

SUPPLEMENTARY INFORMATION FOR

**Oxidation catalysis via visible-light water activation by a [Ru(bpy)₃]²⁺
chromophore BSA-metalloporphyrin couple**

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Figure SI. 3. Transient absorption spectra of a mixture containing 15 μM [Ru(bpy)₃]²⁺ and 10 mM [Ru(NH₃)₆]³⁺ obtained at 1, 10, and 50 μs after 450 nm light excitation.

Figure SI. 4. Transient absorption of a solution containing 15 μM [Ru(bpy)₃]²⁺ and 10 mM [Ru(NH₃)₆]³⁺ in the presence of 15 μM **1**-Mn^{III} at 1, 10, 50, 100, and 200 μs after 450 nm light excitation.

Figure SI. 5. Kinetics of the formation and decay of **1**-Mn^{IV} at 640 nm.

Figure SI. 6: Transient absorption of 7.5 μM **1**-Mn^{III}, 75 μM [Ru(bpy)₃]²⁺, and 20 mM [Ru(NH₃)₆]³⁺ in H₂O/AcN (60:40) in the absence (blue), and presence (red) of 7.5 μM BSA. Excitation: 460 nm, laser energy ~4 mJ. Argon degassed.

Figure SI. 7: HR-ESI MS showing the reaction products from the photo-oxidation of thioanisole using [Ru(bpy)₃]²⁺ and BSA-**1**-Mn^{III}

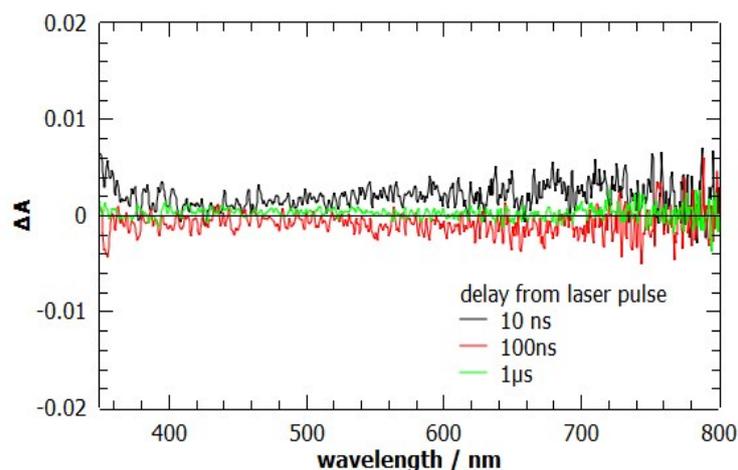


Figure SI.1. Transient absorption spectra of 15 μM solution of **1-Mn^{III}** in water, buffered solution. The lack of spectral features at 10 ns indicates excited lifetime of this species is shorter than the resolution of the apparatus.

