

The ET rates were calculated from Equation 8 in the main text using the ΔG° and λ values given below.

Cc-CcP. For the ET from yeast Cc to the CcP W191⁺ radical, the driving force matches the reorganization energy ($-\Delta G^\circ \approx \lambda$), so that the ET is described by the maximum, activationless rate constant $k_{ET} \approx k_{ET,max}$ [S8]. For the ET to the CcP heme oxyferryl, $\lambda = 0.7$ eV [S9] and $\Delta G^\circ = -797$ mV can be calculated from the reduction potentials (ΔE) of yeast Cc, $\Delta E = 290$ mV [S10], and the CcP oxyferryl, $\Delta E = 1087$ mV [S11].

Cc-Cb₅. For the heme-heme ET between bovine Cb₅ and yeast Cc, $\lambda = 0.7$ eV [S12] and $\Delta G^\circ = -270$ mV is calculated from $\Delta E = 20$ mV for Cb₅ [S13] and $\Delta E = 290$ mV for Cc [S10].

Cc-Cbc₁. The reduction potentials of yeast Cc and Cc₁ hemes are nearly identical (i.e. $\Delta G^\circ \approx 0$) [S2], while the reorganization energy is estimated to be in the range $\lambda = 0.7 - 1$ eV [S2].

Cc-CCO. With $\Delta E = 245$ mV for the CuA site [S14] and $\Delta E = 220$ mV for the horse Cc bound to CCO [S15], $\Delta G^\circ = -25$ mV. The reorganization energy for the intermolecular ET step, λ , can be calculated from the reorganization energies of Cc, $\lambda_1 \approx 0.7$ eV [S16], and the CuA site, $\lambda_2 \approx 0.4$ eV [S17], as $\lambda = (\lambda_1 + \lambda_2)/2 = 0.55$ eV.

Cc-Fcb₂. With $\Delta E = 6$ mV for the heme b₅ of Fcb₂ [S18] and $\Delta E = 290$ mV for the yeast Cc [S10], $\Delta G^\circ = -284$ mV; $\lambda = 0.7$ eV as reported for the Cc-Cb₅ couple [S12].

Cc-SOX. With $\Delta E = 20$ mV for the heme group in Cb₅ [S13] and $\Delta E = 260$ mV for the horse Cc [S19], $\Delta G^\circ = -240$ mV; $\lambda = 0.7$ eV [S12].

Cc-Erv1. Given the values of $\Delta E = 290$ mV for the yeast Cc [S10], $\Delta E = 215$ mV for the Erv1 flavin [S20], and $\Delta E = 150$ mV for the C130-C133 disulfide in Erv1 [S20], the activation energy for the ET from the Erv1 flavin or C130-C133 disulfide is $\Delta G^\circ = -75$ mV or -140 mV, respectively. A range of reorganization energies ($\lambda = 0.7 - 1$ eV) was used in the calculations.