

SUPPLEMENTARY INFORMATION

Electrochemical measurements

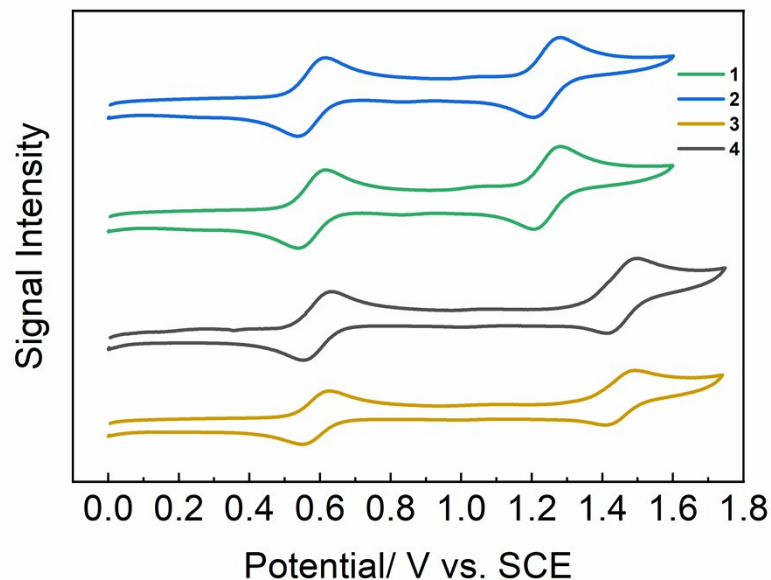


Figure S1. Electrochemical measurements for dyads in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (4:1), 0.1 M tetrabutylammonium hexafluorophosphate

$[\text{Fe}^{\text{II}}(\text{L}_5^2)\text{Cl}]^+$ catalyst excited state

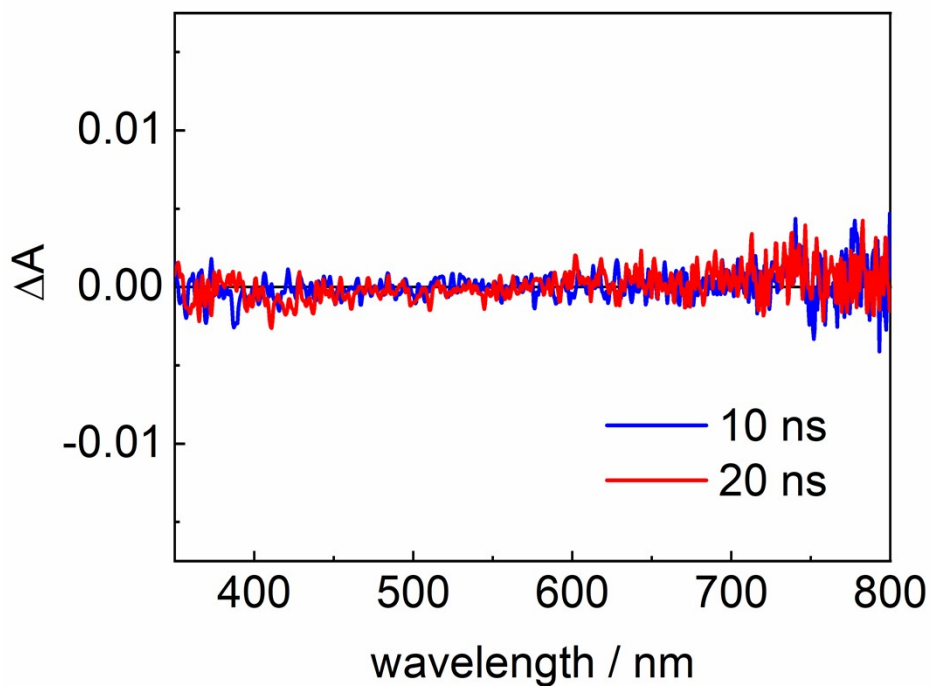


Figure S2. Transient absorption of $[\text{Fe}^{\text{II}}(\text{L}_5^2)\text{Cl}]^+$ catalyst. Excitation at 355 nm. Laser energy: 8 mJ. $A_{355} = 0.20$. Solvent: CH_3CN