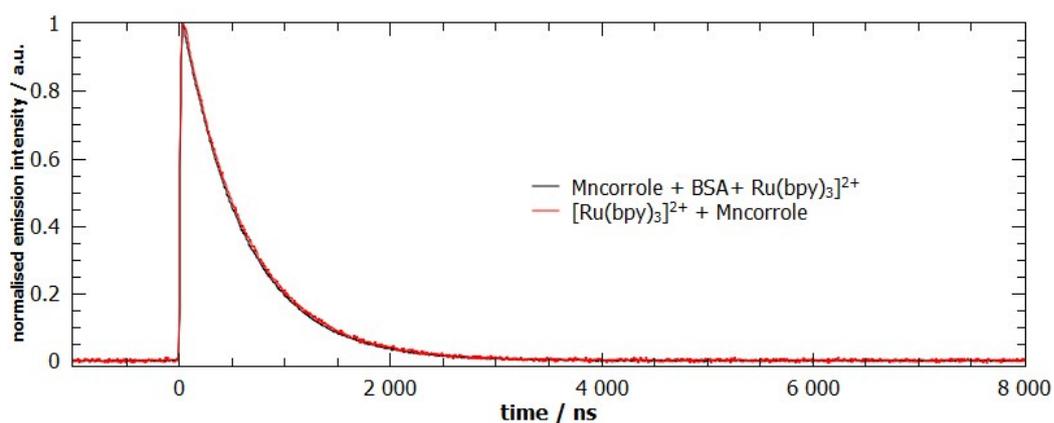


Figure SI.2. Emission kinetics of a mixture of 15 μM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 15 μM **1-Mn^{III}** (black line) and 26 μM $[\text{Ru}(\text{bpy})_3]^{2+}$, 3 μM **1-Mn^{III}** and 7.5 μM BSA (red line) in the absence of electron acceptor in (4:1 water: acetonitrile solvent mixture). Excitation wavelength 450 nm, detection wavelength 610 nm corresponds to emission maximum of ruthenium chromophore. Emission lifetime was 600 ns for both samples.

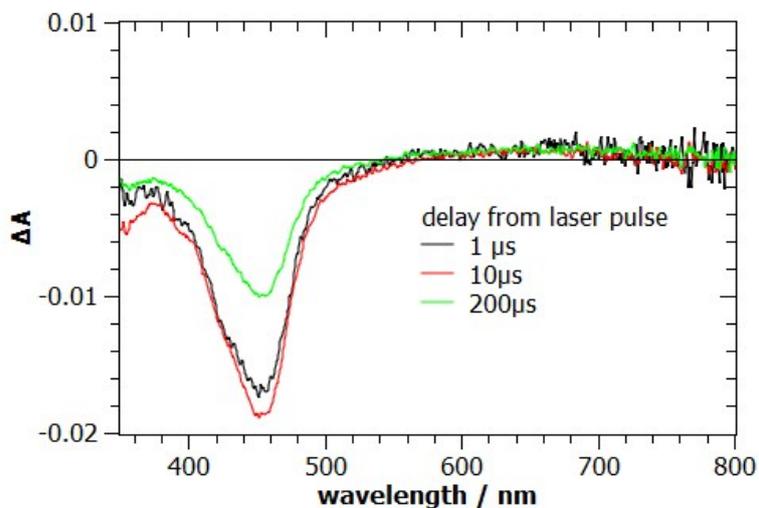


Figure SI.3. Transient absorption spectra of a mixture containing 15 μM $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and 10 mM $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$ obtained at 1, 10, and 200 μs after 450 nm light excitation. The bleach observed at 450 nm corresponds to the formation of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$, denoting the formation of the charge separated state. The recovery of the signal denotes charge recombination between the oxidized chromophore $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ and the reduced electron acceptor $[\text{Ru}^{\text{II}}(\text{NH}_3)_6]^{2+}$. Estimated from the extinction coefficient of the chromophore $\sim 2 \mu\text{M}$ $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ are obtained after electron transfer to $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$. The lifetime of the charge-separated state is $\sim 250 \mu\text{s}$.

