SUPPORTING INFORMATION

Electrochemical Detection of pH-Responsive Grafted Catechol and Immobilized Cytochrome *c* Onto Lipid Deposit-Modified Glassy Carbon Surface

Estelle Lebègue[†,*], Ricardo O. Louro[‡] and Frédéric Barrière[†,*]

[†] Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes - UMR 6226, F-35000 Rennes, France.

[‡] Instituto de Tecnologia Química e Biológica, António Xavier, Universidade NOVA de Lisboa, 2780-157 Oeiras, Portugal.

Content:

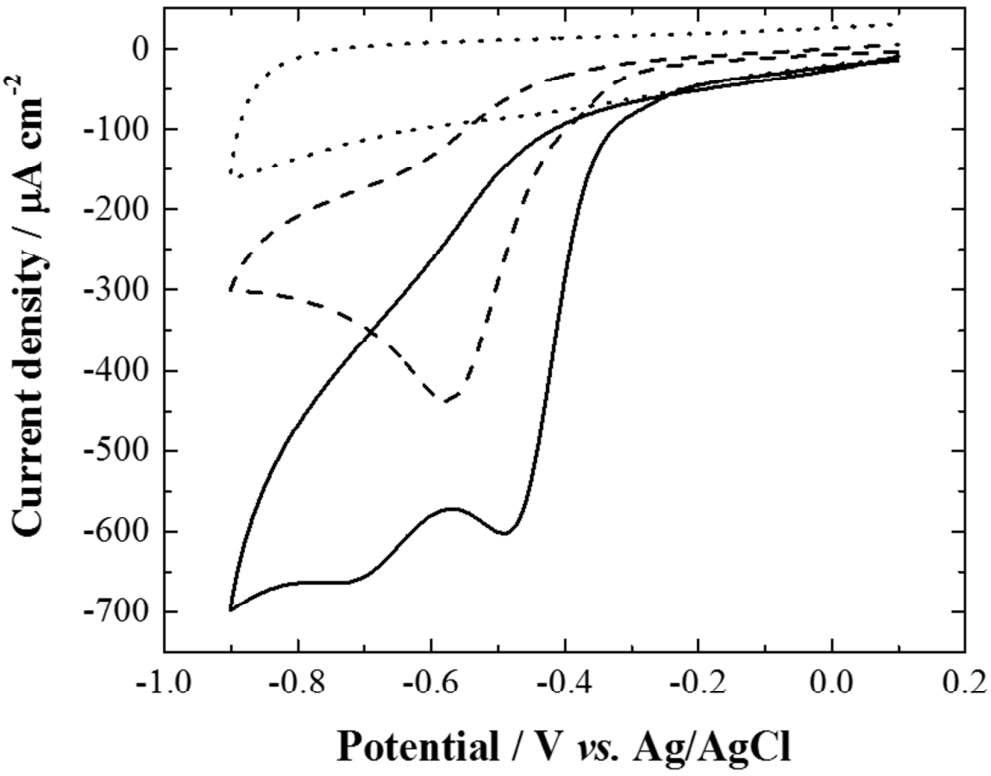

Figure S1. Cyclic voltammograms (1st cycle shown) recorded at 50 mV s^{-1} on bare glassy carbon electrode in 0.1 M HCl as aqueous electrolyte under inert atmosphere (Ar) in the absence (dotted line) and in the presence of 1 mM 4-nitrocatechol (dashed line) and 1 mM 4-nitrocatechol + 3 mM $NaNO_2$ (solid line).

