# SIMULTANEOUS TRUE, GATED, AND COUPLED ELECTRON-TRANSFER REACTIONS AND ENERGETICS OF PROTEIN REARRANGEMENT

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## Supplementary Information

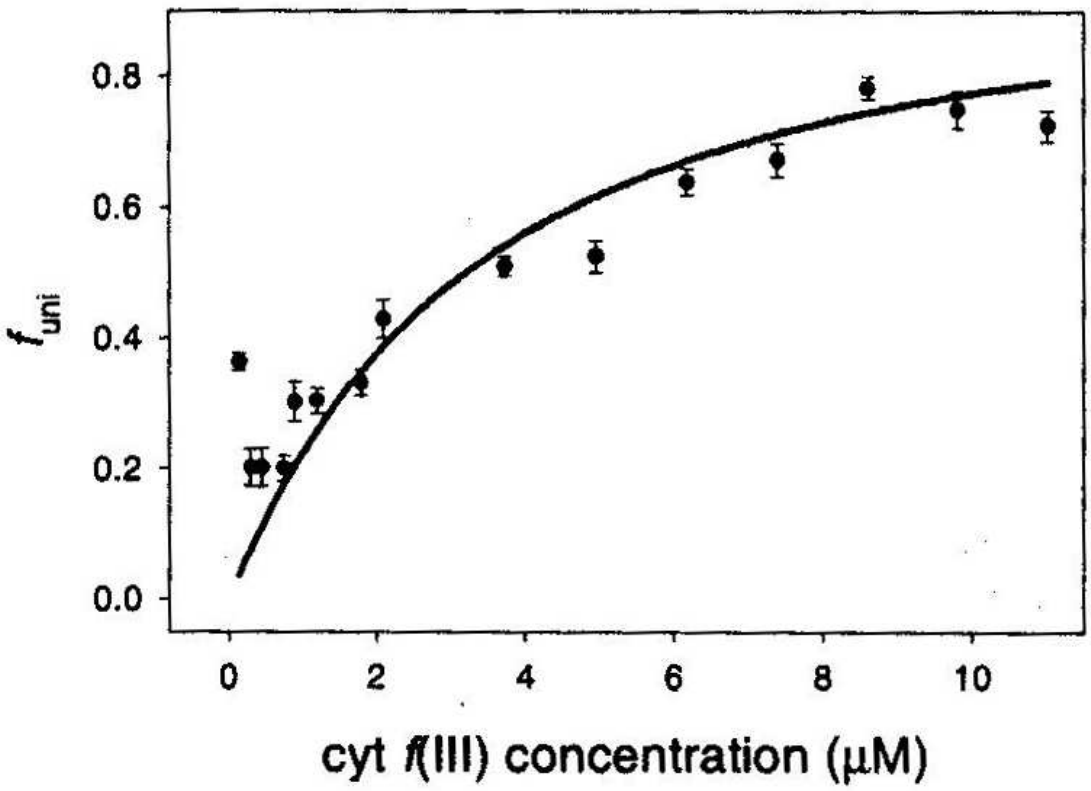


**Fig. S1.** Fraction of the reaction occuring by the unimolecular mechanism, via the persistent complex in Scheme 1, as a function of the cytochrome *f*(III) concentration.