Emission kinetic analysis

Emission values given in Table 2 have been obtained fitting the experimental decays with the biexponential decay equation given below:

$$A = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

The values τ_1 and τ_2 have been reported in Table, together with percentages calculated as

$$\frac{A_1}{A_1 + A_2} \times 100$$

and

$$\frac{A_2}{A_1 + A_2} \times 100$$

Chromophore-catalyst complexes gated emission spectra

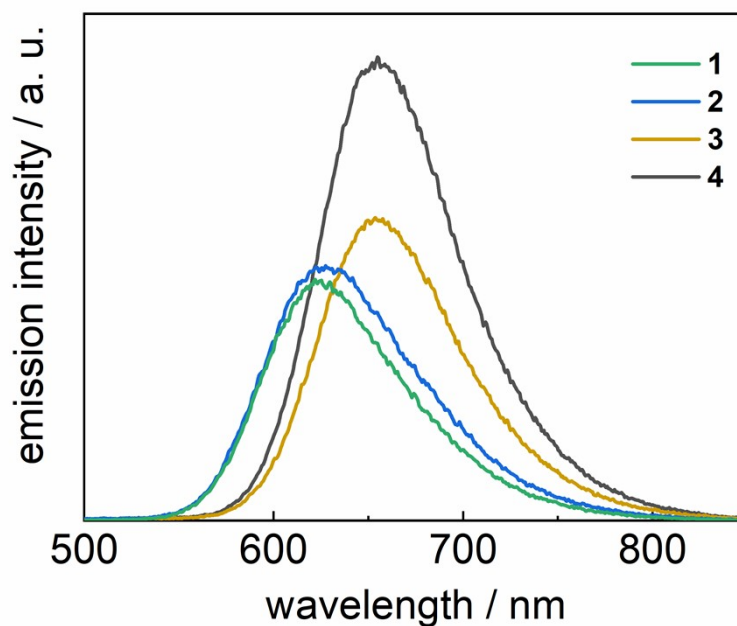


Figure S3. Gated (gate = 10 ns) emission spectra for the different dyads, obtained 10 ns after excitation with 460 nm laser pulse (10 mJ energy) in a H₂O/CH₃CN (4:1) mixture.

