Supporting Information

The electrochemical response of cytochrome *c* immobilized on smooth and roughened silver and gold surfaces chemically modified with 11-mercaptounodecanoic acid

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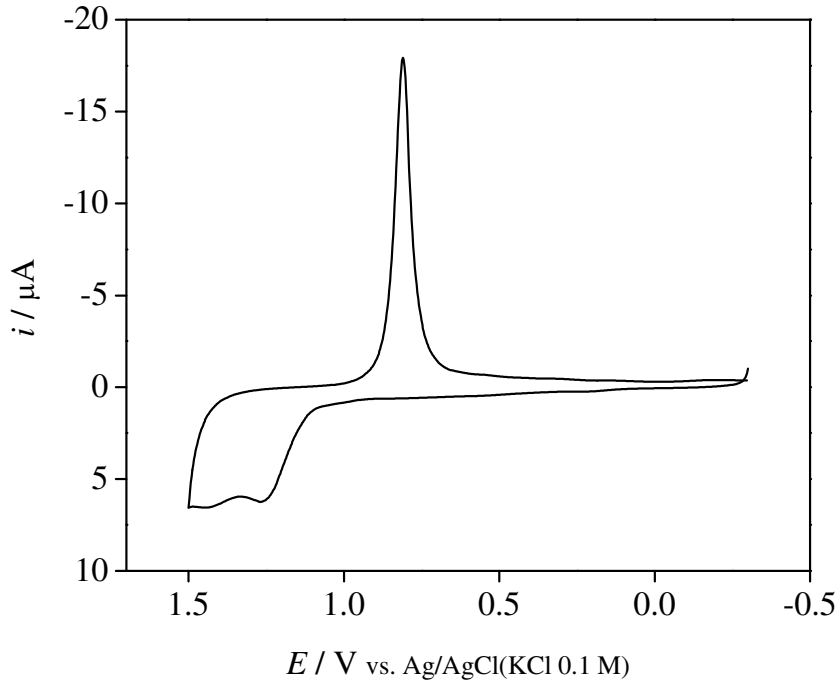

Figure S1. Electrochemical treatment of gold electrodes performed in 1 M H_2SO_4 at scan rate of 0.1 Vs^{-1}.

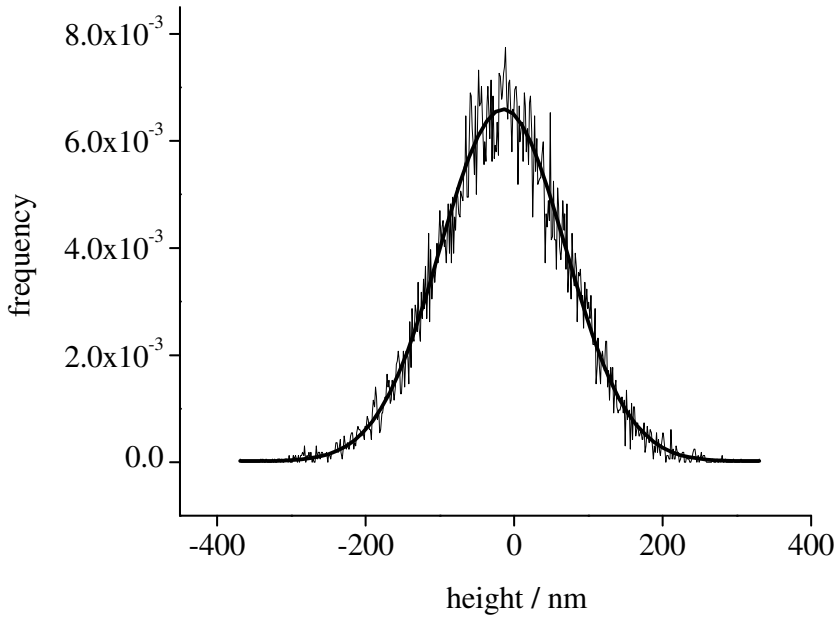

Figure S2. Gaussian distribution of surface feature dimensions on roughened silver electrodes. The thick solid line represents the fit to the experimental data.