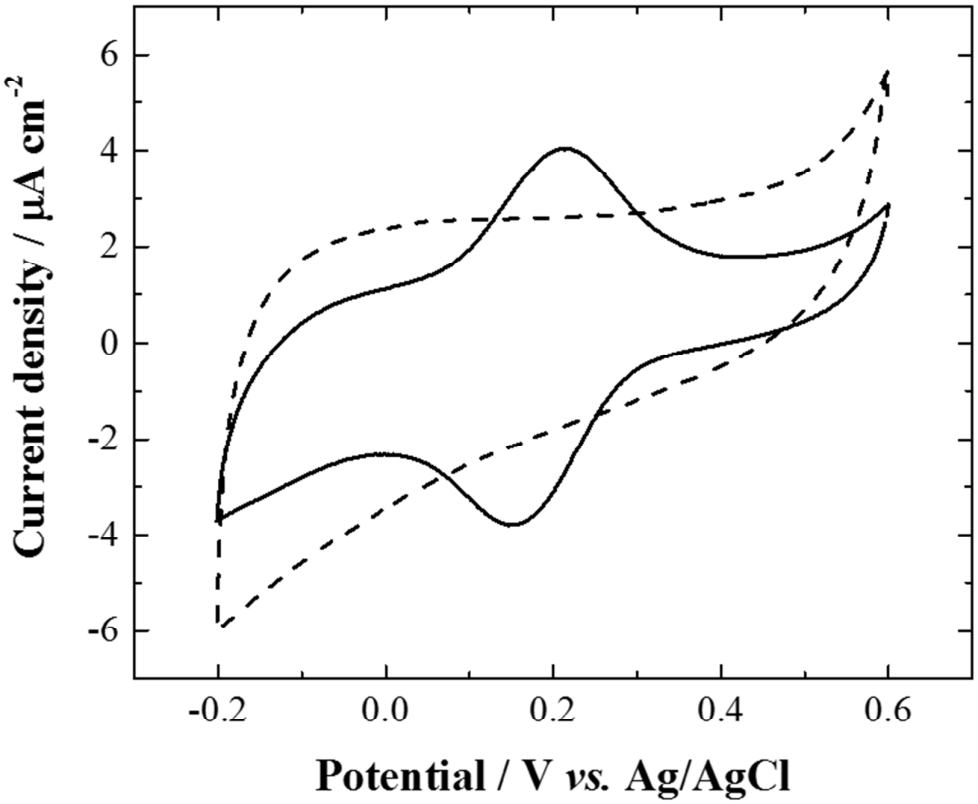

Figure S2. Cyclic voltammograms (3rd cycle shown) recorded at 20 mV s^{-1} on unmodified (dashed line) and catechol-modified (solid line) glassy carbon electrode in 10 mM phosphate buffer aqueous electrolyte at pH 7.2 under inert atmosphere (Ar).

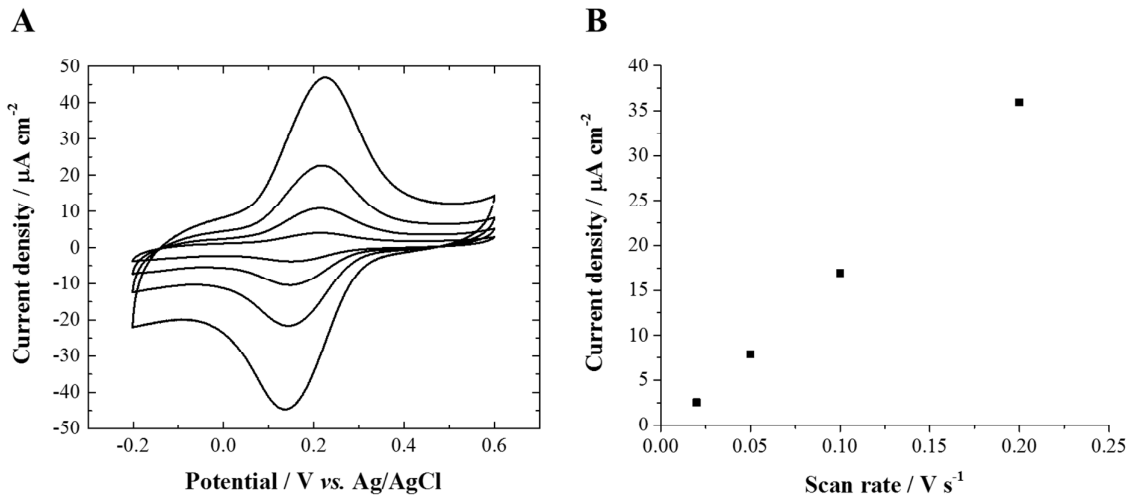

Figure S3. **A**. Cyclic voltammograms recorded at different scan rates (20, 50, 100 and 200 mV s^{-1}) in 10 mM phosphate buffer aqueous electrolyte at pH 7.2 under Ar on catechol-modified glassy carbon electrode. **B**. The corresponding variation of the anodic peak current (i_{pa}) as a function of the scan rate.