Transient absorption kinetics

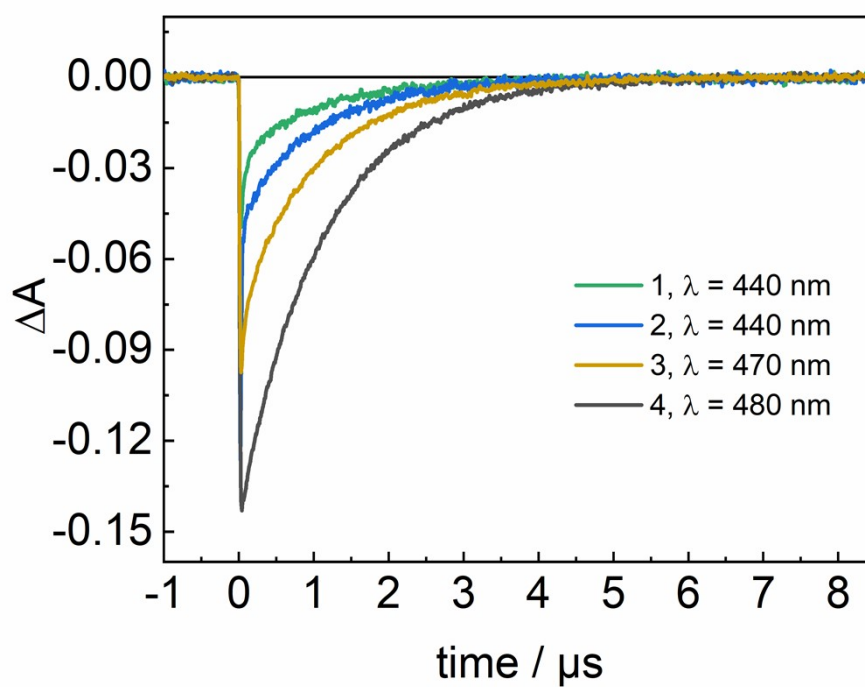


Figure S4. Transient kinetics obtained for the dyads at indicated wavelengths in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (4:1). Optically matched absorption at 460 nm ($A_{460} = 0.40$). Size of the signals agree with the excited state lifetimes

PET in the presence of 20 mM MV²⁺

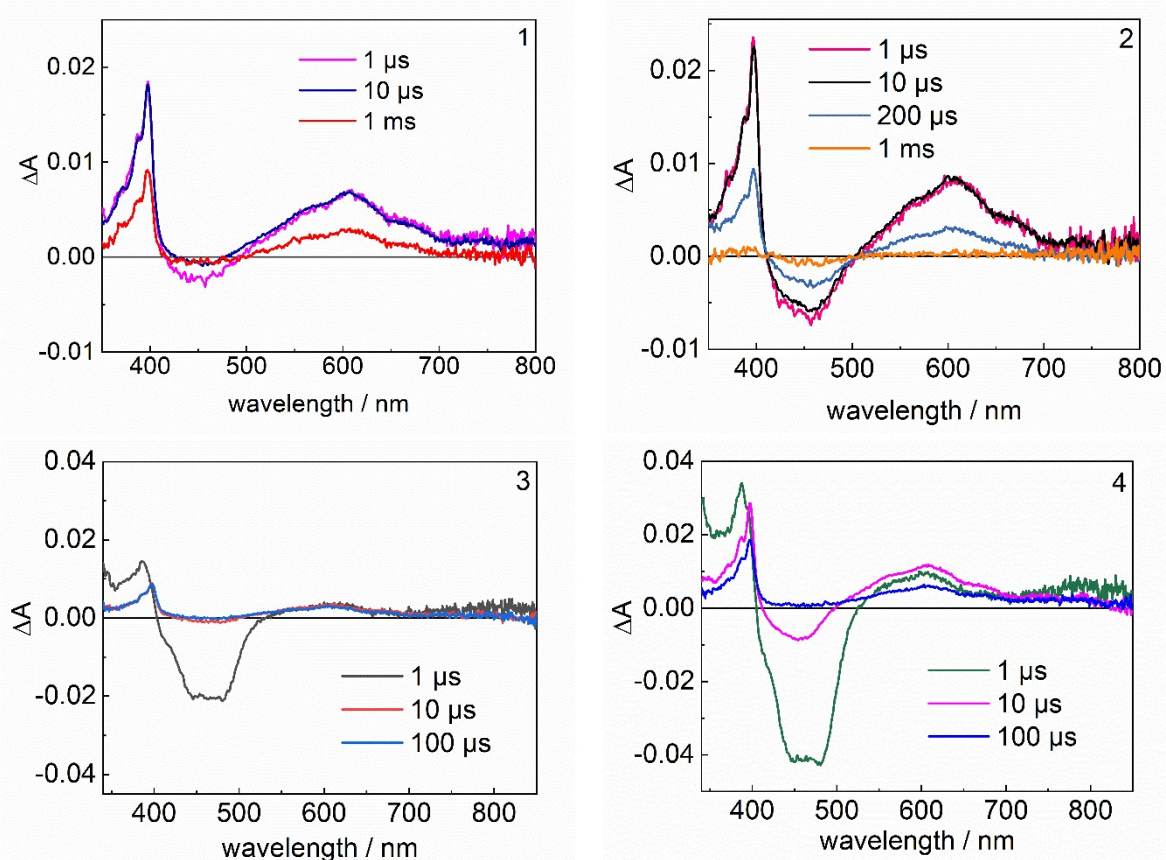


Figure S5. Differential transient absorption spectra in the presence of 20 mM MV²⁺ for the different compounds in H₂O/CH₃CN (4:1) argon-purged solution. Solutions excited at 460 nm with a laser energy ~10 mJ, absorption at excitation wavelength: 0.40

