SUPPORTING INFORMATION

Hole Hopping through Tryptophan in Cytochrome P450

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Additional Experimental Details

Laser transient spectroscopy. Excitation pulse energies were in the range of 5-10 mJ/pulse. Samples were held in cuvettes with 1- cm optical path lengths and the absorbance at the 480-nm excitation wavelength was approximately 0.15.

The transient kinetics shown in manuscript Figures 3 and 4 are normalized to the prompt bleach at 440 nm. This bleach signal corresponds to formation of the $*Ru^{2+}$ excited state. By normalizing to the initial excited state concentration, the signals for the different proteins reflect the relative yields of subsequent intermediates that form.

Sample spectra. Absorption spectra of $[Ru(bpy)_2(IAphen)]^{2+}$, CYP102A1, Ru_{C97}(CYP102A1)W96, and *p*MeODMA$^{•+}$ have been reported previously.[1, 2]

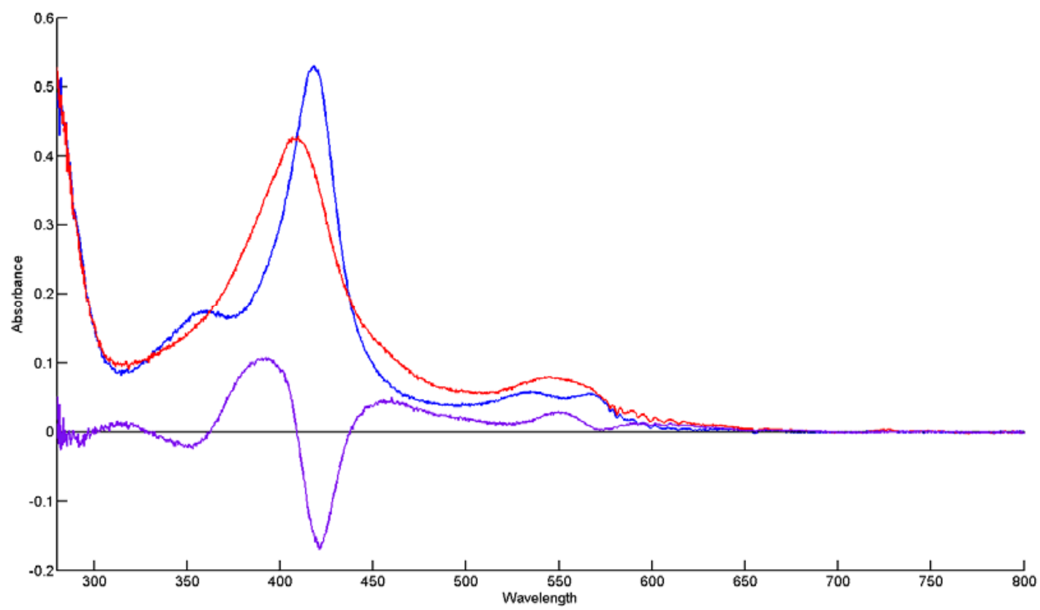

Figure S1. Spectra of ferric (blue) and ferrous (red) wild-type P450-BM3, and the ferrous - ferric difference spectrum (purple).

Electron Transfer Rate Calculations

Electron-transfer rate constants were estimated using the following semiclassical expression:[3]

$$k_{ET} = \left(10^{13}\,s^{-1}\right) \times e^{-\beta(r-r_o)} \times e^{-\frac{(\Delta G^\circ+\lambda)^2}{4\lambda k_B T}}$$

The following parameters were used for all estimated rate constants in Table S1: β = 1.1 Å^{-1}; r_o = 3 Å; λ = 0.8 eV; k_B = 8.6165 × 10^{-5} eV K^{-1}; T = 295 K.

Table S1. Estimated electron transfer rate constants

Reaction	ΔG°, eV	r, Å	k_{ET}, s^{-1}	$\tau_{ET} = k_{ET}^{-1}$
Ru_{C97}^{3+}-$Fe^{3+}P \rightarrow Ru_{C97}^{2+}$-$Fe^{3+}P^{\bullet+}$	–0.2	20.8	3.8×10^2	2.7 ms
Ru_{C97}^{3+}-W96 $\rightarrow Ru_{C97}^{2+}$-$W96^{\bullet+}$	–0.1	11.88	1.4×10^6	0.7 μs
$W96^{\bullet+}$- $Fe^{3+}P \rightarrow$ W96 - $Fe^{3+}P^{\bullet+}$	–0.1	7.15	2.5×10^8	4 ns
Ru_{C97}^{+}-$Fe^{3+}P \rightarrow Ru_{C97}^{2+}$-$Fe^{2+}P$	–0.9	19.5	1.2×10^5	8.6 μs
Ru_{C97}^{+}-$Fe^{3+}P \rightarrow Ru_{C97}^{2+}$-$Fe^{2+}P$	–0.9	23.8	1.0×10^3	1 ms

References

[1] Ener, M. E., Lee, Y. T., Winkler, J. R., Gray, H. B., and Cheruzel, L. (2010) Photooxidation of cytochrome P450-BM3, *Proc. Natl. Acad. Sci. USA 107*, 18783-18786.

[2] Sassoon, R. E., Gershuni, S., and Rabani, J. (1992) Photochemical generation and consequent stabilization of electron-transfer products on separate like-charged polyelectrolytes, *J. Phys. Chem. 96*, 4692-4698.

[3] Winkler, J. R., and Gray, H. B. (2014) Electron Flow through Metalloproteins, *Chem. Rev. 114*, 3369-3380.