Table S1. Apparent normal potential of cytochrome *c* detected by cyclic voltammetry (data from Figure 4 in the manuscript) at glassy carbon electrodes modified with lipid deposits of different DOPC/CL ratio, in a 0.05 mM cytochrome *c* solution in 10 mM phosphate buffer aqueous electrolyte at pH 7.2 under inert atmosphere (Ar).

Lipid deposit composition	**Apparent normal potential of cytochrome *c* (V *vs*. Ag/AgCl)**
100% CL	-0.002 V
25% DOPC/75% CL	+0.004 V
50% DOPC/50% CL	+0.008 V
75% DOPC/25% CL	+0.013 V

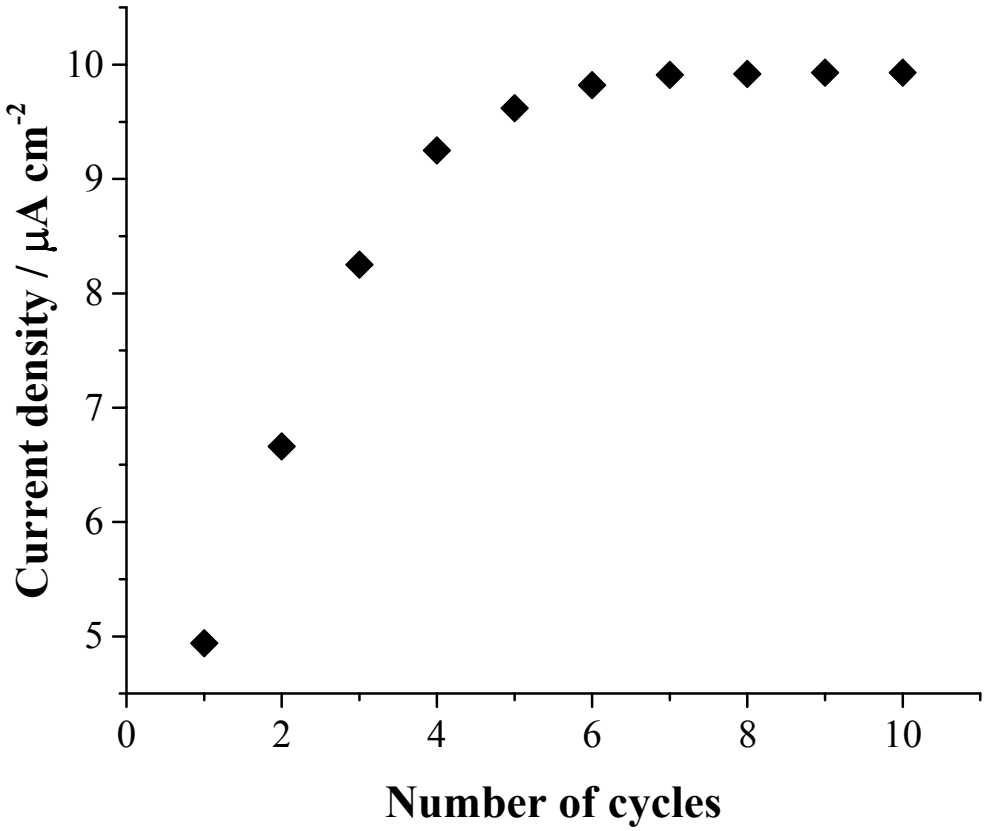

Figure S4. Anodic peak current density as a function of the number of cycles recorded by cyclic voltammetry (data from Figure 5A in the manuscript) at a 75% DOPC/25% CL lipid deposit-modified glassy carbon electrode in a 0.15 mM cytochrome *c* solution in 10 mM phosphate buffer aqueous electrolyte at pH 7.2 under inert atmosphere (Ar).