Simulations

All the parameters resulting from simulations are given in the table below: k_{ET} is the rate constant for interaction with MV²⁺, k_{IET} is the rate for Fe^{II} oxidation, k_{IET1} the recombination rate between MV^{•+} and Ru^{III}, while k_{IET2} is that between MV^{•+} and Fe^{II}. Φ_{IET} is the yield for the intramolecular oxidation of Fe^{III}, obtained as the ration of Fe^{III} maximum concentration over the Ru^{III} concentration.

Compound	$k_{ET} / \text{M}^{-1} \text{s}^{-1}$	k_{IET} / s^{-1}	$k_{REC1} / \text{M}^{-1} \text{s}^{-1}$	$k_{REC2} / \text{M}^{-1} \text{s}^{-1}$	Φ_{IET}
1	3.2×10^8	3100	2.2×10^9	2.3×10^9	0.55
2	3.2×10^8	620	2.0×10^9	2.0×10^9	0.24
3	3.5×10^7	11000	2.7×10^9	2.4×10^9	0.87
4	3.5×10^7	8300	2.6×10^9	2.3×10^9	0.75

Table S1. Summary of the simulations results.

Fits results

Complex 1

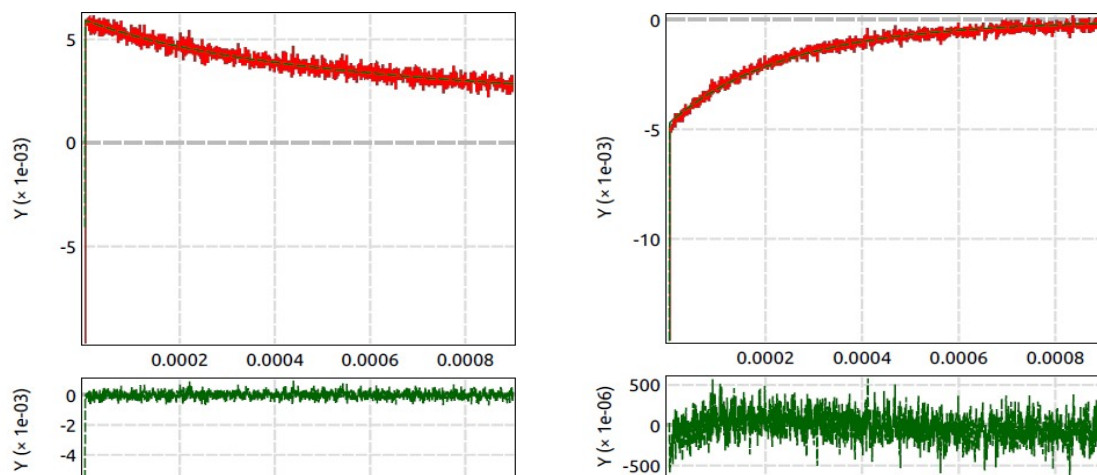


Figure S6. Global fit obtained for complex 1: left, 605 nm; right 450 nm

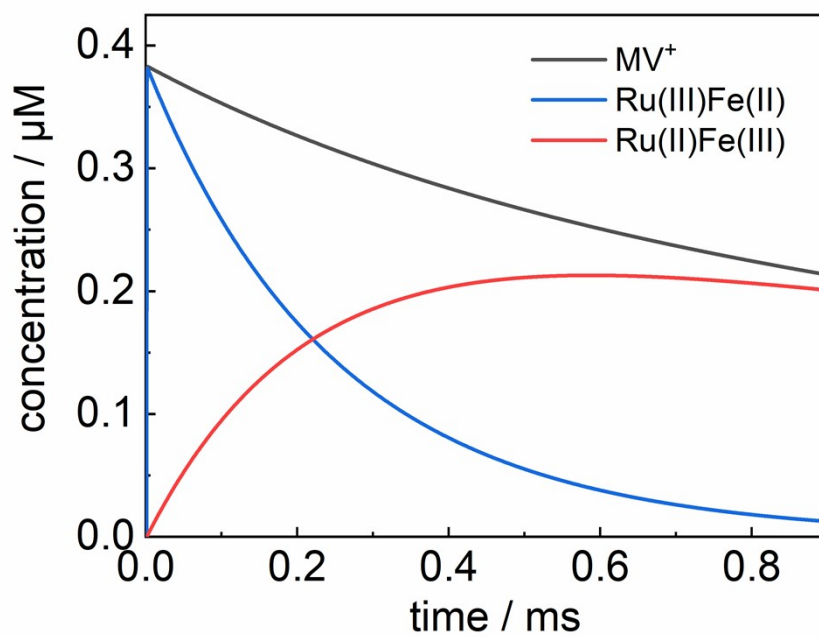


Figure S7. Time-evolution of concentration of different species for 1 and MV^{2+}