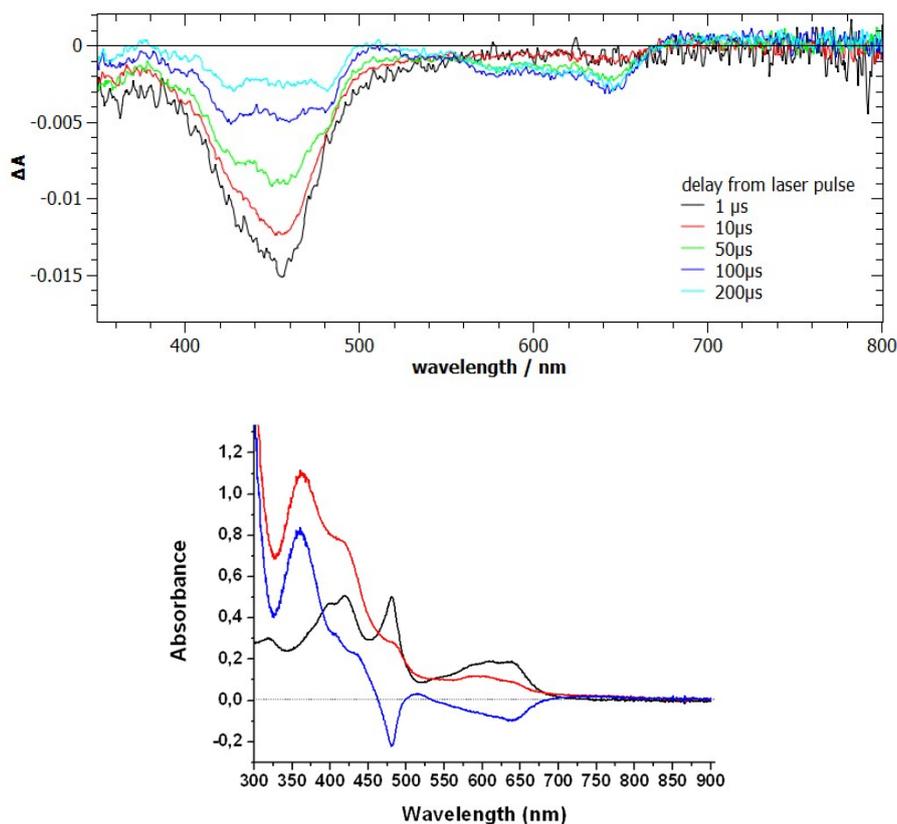


Figure SI.4. Top. Transient absorption of a solution containing 15 μ M $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and 10 mM $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$ in the presence of 15 μ M **1-Mn^{III}** at 1, 10, 50, 100, and 200 μ s after 450 nm light excitation. Bleach at 450 nm corresponds to the formation of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$. Bleach in the 600-650 nm region appearing after 50 μ s corresponds to the formation of Mn^{IV}-corrole. Bottom. UV/Vis spectra of 20 μ M **1-Mn^{III}** in acetonitrile (black trace), **1-Mn^{IV}** (red trace) obtained by treatment of **1-Mn^{III}** with 0.5 eq. I_2 , and difference spectrum **1-Mn^{IV}** - **1-Mn^{III}** (blue trace) showing bleach in the 550-650 nm region and at 480 nm as well.

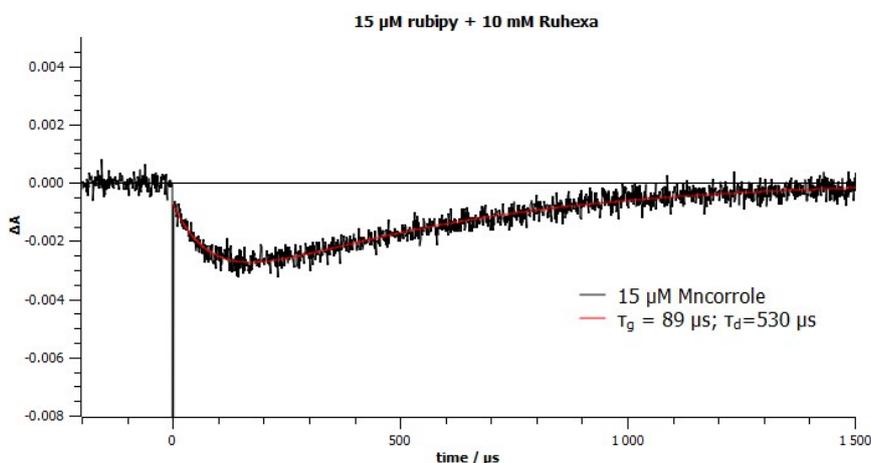


Figure SI.5. Kinetics of the formation and decay of **1-Mn^{IV}** followed at 640 nm in a mixture of 15 μ M **1-Mn^{III}**, 15 μ M $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and 10 mM $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$ after 450 nm light excitation.