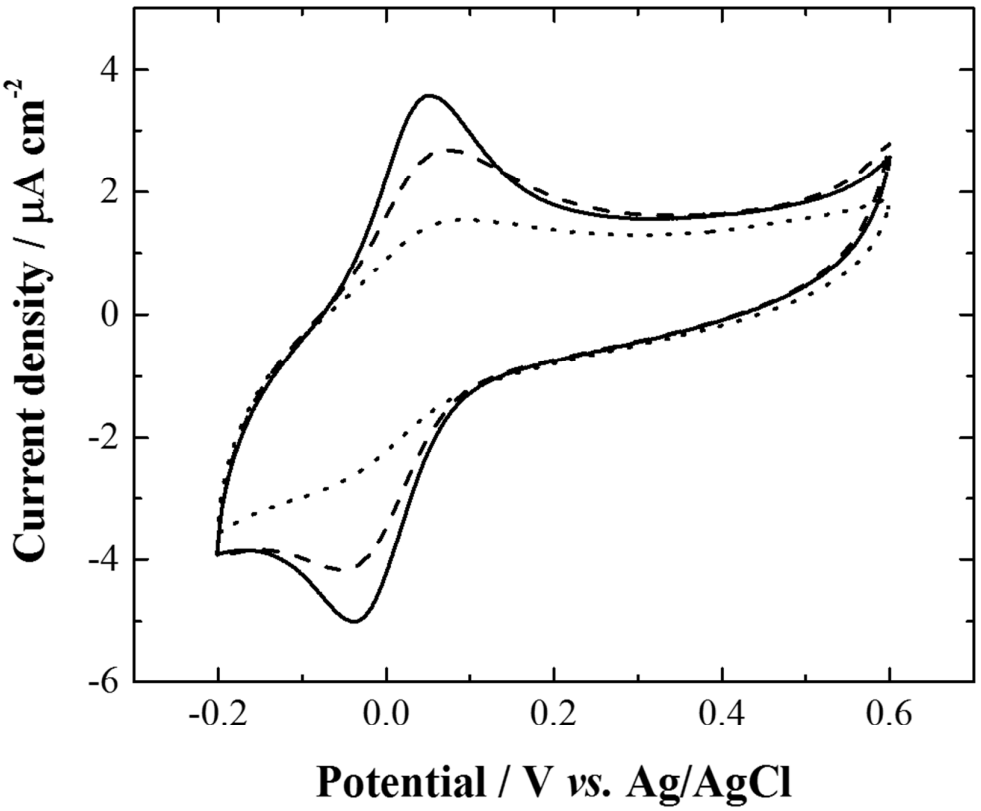

Figure S5. Cyclic voltammograms (3rd cycle shown) successively recorded at 20 mV s^{-1} on cytochrome *c*-modified glassy carbon electrode in 10 mM phosphate buffer aqueous electrolyte at pH 7.2 (solid line), pH 9 (dashed line) and pH 5 (dotted line) under inert atmosphere (Ar). The peaks current decreasing from the first cyclic voltammograms (pH 7.2) to the last cyclic voltammograms (pH 5) is due to the protein desorption.