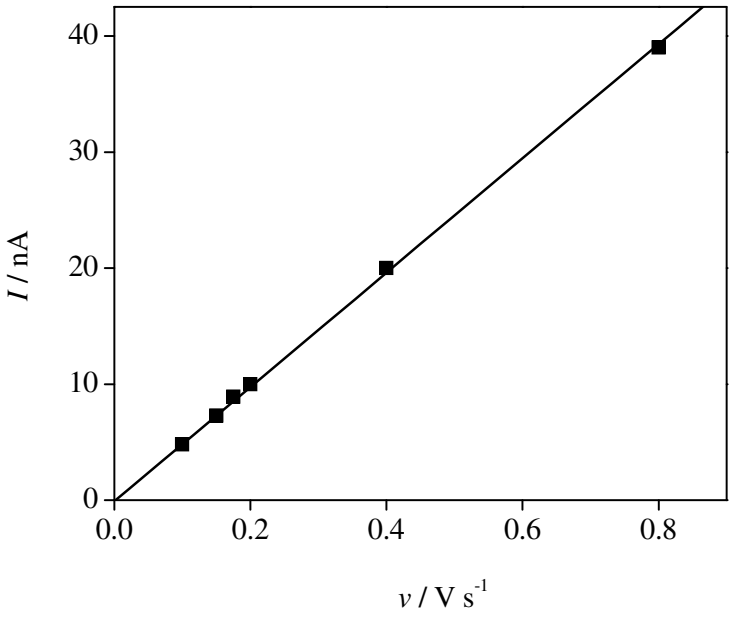

Figure S3. Linear plot of peak current vs. scan rate for Ag^{S}/MUA/cyt-c electrodes.

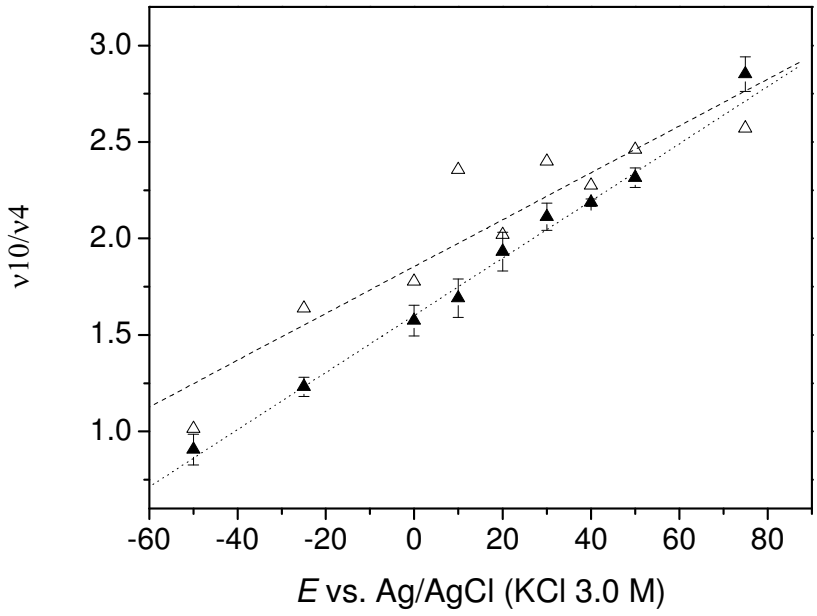

Figure S4. Ratio between the intensities of the ν_{10} and ν_4 modes in the SERR spectra of of cyt-*c* immobilized at Ag^R/MUA electrodes as a function of the applied potential immediately after protein incubation (full triangles), and after 24 hours of incubation at 4 °C in 10 mM phosphate buffer (open triangles). Potentials are expressed in mV vs. the Ag/AgCl (KCl 3.0 M). SERRS experiments were performed with 514-nm excitation.