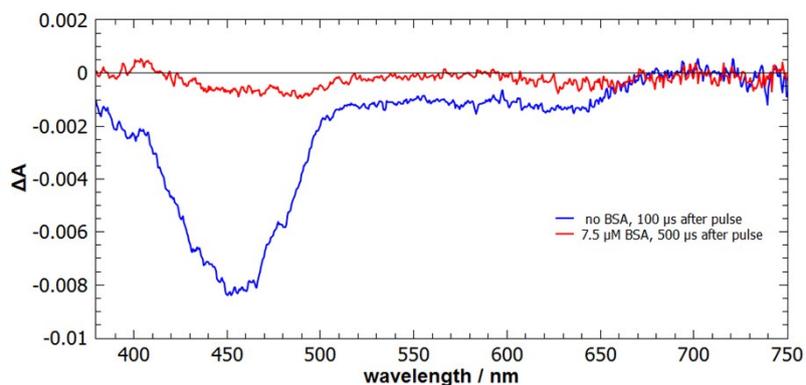


Figure SI. 6. Transient absorption of 7.5 μM **1-Mn^{III}**, 75 μM $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$, and 20 mM $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$ in $\text{H}_2\text{O}/\text{AcN}$ (60:40) in the absence (blue), and presence (red) of 7.5 μM BSA. Excitation: 460 nm, laser energy ~ 4 mJ. Argon degassed.

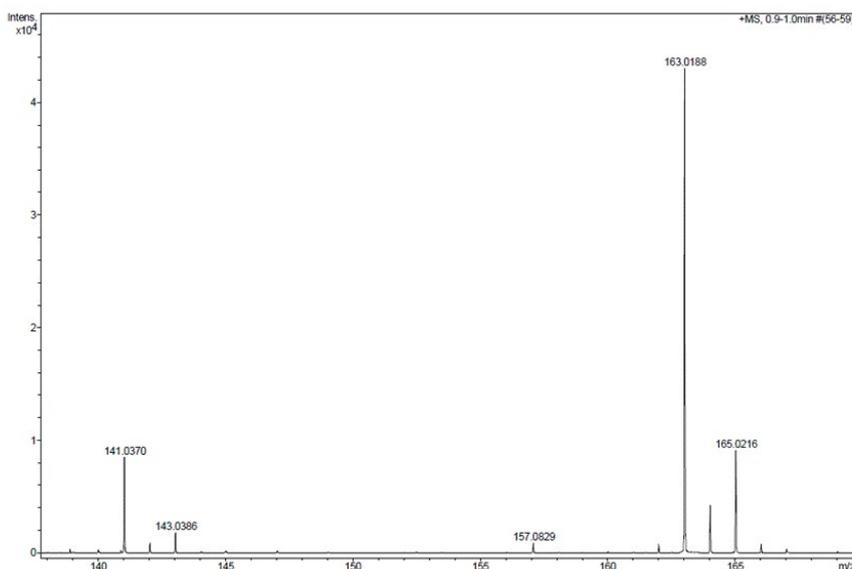


Figure SI. 7. HR-ESI MS showing the reaction products from the photo-oxidation of thioanisole using $[\text{Ru}(\text{bpy})_3]^{2+}$ and **BSA-1-Mn^{III}**. Peaks at 141.0371 and 143.0386 correspond to $[\text{M}+\text{H}]^+$ and peaks at 163.0188 and 165.0216 correspond to $[\text{M}+\text{Na}]^+$. $[\text{M}]$ = methyl phenyl sulfoxide $\text{CH}_3\text{SOC}_6\text{H}_5$ or $\text{CH}_3\text{S}^{18}\text{OC}_6\text{H}_5$.