Complex 2

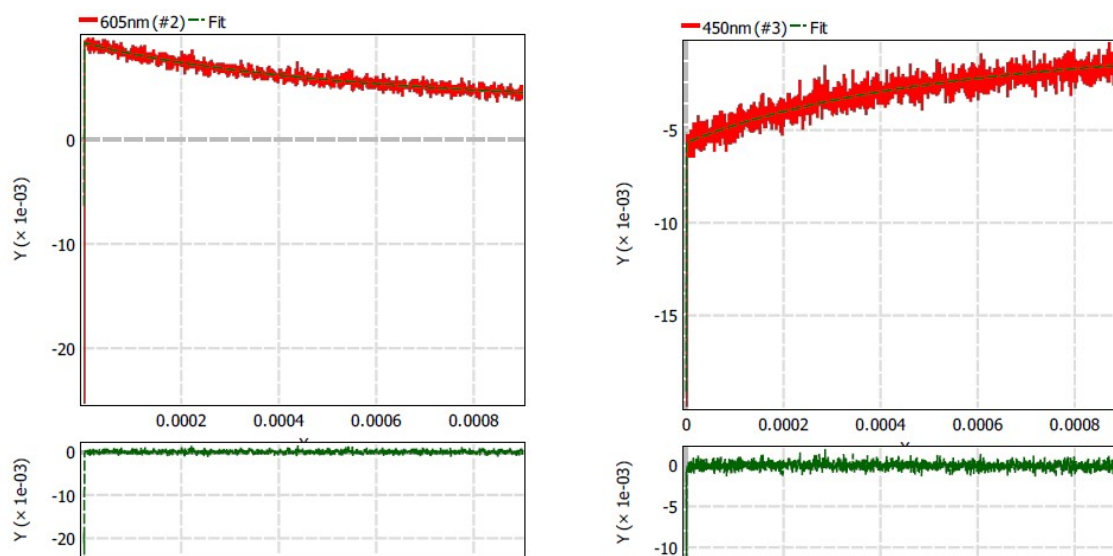


Figure S 8. Global fit obtained for complex 2: left, 605 nm; right 450 nm

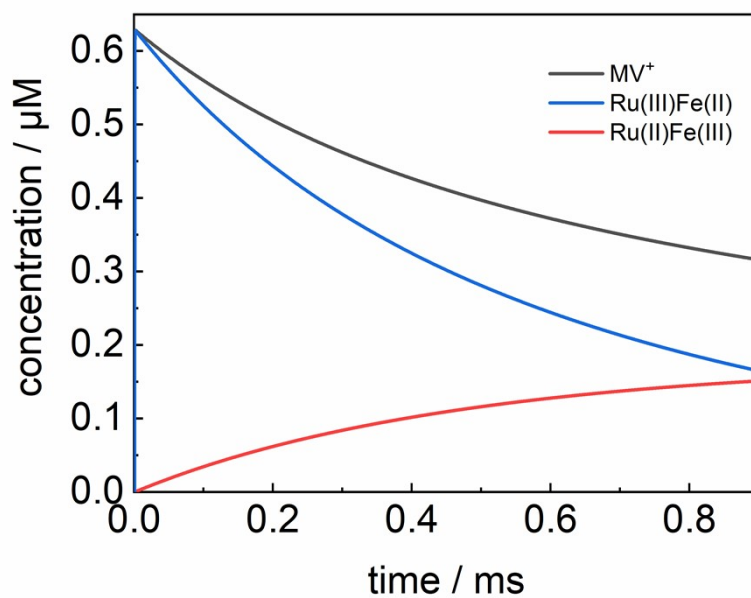


Figure S 9. Time-evolution of concentration of different species for 2 and MV^{2+}

