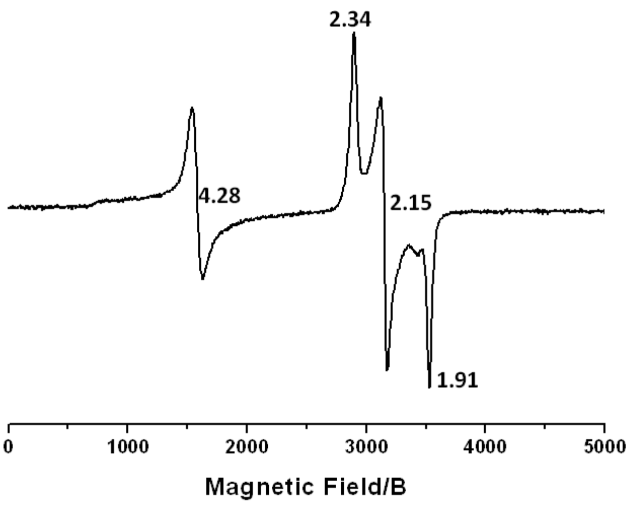

Figure SI 10. X-band EPR spectrum of complex **2-OH$_2$** in a 4:1 H_2O:CH_3CN solvent mixture after addition of 2 eq. H_2O_2. The weak resonance at *g* = 4.28 is due to ubiquitous S=5/2 Fe^{III} species.

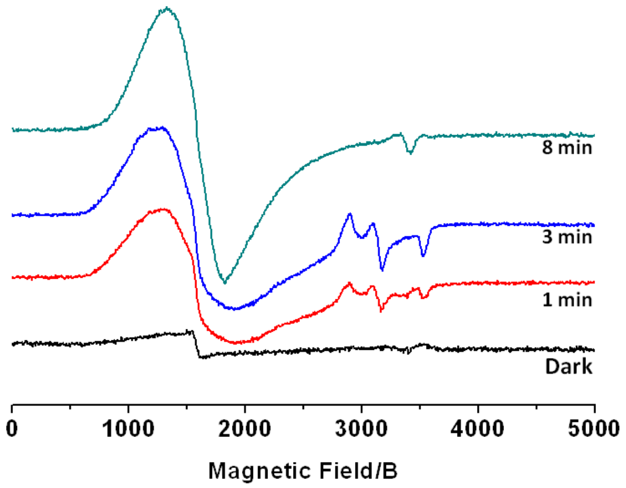

Figure SI 11. X-band EPR signal of a mixture of 0.9 mM complex **1-OH$_2$** and 16.5 mM $[Co^{III}(NH_3)_5Cl]^{2+}$ in a 4:1 H_2O:CH_3CN solvent mixture after illumination with 455 nm light at *t* = 0 (black), 1 min (red), 3 min (blue), 8 min (green). Mw freq 9.49 GHz, mw power 0.40 mW, T= 5K, 5 scans.

Flash photolysis experiments of Ru^{II}-Fe^{III}(OH) (prepared with H_2O_2) in presence of MV^{2+} was investigated in a circulating system in order to avoid accumulation of different oxidation states of the complexes during data acquisition. The light-induced charge separated state EA^{-} + Ru^{III}-Fe^{III} (Eq. 5) was attained as shown by the loss of absorption at 450 nm due to formation of Ru^{III}-Fe^{III} and formation of absorption at 605 nm due to MV$^{\bullet+}$. However, oxidation of Fe^{III} to Fe^{IV} could not be observed due to the competition between this reaction (Eq. 6) and the recombination pathway given by (Eq. 8). This latter pathway is significantly faster than the recombination pathway between the reduced EA and the oxidized chromophore (Eq. 9) since the initial species Ru^{II}-Fe^{III}(OH) is in large excess (~20 µM) as compared to the concentration (< 1 µM) of Ru^{III}-Fe^{III}(OH) formed by laser flash excitation. This is evidenced by the observation that MV$^{\bullet+}$ (605 nm) disappears faster than Ru^{III} (450 nm) (Fig. SI 12) due to reaction (8), prevailing over reaction (6).