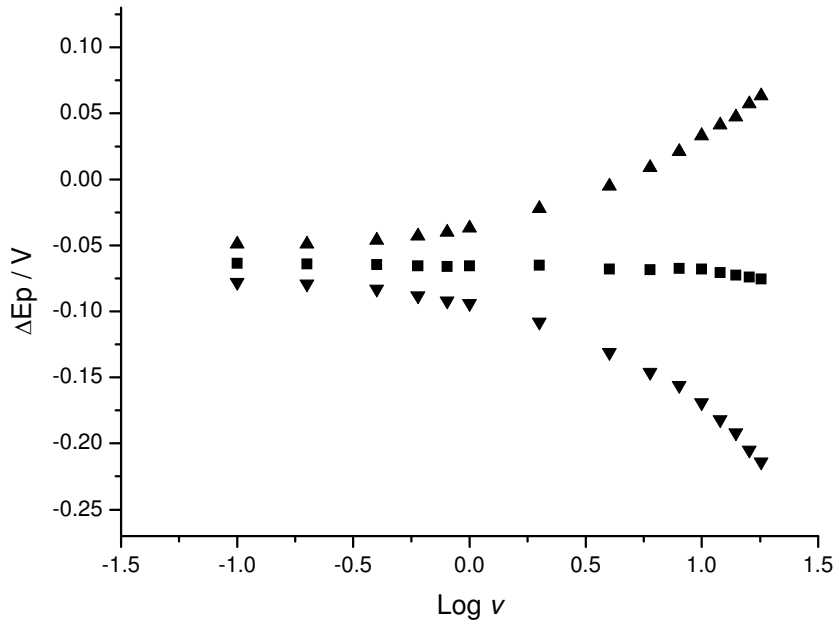

Figure S5. Trumpet plot for the Au/MUA/cyt-*c* system.

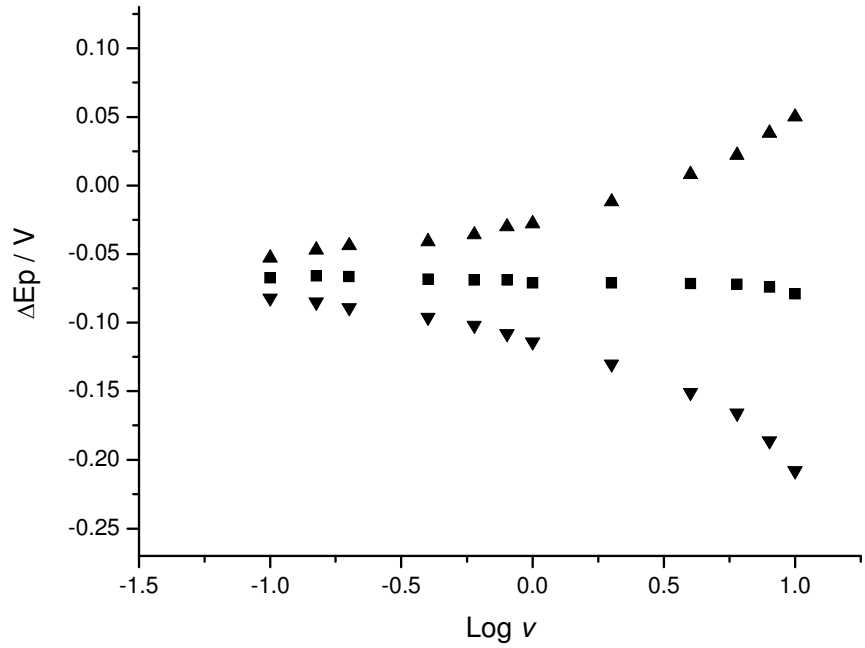

Figure S6. Trumpet plot for the Ag^{S}/MUA/cyt-*c* system.

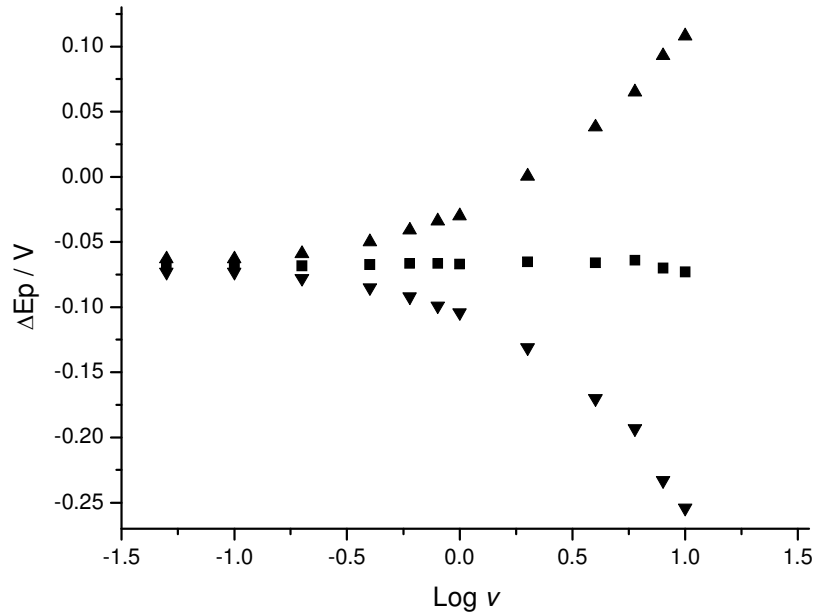

Figure S7. Trumpet plot for the Ag^R/MUA/cyt-*c* system immediately after protein immobilisation.