Complex 3

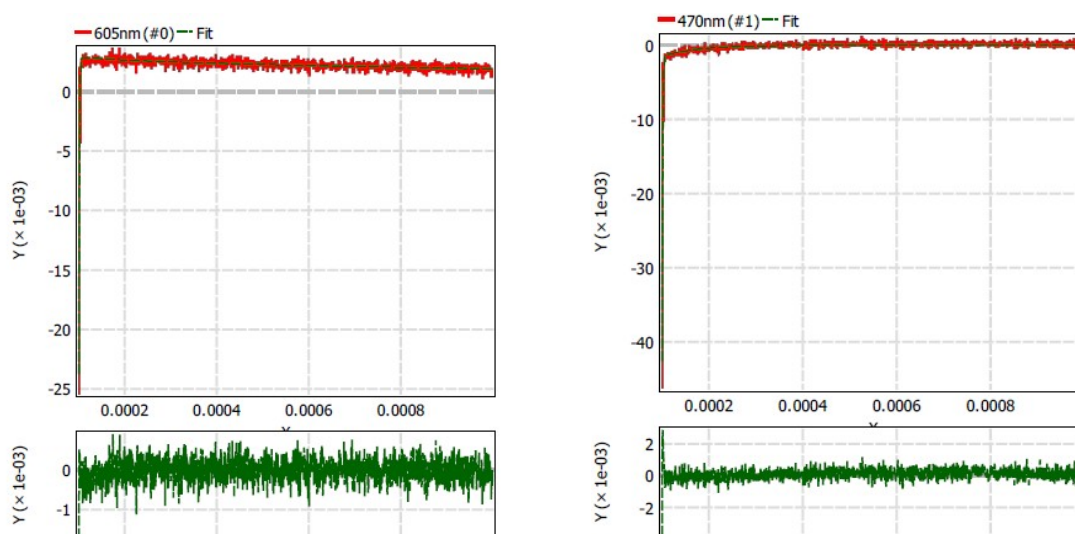


Figure S10. Global fit obtained for complex 3: left, 605 nm; right 470 nm

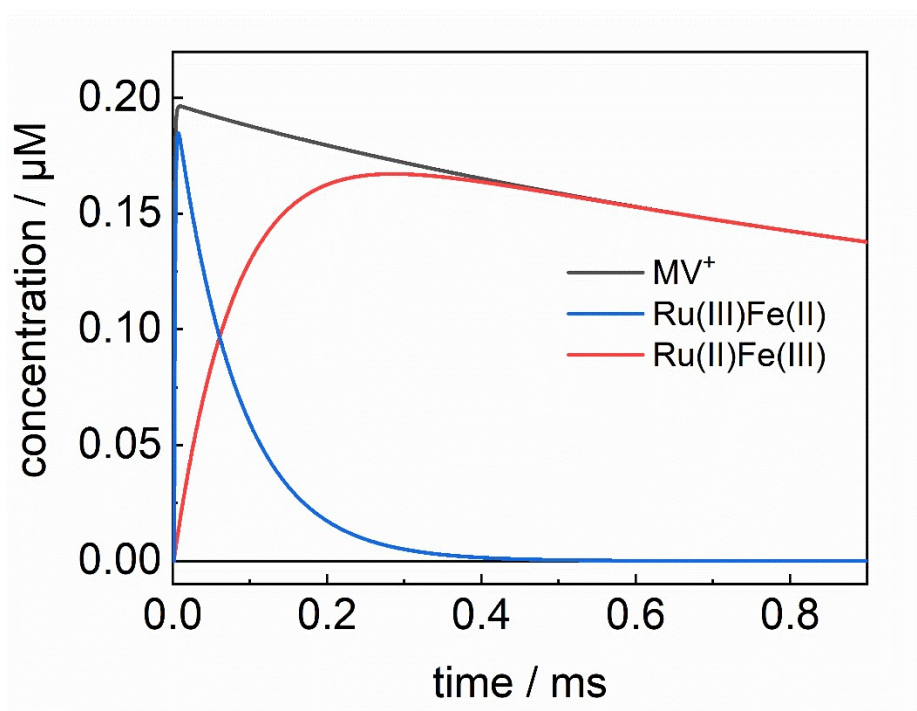


Figure S11. Time-evolution of concentration of different species for 3 and MV²⁺

Complex 4

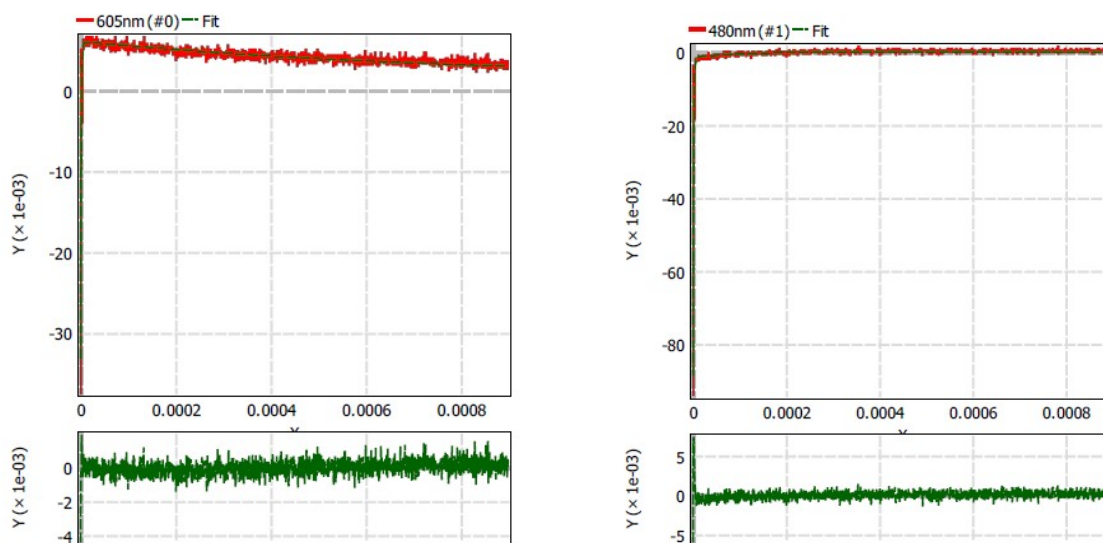


Figure S12. Global fit obtained for complex 4: left, 605 nm; right 480 nm

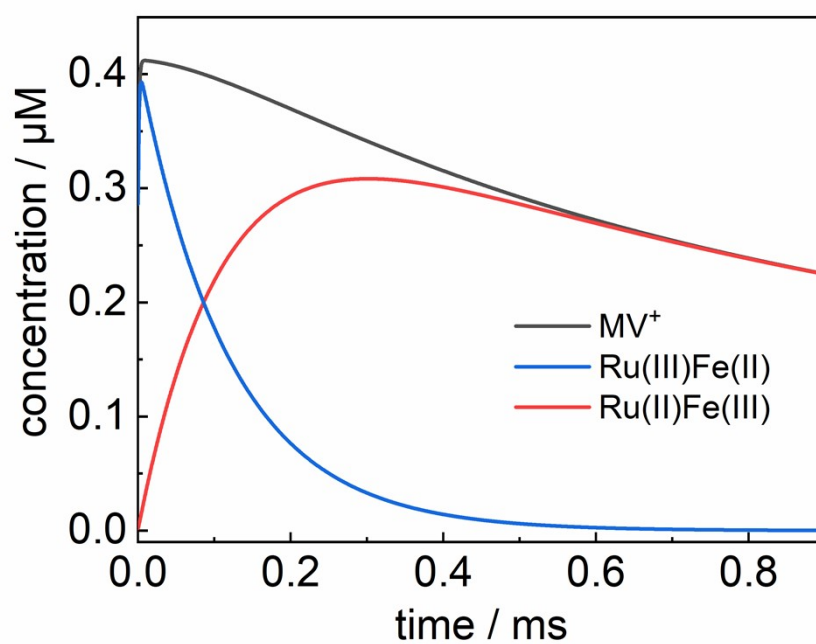


