Further Plots Showing the Luminescence Decay and Transient Absorbance of Wire:NOS Conjugates:

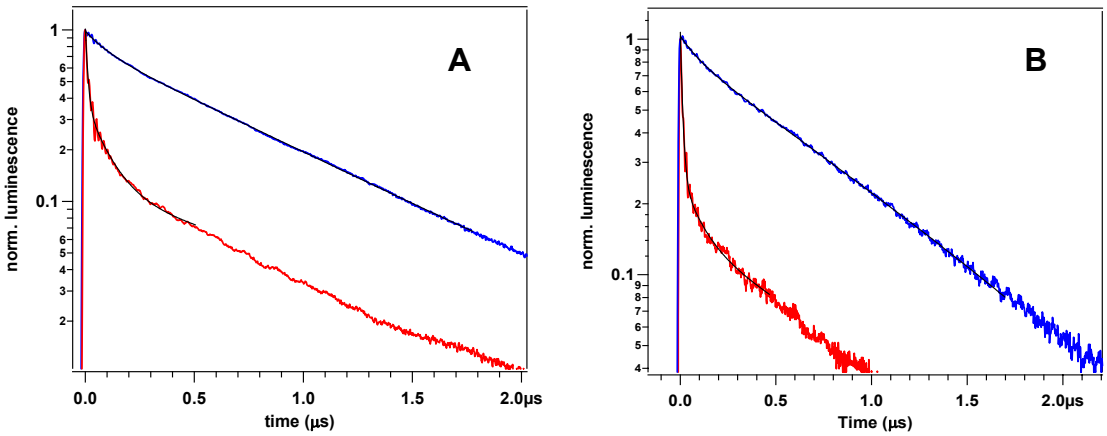


Figure S1. Semilog plot of luminescence at 560 nm vs. time for a) **2** (blue) and a 1:1 mixture of **2** and Δ65 (red) and b) **4** (blue) and a 1:1 mixture of **4** and Δ65 (red). The wire-only traces were fit to a bi-exponential decay with $k_{em1} = 1.0(1) \times 10^7$ s^{-1} and $k_{em2} = 1.35(5) \times 10^6$ s^{-1}. The protein plus wire traces were fit to three exponentials with k_{em1} and k_{em2} held constant at the values found for the wire-only traces. In the fits shown in black above, $k_{em3} = 9.1(6) \times 10^7$ s^{-1}, a number that is indistinguishable from the instrument response.

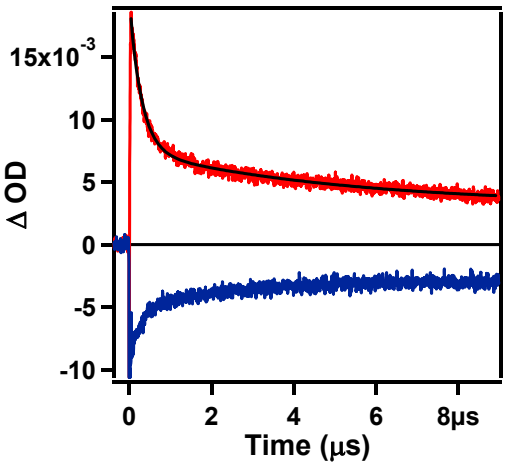


Figure S2. Transient absorbance of an approximate 1:1 mixture of **2** and Δ65 (5 µM) showing the prompt formation and initial decay of Fe(II). λ_{ex} = 355 nm, λ_{obs} = 445 nm (red), λ_{obs} = 422 nm (blue), bi-exponential fit ($k_{b1} = 4(1) \times 10^6$ s^{-1}, $k_{b2} = 2.1(1) \times 10^5$ s^{-1}, black).

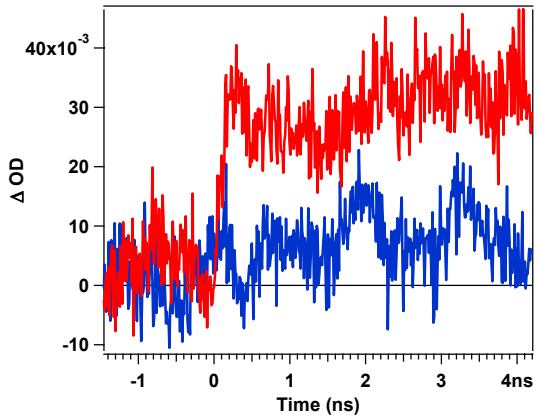


Figure S3. Transient absorbance at 442 nm of Δ65 (16 μM) bound to approximately 1.5 eq. **2** (red) or **4** (blue). The red trace shows the rapid formation (≤ 300 ps) of hemeFe(II) while the blue trace shows no indication of Fe(II) formation. λ_{ex} = 355 nm.

