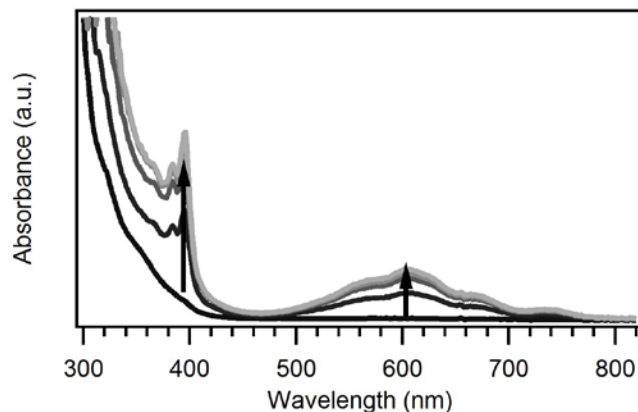


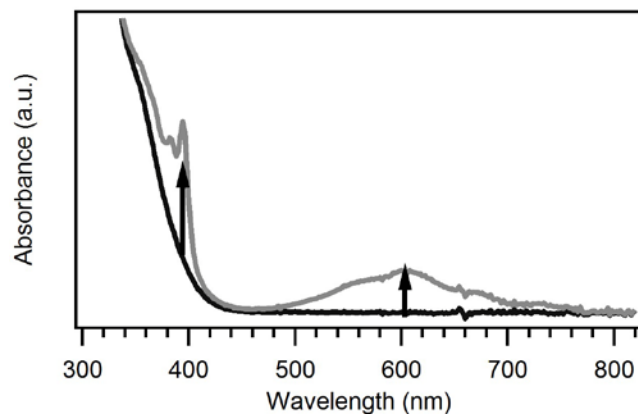
## Supporting Information

### Redox Reactivity of Photogenerated Osmium(II) Complexes

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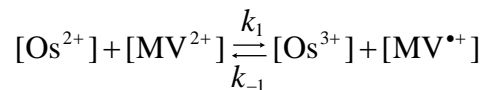


**Figure S1** Steady-state absorbance spectra obtained at intervals upon irradiation ( $\lambda=355$  nm) of  $[\text{Os}(\text{NH}_3)_5\text{N}_2][\text{PF}_6]_2$  and  $[\text{MV}][\text{PF}_6]_2$  in acetonitrile solution indicate the formation of reduced methyl viologen ( $\text{MV}^{\bullet+}$ ). Sample conditions: 3.5 mM  $[\text{Os}(\text{NH}_3)_5\text{N}_2][\text{PF}_6]_2$ , 1.2 mM  $[\text{MV}][\text{PF}_6]_2$ , 100 mM  $[\text{tBu}_4\text{N}][\text{PF}_6]$ .



**Figure S2** Steady-state absorbance spectra obtained at intervals upon irradiation ( $\lambda=355$  nm) of  $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$  and  $[\text{MV}]\text{Cl}_2$  in aqueous solution indicate the formation of reduced methyl viologen ( $\text{MV}^{\bullet+}$ ). Sample conditions: 3.5 mM  $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ , 0.5 mM  $[\text{MV}]\text{Cl}_2$ , 100 mM NaPi, pH 3.

## Kinetics Simulations



In acetonitrile, the standard free-energy change for the reaction, is likely to be greater than zero, implying that  $k_1 < k_{-1}$ . In this case, the kinetics of the reverse reaction must be taken into account, and the simple pseudo-first-order approximation will not necessarily be valid.

The differential equation describing the rate of  $[\text{MV}^{\bullet+}]$  formation is:

$$\frac{d[\text{MV}^{\bullet+}]}{dt} = k_1[\text{Os}^{2+}][\text{MV}^{2+}] - k_{-1}[\text{Os}^{3+}][\text{MV}^{\bullet+}] = (k_1 - k_{-1})[\text{MV}^{\bullet+}]^2 - k_1([\text{Os}^{2+}]_0 + [\text{MV}^{2+}]_0)[\text{MV}^{\bullet+}] + k_1[\text{Os}^{2+}]_0[\text{MV}^{2+}]_0$$