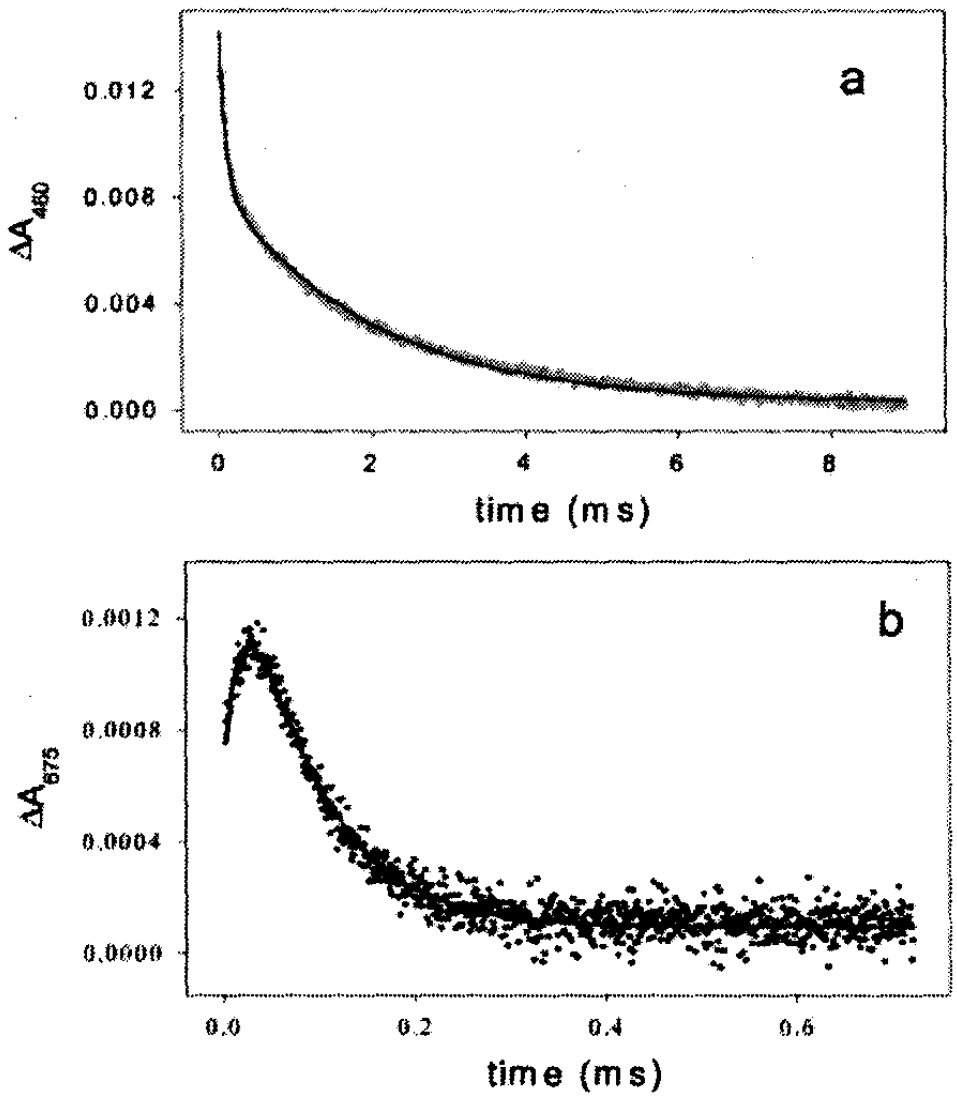


**Fig. S2.** Transient absorbance changes in a solution initially containing 1.0 μM zinc cytochrome $c_6$ and 3.0 μM cytochrome *f*(III) at pH 7.00 and room temperature. (a) Disappearance of the triplet state monitored at 460 nm. (b) Formation and disappearance of the cation radical monitored at 675 nm.

