Supplementary Material to

Interfacial bridge-mediated electron transfer: mechanistic analysis based on electrochemical kinetics and theoretical modelling

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DATA ANALYSIS

The open circuit potential (ILIT) transients were fit to[1, 2]

$$\Delta E_{oc}(t) = A'\Delta T^*(t) + B'k_m(E_i)\int_0^t \exp[-k_m(E_i)(t-\tau)]\Delta T^*(\tau)\,d\tau \qquad (S1)$$

where $\Delta E_{oc}(t)$ is the change in the open circuit potential as a function of time, A' is the amplitude of the initial thermal response, B' is the amplitude associated with the ET relaxation (see eqn (S2) below), and $k_m(E_i)$ is the measured (experimental) rate constant (s^{-1}) for this relaxation at the initial applied potential (E_i). The quantities A' and B' include E_{Soret} (see Fig. 4). (E_{Soret} is an effect of the temperature perturbation of the electrode, which causes a temperature gradient in the electrolyte solution , and this in turn causes a different free energy gradient for each type of ion in the solution; these free energy gradients induce a small potential difference in the electrolyte beyond the diffuse double layer.) $\Delta T^*(t \text{ and } \tau)$ in eqn (S1) is the convolution of the temperature perturbation at the working electrode/electrolyte interface and the ILIT instrument response function[3] divided by the interfacial potential change (ΔT_{eq}) that would be produced if all of the absorbed heat were uniformly distributed and none of this heat were lost to either the quartz disk or the electrolyte solution.[1-3] The parameter B' is defined by (for the equivalent circuit in Fig. 4)[2]

$$B' = \frac{\Delta E_{redox} - A'}{1+(1/\gamma)[(1+\omega(E_i))^2 / \omega(E_i)]} \qquad (S2)$$

where[4]

$$\gamma = \frac{N_T F^2}{RTC_{film}} \qquad (S3)$$

in which $N_T \ (= A(\Gamma_{ox} + \Gamma_{red}))$ is the total number of redox moieties in the mixed monolayer. The parameters ΔE_{redox} and $\omega(E_i)$ in eqn (S2) are defined by

$$\Delta E_{redox} = \Delta T_{eq} \frac{dE^{0'}}{dT} + \frac{\Delta T_{eq}}{T} (E_i - E^{0'}) \qquad (S4)$$

and

$$\omega(E_i) = \frac{\Gamma_{ox}}{\Gamma_{red}} = \exp[\ \frac{F}{RT} (E_i - E^{0'})\ ] \qquad (S5)$$

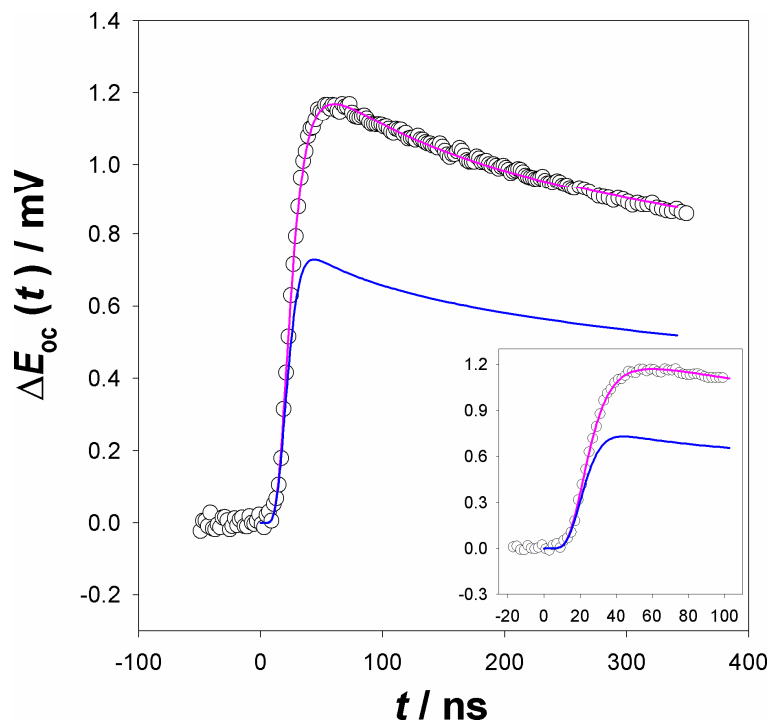An example of an ILIT transient (and the fit of this transient to eqn (S1)) is shown in Fig. S1.