Simulation of the Proposed Electron Hopping Kinetics in Wire:NOS Conjugates:

The proposed electron hopping mechanism was simulated according to the expanded model shown in Scheme S1, leading to the following differential equations:

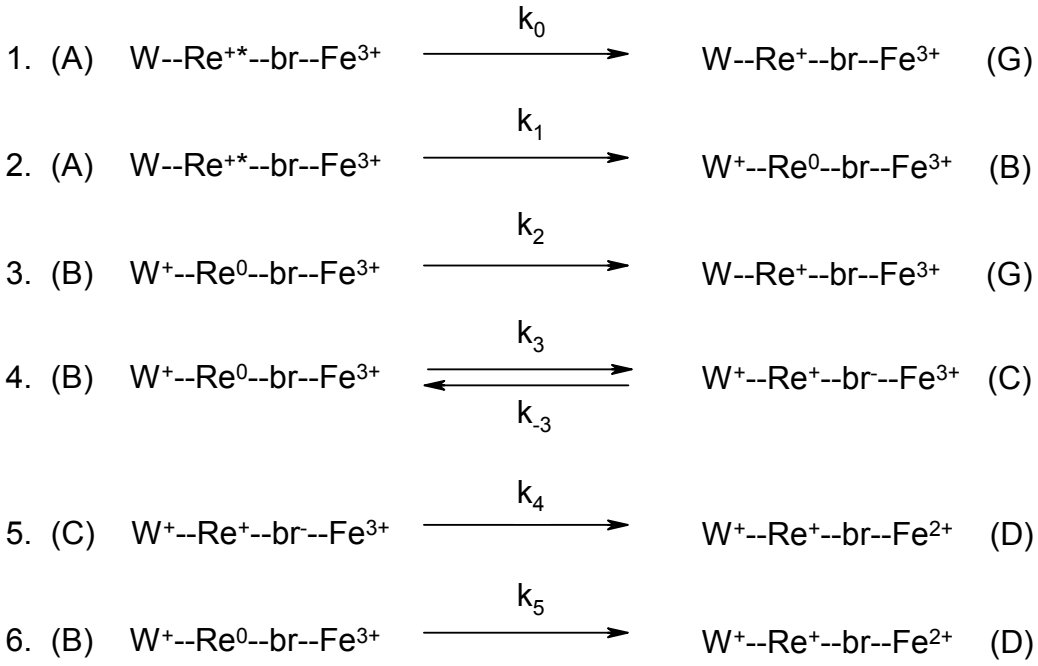
$$\frac{\partial A}{\partial t} = -(k_0 + k_1)A \qquad \text{(S1)}$$

$$\frac{\partial B}{\partial t} = k_1 A - (k_2 + k_3 + k_5)B + k_{-3}C \qquad \text{(S2)}$$

$$\frac{\partial C}{\partial t} = k_3 B - (k_{-3} + k_4)C \qquad \text{(S3)}$$

$$\frac{\partial D}{\partial t} = k_4 C + k_5 B \qquad \text{(S4)}$$

These equations were solved numerically in Matlab using the estimated distance and driving force parameters shown in Table S1 and λ = 0.8 V. The resulting ET kinetics are shown graphically in Figure S4.



Scheme S1. Expanded model for simulation of the hopping kinetics in photoexcited Re-Im-F_8bp-Im:Δ65. br ≡ perfluorobiphenyl bridge.

Table S1. Distance and driving force parameters for simulation of hopping kinetics.

Reaction (Scheme S1)	*estimated r (Å)*	*estimated -ΔG (V)*
1	NA	NA
2	3	0.35
3	3	2.4
4	6	-0.1-0.2
4 (reverse)	6	0.1-0.2
5	6	1.15-1.25
6	20	1.05

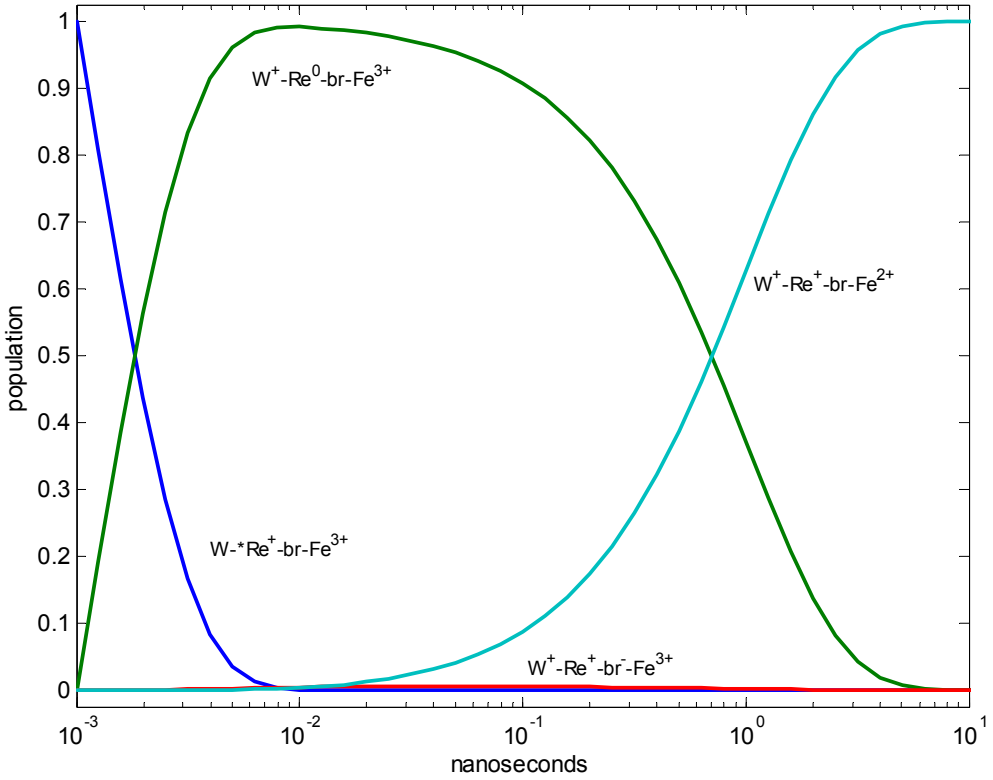


Figure S4. Simulation of the kinetics of formation and decay of the various redox states in the proposed hopping mechanism for ultrafast formation of Fe(II) (light blue trace).