$$\mathrm{Ru^{III}\text{-}Fe^{III}(OH)} \rightarrow \mathrm{Ru^{II}\text{-}Fe^{IV}(O)} \qquad \text{(Eq. 6)}$$

$$\mathrm{EA^{-} + Ru^{II}\text{-}Fe^{III}(OH)} \rightarrow \mathrm{EA + Ru^{II}\text{-}Fe^{II}(OH_2)]} \qquad \text{(Eq. 8)}$$

$$\mathrm{EA^{-} + Ru^{III}\text{-}Fe^{III}(OH)} \rightarrow \mathrm{EA + Ru^{II}\text{-}Fe^{III}(OH_2)]} \qquad \text{(Eq. 9)}$$

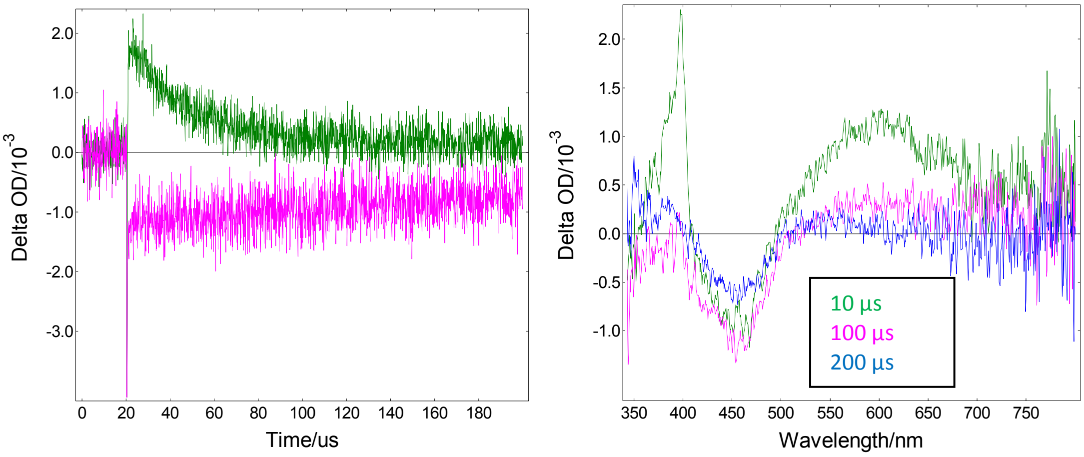

Figure SI 12. Flash photolysis of Ru^{II}-Fe^{III}-OH, prepared by chemical oxidation of **1-OH$_2$** with 2 eq. H_2O_2, in presence of 20 mM methyl viologen. Left) decay of MV$^{\bullet+}$ to MV^{2+} followed at 605 nm (green trace); recovery of Ru^{2+} from Ru^{3+} monitored at 450 nm (pink trace). Right) Transient absorption spectra of **1-OH$_2$** recorded at 10, 100, and 200 µs after laser flash excitation.

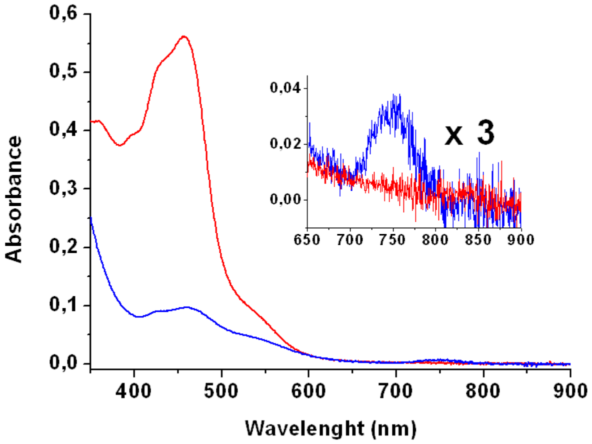

Figure SI 13. UV/Vis spectra of a solution containing 34 µM **1-OH$_2$** and 400 µM [Co^{III}(NH$_3$)$_5$Cl]$^{2+}$ before (red) and after (blue) illumination with 450 nm light.

