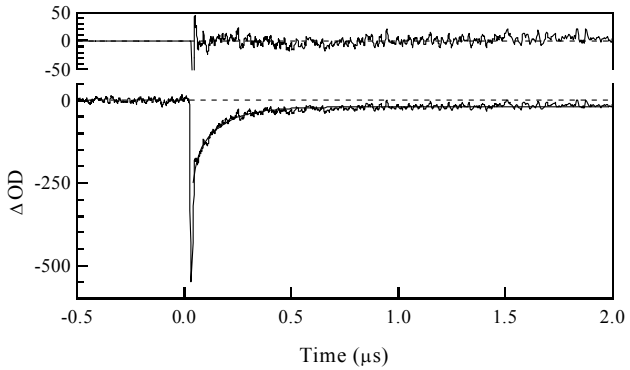
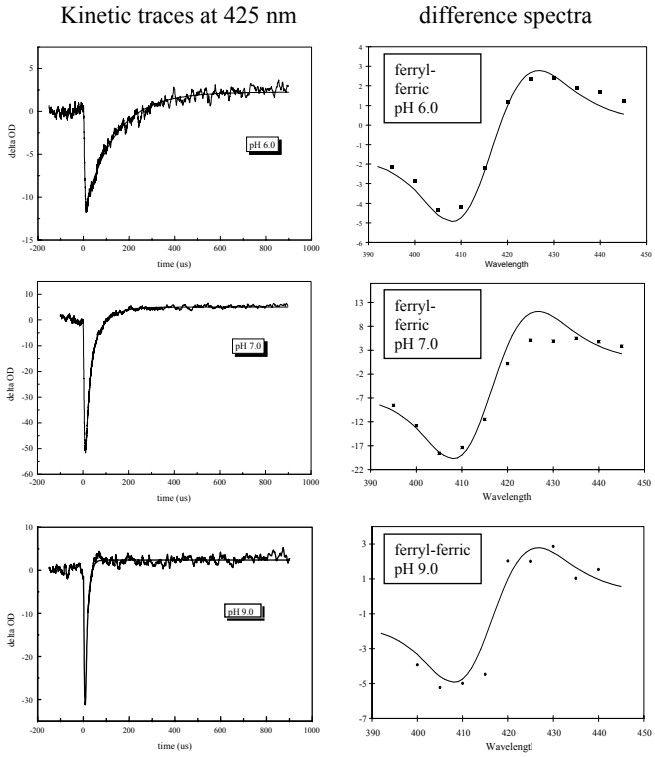
Electron Transfer Chemistry of Ru-linker-(heme)-modified Myoglobin: Rapid Intraprotein Reduction of a Photogenerated Porphyrin Cation Radical. *Chad E. Immoos, Angel J. Di Bilio, Michael S. Cohen, Wytze Van der Veer, Harry B. Gray, and Patrick J. Farmer*

(Suppoting Information)

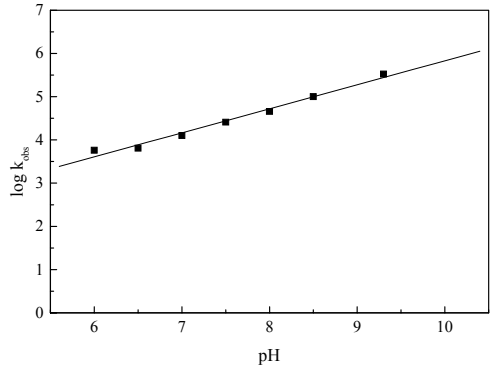


S1. Transient absorbance change at 410 nm (pH 7 buffer) of a 4 μM solution of RuC7MbFe^{3+} upon pulsed excitation at 480 nm. Top trace is the residual from the fit of back electron transfer ($Ru^{3+}Fe^{2+} \rightarrow Ru^{2+}Fe^{3+}$; $k = 1.7 \times 10^7$ sec^{-1}). The $Ru^{3+}Fe^{2+}$ state is formed at $>10^8$ s^{-1}. In the transient difference spectra (not shown), the absorbance increase due to formation of RuC7MbFe^{2+} and the corresponding bleach due to loss of RuC7MbFe^{3+} both occur within 10 ns.

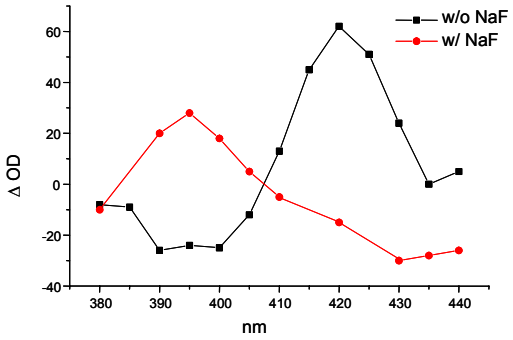
pH Dependence of Ferryl Formation



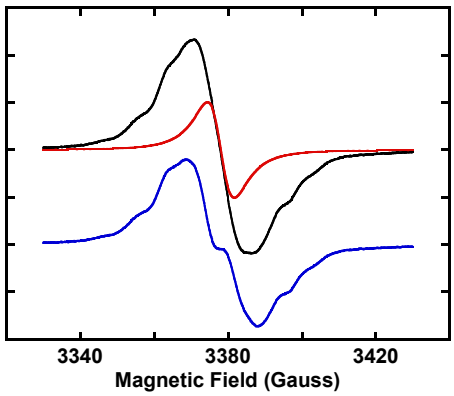
S2. Kinetics traces (425 nm) and transient difference spectra after 1 ms for oxidative flash-quench experiments at variable pH. Note that while the rate of porphyrin cation radical ($P^{\bullet+}$) reduction increases dramatically, the overall yield of ferryl (as measured by the rise over baseline after 1 ms) does not significantly increase with rising pH. This suggests that the competitive reduction by protein residues is likewise pH dependent.



S3. pH dependence of log*k* for $P^{\bullet+}$ reduction (monitored at 425 nm) in RuC7Mb. The slope of the line is ca. 0.5, much less than that predicted for simple ferryl formation.



S4. Comparative transient difference spectra recorded 1 ms after flash-quench (pH 7) for RuC7Mb in the presence and absence of NaF, demonstrating the F^- inhibition of ferryl formation.



S5. Subtraction of the EPR signal in Figure 4**B** (see main text) from the signal in Figure 4**A** (taking into account that thawing/refreezing reduces the intensity of the first signal to about 20% of its original value) gives a spectrum (blue trace) with a hyperfine pattern that is strongly reminescent of a tyrosyl radical. However, this procedure gives only qualitative results, as the actual intensity of the "narrow" signal prior to thawing/refreezing and the contribution of $W14^{\bullet}$ are unknown.