Supporting Information for
Electron Transfer and Conductance Quantum

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1 Materials and Methods

Polycrystalline Gold Disk Electrodes (GDE) (METROHM, 2 mm diameter) were cleaned following the IUPAC procedure (*1*). After cleaning procedure the GDE is immersed in a 1 mM 11-ferrocenyl-undecanethiol (Sigma-Aldrich) ethanolic solution (for 12 h at room temperature). Electrodes were then rinsed with ethanol and water and dried under nitrogen prior to immersion in the electrochemical cell (a 5 mL volume compartment cell with the functionalized GDE working electrode, an Ag|AgCl reference and a platinum gauze counter electrode). Electrochemical Impedance Spectroscopy (EIS) measurements were carried out using a PC controlled AUTOLAB potentiostat PGSTAT30 equipped with an ADC750 and a FRA (Frequency Response Analyser) module. AC frequencies ranged from 1 MHz to 10 mHz, with an amplitude of 10 mV. All EIS data were checked regarding compliance with the constraints of linear systems theory by Kramers-Kronig using the appropriate routine of the FRA AUTOLAB software. Supporting electrolyte was 100 mM tetrabutylammonium hexafluorophosphate (Sigma Aldrich) in dichloromethane (Sigma Aldrich).

The electrolyte was de-oxygenated with bubbling argon and surface purging for the dura-

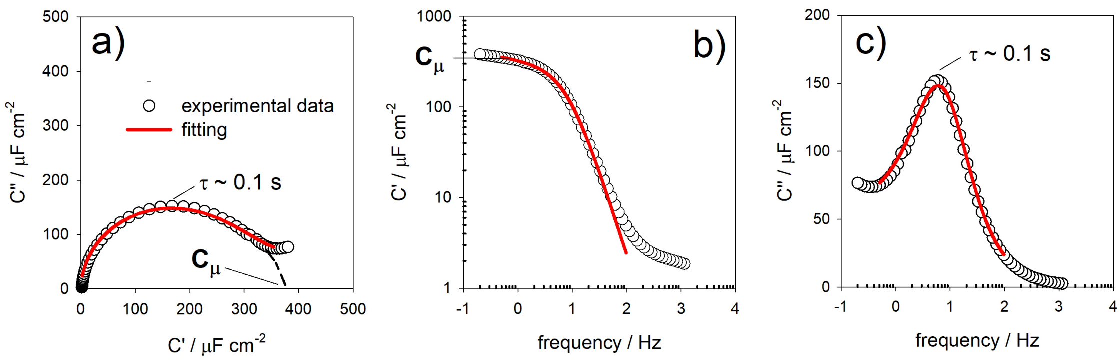

Figure 1: (a) Nyquist capacitive plot, being (b) and (c) Bode capacitive diagrams of $C^*(\omega)$. This type of capacitive spectra corresponds to the average response of the molecular ensemble and provides the values of C_μ and τ from where G can be obtained from the relationship $k = G/C_\mu$. C_μ can be obtained at the lower frequency as the diameter of the semicircle in (a) or in (b) as shown. τ is the product of R_{ct} and C_μ and $k = \tau^{-1} = G/C_\mu$, where $G = 1/R_{ct}$.

tion of the experiment. The obtained complex impedance $Z^*(\omega)$ function was converted into complex capacitance $C^*(\omega)$ using the following relationship $C^*(\omega) = 1/j\omega Z^*(\omega)$ in which ω is the angular frequency and $j = \sqrt{-1}$ the imaginary number. An example of data obtained at the formal potential (E_F) is exemplified in Figure 1 of this support information document from where k, G and C_μ were obtained, as a function of the electrode potential, as shown in the main text. The k, G and C_μ values can be obtained by either graphical analysis or alternatively by a mathematical fitting of data to an equivalent resistive-capacitive RC circuit. The later is exemplified in Figure 1 (observe the red line curve as the fitting of the RC-model to the experimental data points).

References and Notes

1. S. Trasatti, *Pure and Applied Chemistry* **63**, 711 (1991).