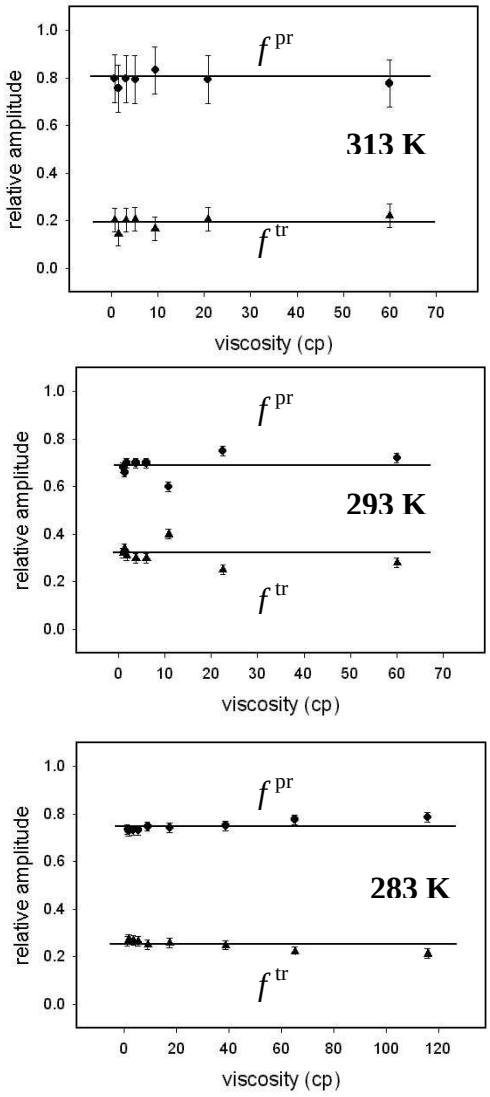


**Fig. S3.** Independence of solution viscosity of the relative amplitudes $f^{pr}$ and $f^{tr}$, respectively, of the electron-transfer reaction occurring within persistent (●) and transient (▲) protein complex in Scheme S1 at different temperatures. Viscosity of the sodium phosphate buffer solution at pH 7.0 and ionic strength 10 mM was adjusted with glycerol.

**Temperature Dependence of Association between Zinc Cytochrome $c_6$ and Cytochrome *f*(III).** Temperature effects on the association constant were studied in the temperature range from 0.5 to 40 $^{o}$C. The results in Figure S4 were fitted to equation S3.

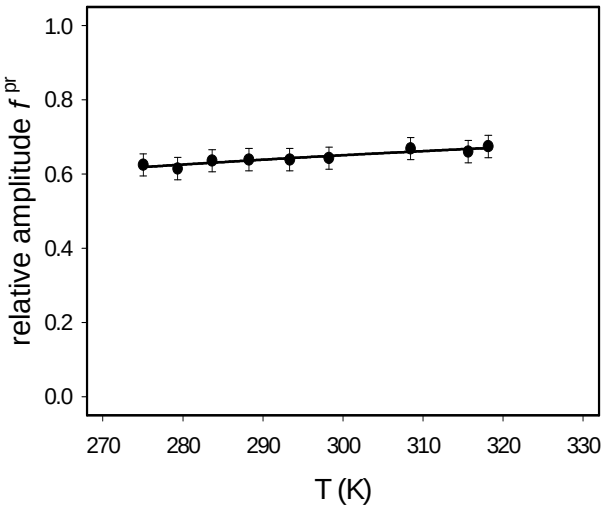


**Fig. S4.** Temperature dependence of the relative amplitude $f^{pr}$ for the reaction between $^3$Zncyt$c_6$ and cyt *f*(III), in sodium phosphate buffer at pH 7.0 and ionic strength 10 mM. The solid line is fitting to eq S3.

$$K_a=\exp(-\Delta G_a/RT) \quad \text{(S1)}$$

$$K_a=\exp(\Delta S_a/R)\exp(-\Delta H_a/RT) \quad \text{(S2)}$$

$$f^{pr}=(1/2[\text{Zncyt}c_6]_0)*\{[\text{Zncyt}c_6]_0 + [\text{cyt } f(\text{III})]_0 +(\exp(\Delta S_a/R)\exp(-\Delta H_a/RT))^{-1} - (([\text{Zncyt}c_6]_0+ [\text{cyt } f(\text{III})]_0 + (\exp(\Delta S_a/R)\exp(-\Delta H_a/RT))^{-1})^2 - 4[\text{Zncyt}c_6]_0[\text{cyt } f(\text{III})]_0)^{0.5}\} \quad \text{(S3)}$$

Values for enthalpy and entropy of association obtained from the fitting are $\Delta H_a$=(4±1) kJ/mol, and $\Delta S_a$=(127±4) JK$^{-1}$mol$^{-1}$. Free energy of association calculated from these two

parameters is $\Delta G_a$= - 33 kJ/mol. From the kinetic experiments, using relative amplitudes, we calculated the equilibrium constant [1], $K_a$=(6±2) $10^5$ $M^{-1}$, and from the eq S1 $\Delta G_a$= - 33 kJ/mol. These values of $\Delta G_a$ are obtained from the two different sets of experiments and are in full agreement.

[1] T. Ž. Grove, N. M. Kostić, J. Am. Chem. Soc. 125 (2003) 10598-10607.