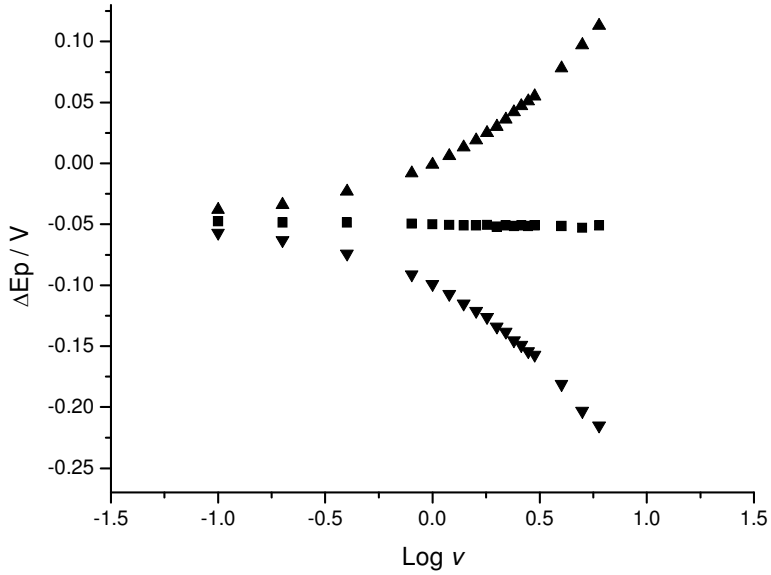

Figure S8. Trumpet plot for the time-dependent Ag^R/MUA/cyt-*c* system after 24 hours incubation.

Determination of the area of roughened Ag electrodes

The area of the roughened Ag electrode was determined according the capacitive current method as described by Hupp et al. (Hupp, J. T.; Larkin, D.; Weaver, M. J. *Surf. Sci.* **1983**, 125, 429-451).

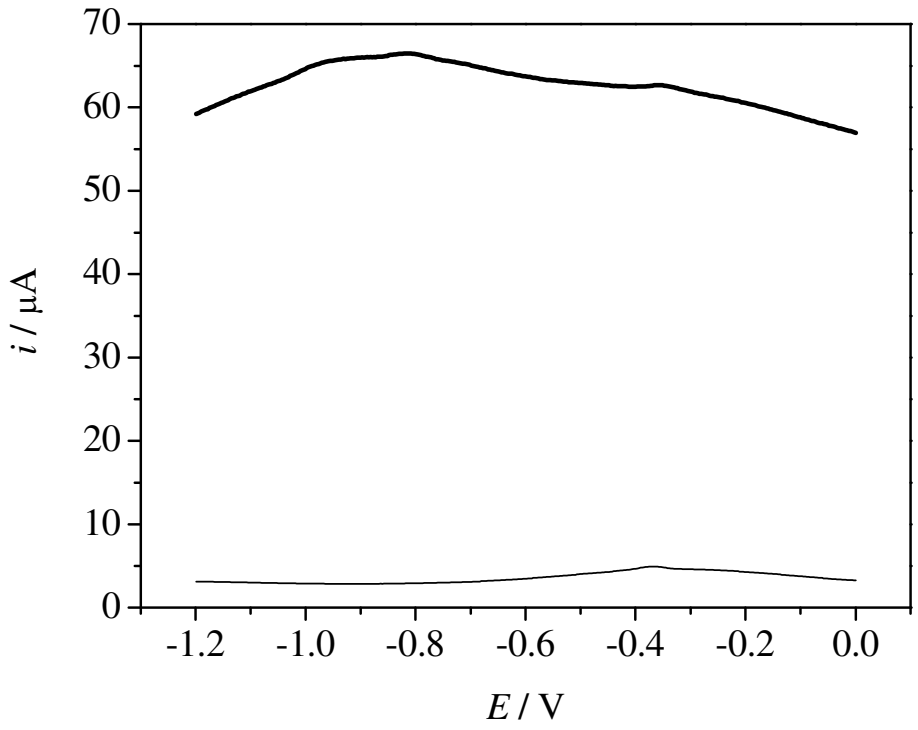

Figure S9. Capacitive plots of roughened (darkest trace) and smooth (lighter trace) Ag electrodes. The electrodes were treated as described in the Section 2.3. The roughening procedure described affords a roughness factor (R_f) of 20.6 ±0.8. The procedure adopted for the R_f determination was the same as described by Hupp *et al.* (Hupp, J. T.; Larkin, D. Wheaver, M. *J. Surf. Sci.* **1983**, *125*, 429-451).