In this expression,  $[\text{Os}^{2+}]_0$  is the concentration of  $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{CH}_3\text{CN})]^{2+}$ , formed by the laser flash, prior to reaction with  $\text{MV}^{2+}$ , and  $[\text{MV}^{2+}]_0$  is the total concentration of  $\text{MV}^{2+}$  added to the solution. The solution

$$[\text{MV}^{\bullet+}] = \gamma \frac{[\gamma + u_0 - (\gamma - u_0)e^{-2\gamma(k_{-1}-k_1)t}]}{[\gamma + u_0 + (\gamma - u_0)e^{-2\gamma(k_{-1}-k_1)t}]} - \frac{k_1([\text{Os}^{2+}]_0 + [\text{MV}^{2+}]_0)}{2(k_{-1} - k_1)}$$

to this differential equation in the limit where  $k_1 < k_{-1}$  is:

where

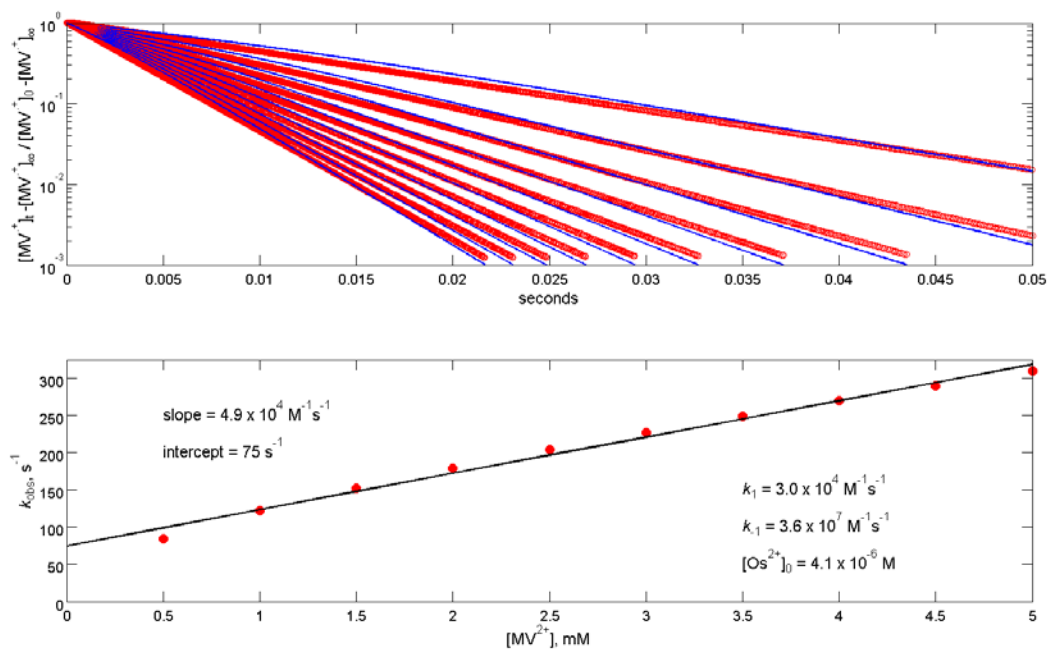
In the general case, the kinetics of  $[\text{MV}^{\bullet+}]$  formation will be nearly exponential, but not exactly so. Simulations of the kinetics using selected values of  $k_1$ ,  $k_{-1}$ ,  $[\text{Os}^{2+}]_0$ , and a range of  $[\text{MV}^{2+}]_0$  concentrations

$$\gamma^2 = \frac{k_1^2([\text{Os}^{2+}]_0 + [\text{MV}^{2+}]_0)^2}{4(k_{-1} - k_1)^2} + \frac{k_1[\text{Os}^{2+}]_0[\text{MV}^{2+}]_0}{(k_{-1} - k_1)} \quad \text{and} \quad u_0 = \frac{k_1([\text{Os}^{2+}]_0 + [\text{MV}^{2+}]_0)}{2(k_{-1} - k_1)}$$

are shown in Figure S3. It is clear that the kinetics are not single exponential, but the deviation of exponential behavior would be difficult to detect with modest noise on the experimental data.

The lower pane in Figure S3 shows that, with the indicated parameters, a plot of  $k_{\text{obs}}$  vs.  $[\text{MV}^{2+}]_0$  agrees reasonably well with that shown in Figure 3 of the text. In particular, the plot exhibits a nonzero intercept.

The  $k_1/k_{-1}$  ratio ( $8.3 \times 10^{-4}$ ) implies that  $\Delta G^\circ = +0.18$  eV, in remarkably good agreement with values extracted from electrochemical measurements (see text).



**Figure S3.** (*upper*) Simulated  $[MV^{2+}]$  kinetics (represented as a fractional completion function, blue line) and best exponential fits to the data (red circles). The different plots correspond to  $[MV^{2+}]_0^0$  values of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 mM, using:  $k_1 = 3.0 \times 10^4 M^{-1} s^{-1}$ ;  $k_{-1} = 3.6 \times 10^7 M^{-1} s^{-1}$ ; and  $[Os^{2+}]_0 = 4.1 \times 10^{-6} M$ . (*lower*) Best-fit rate constants extracted from the simulations in the upper panel (red circles) plotted as a function of  $[MV^{2+}]_0$ . The black line is the best linear fit to the data with the indicated slope and intercept.