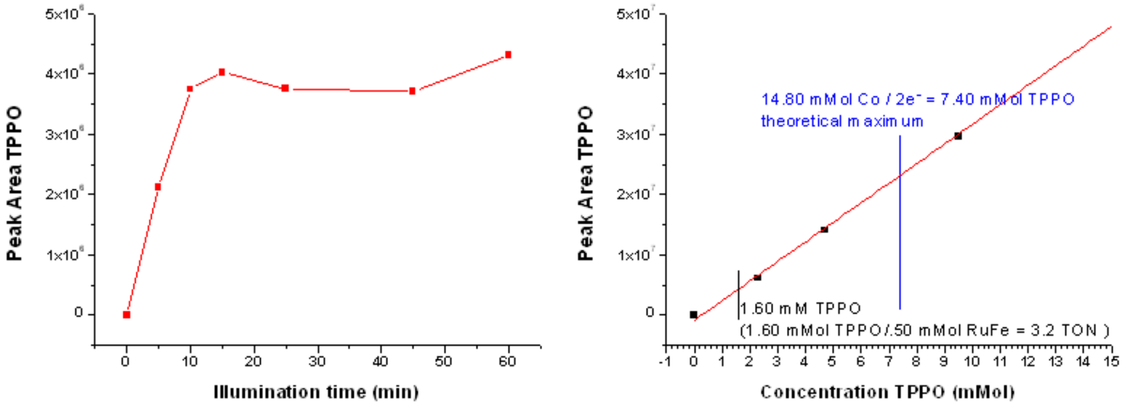

Figure SI 14. Left) Time profile of the photocatalytic reaction as described in the Experimental Section. Right) Calibration curve for triphenylphosphine oxide (TPPO). Black line indicates maximum amount of triphenylphosphine oxide obtained during photocatalysis after 10 min irradiation. Blue line indicates maximum theoretical yield for triphenylphosphine oxide production based on concentration of electron acceptor.

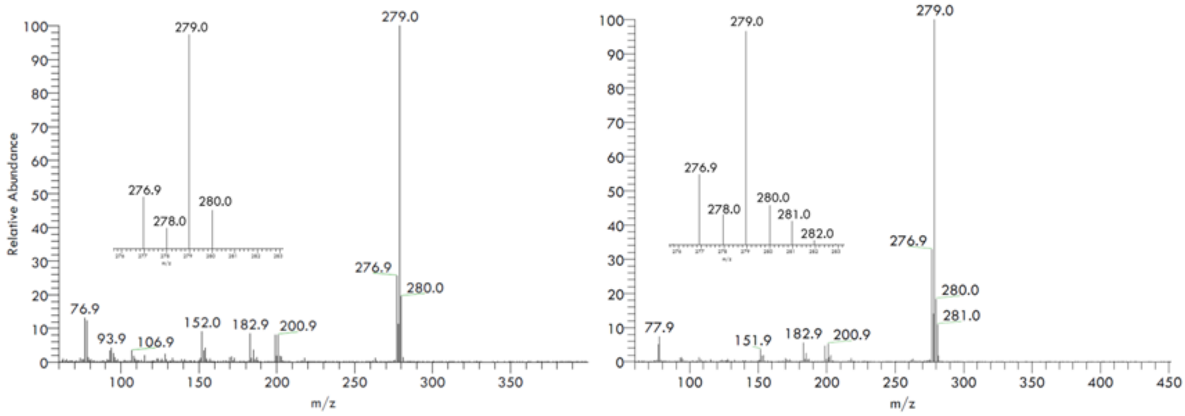

Figure SI 15. MS of the peak corresponding to the triphenylphosphine oxide (TPPO) product produced in H_2O (left) and with 16 % $H_2^{18}O$ (right) with m/z = 279 corresponding to $[TPPO+H]^+$ and m/z = 281 corresponding to $[TPP^{18}O + H]$. $TPP^{18}O$ obtained corresponds to > 12 % of total product.

[1] Bernal, I.; Jensen, I. M.; Jensen, K. B.; McKenzie, C. J.; Toftlund, H.; Tuchagues, J. P. *J. Chem. Soc., Dalton Trans.* **1995**, 3667.

[2] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Vonzelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85-277.