Fig. S1. ILIT response (open circles) from a Au electrode coated with a mixed monolayer composed of Fc-OPV (n=2, number ii (see Fig. 5)) and $HS(CH_2)_9CH_3$ in contact with a 1.0M $HClO_4$ electrolyte solution at E_i = 325mV vs SSCE ($E^{0'}$ = 172mV vs SSCE (see Fig. S2)), T = 298K and ΔT_{eq} = 4.4K. The pink curve describes a fit of these data to eq. S1 resulting in A' = 0.88mV, B' = 0.60mV and $k_m(E_i)$ = 7.8x10^{7}s^{-1}. The blue curve represents the response that would be observed if there were no relaxation of the ILIT signal caused by electron-transfer between the electrode and the Fc redox couple. The insert contains these same data over a shorter time range.

From the definition of B' in eqn (S2), it is apparent that B' becomes negligibly small when either $\omega(E_i)$ >> 1.0 or $\omega(E_i)$ << 1.0. This observation ensures that we can never measure an electron-transfer rate constant at more than "moderate" reaction free energies ($|E_i - E^{0'}|$) in our ILIT experiments so that assuming that these rate constants behave (as a function of E_i) according to the Butler-Volmer formulation is always valid. The quantity $k_m(E_i)$, therefore, varies with potential according to[4]

$$k_m(E_i) = \frac{k^0\,\gamma\,\omega(E_i)^{1/2}}{1+\omega(E_i)}\left\{1+\frac{[1+\omega(E_i)]^2}{\gamma\,\omega(E_i)}\right\} \tag{S6}$$

and values for the parameters k^0, $E^{0'}$ and γ may be obtained from fits of the $k_m(E_i)$ versus E_i data to eqns (S5) and (S6). Figure S2 demonstrates a fit of $k_m(E_i)$ measured as a function of potential to eqn (S6). We emphasize that evaluations of γ and $E^{0'}$ obtained from fits such as those shown in Fig. S2 are the same (within experimental error) as those obtained from cyclic voltammograms.[4]
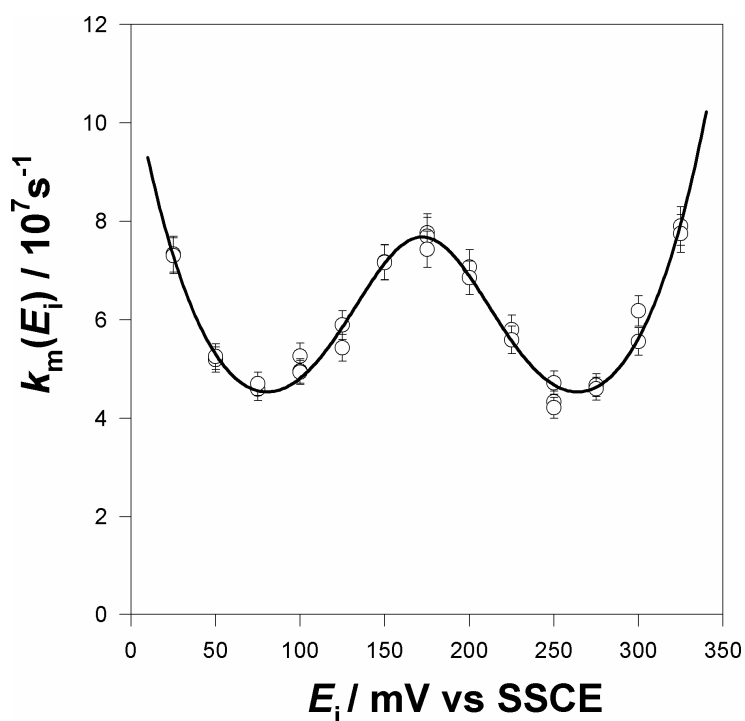

Fig. S2. $k_m(E_i)$ as a function of E_i at $T = 298K$ for the Au electrode/mixed monolayer combination described in the legend of Fig. S1. The solid line curve describes the fit of these data to eq. S6 resulting in $k^0 = 3.7\times10^6\,s^{-1}$, $E^{0'} = 172mV$ vs SSCE and $\gamma = 38$ (the γ calculated from the cyclic voltammogram of this monolayer is also 38).

[1]   J. F. Smalley, L. Geng, S. W. Feldberg, L. C. Rogers, and J. Leddy, *J. Electroanal. Chem.*, 1993, **356**, 181.

[2]   J. F. Smalley, S. W. Feldberg, C. E. D. Chidsey, M. R. Linford, M. D. Newton, and Y.-P. Liu, *J. Phys. Chem.*, 1995, **99**, 13141.

[3]   S. W. Feldberg, M. D. Newton, and J. F. Smalley, in 'Electroanalytical Chemistry', ed. A. J. Bard and I. Rubinstein, New York, NY, 2003, Vol. 22, pp. 101-180.

[4]   J. F. Smalley, Newton, M.D., and Feldberg, S.W., *Electrochem. Commun.*, 2000, 832.