Figure S13. Time-evolution of concentration of different species for 4 and MV^{2+}

Activation energy plots

Values of λ and H_{AB} have been obtained from Marcus equation¹⁶

$$k_{IET} = \frac{2}{\hbar} H_{AB}^2 \frac{1}{\sqrt{4\pi k_B \lambda T}} \times e^{-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}}$$

Where \hbar is the reduced Plank constant (6.58×10^{-16} eV s⁻¹) and k_B is the Boltzmann constant (0.86×10^{-4} eV). By plotting $\ln(k_{IET} \times T^{1/2})$ vs $1/T$, the slope of the linear fit corresponds to the activation energy E_A

$$E_A = \frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B}$$

and the intercept to

$$\ln\left(\frac{H_{AB}^2}{\hbar} \sqrt{\frac{4\pi}{\lambda k_B}}\right)$$

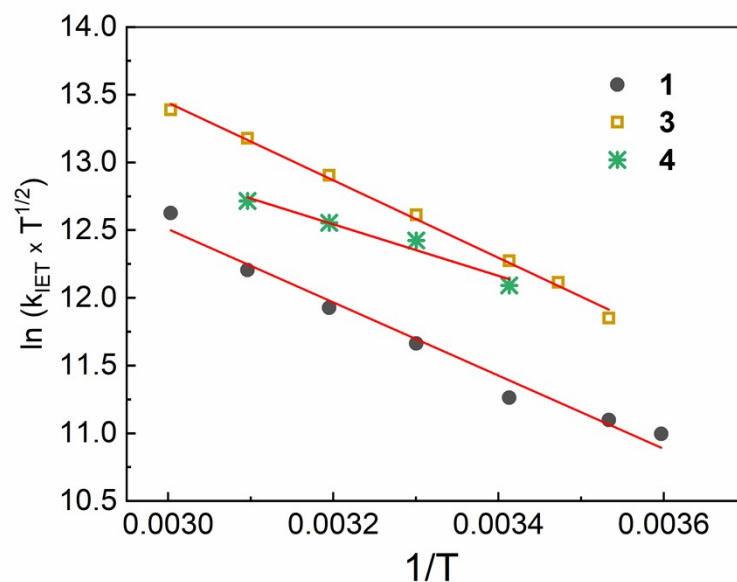


Figure S14. Activation energy plots for complexes **1**, **2** and **4** in H₂O/CH₃CN (4:1) in the presence of 20 mM MV²⁺