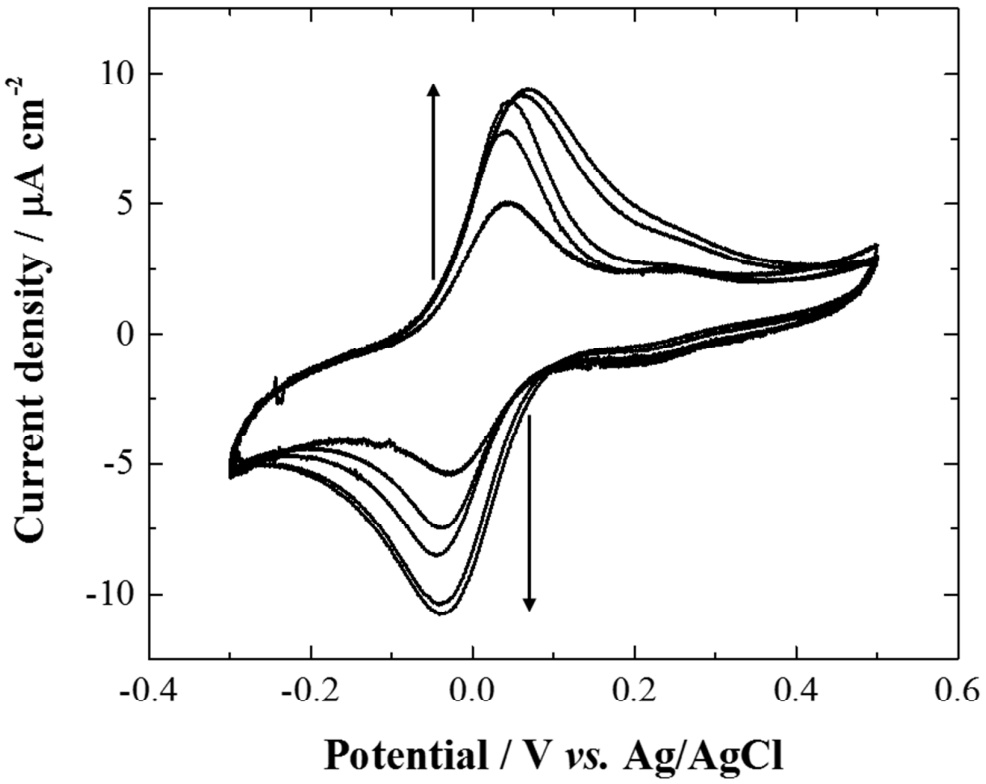

Figure S6. Cyclic voltammograms (1st, 2nd, 3rd, 6th and 10th cycles shown) recorded at 20 mV s^{-1} on glassy carbon electrode modified by catechol and a 75% DOPC/25% CL lipid deposit in 0.15 mM cytochrome *c* solution 10 mM phosphate buffer aqueous electrolyte at pH 7.2 under inert atmosphere (Ar). The redox potential of the protein and of the catechol are located at ca. 0 V and +0.2 V, respectively.

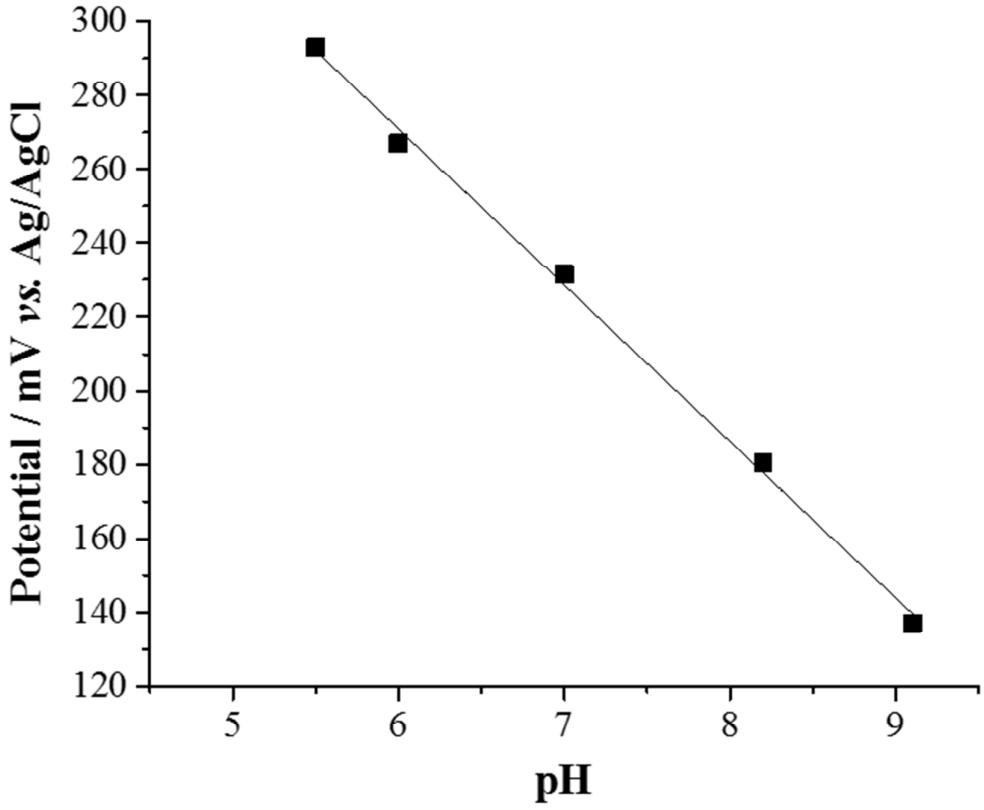

Figure S7. pH dependence of the apparent normal potential of the grafted catechol at the catechol/lipid deposit/cytochrome *c*-modified glassy carbon electrode (data from Figure 6 and Table 1).

Linear regression analysis: $y = -42x + 525$, $R^2 = 0.9976$.

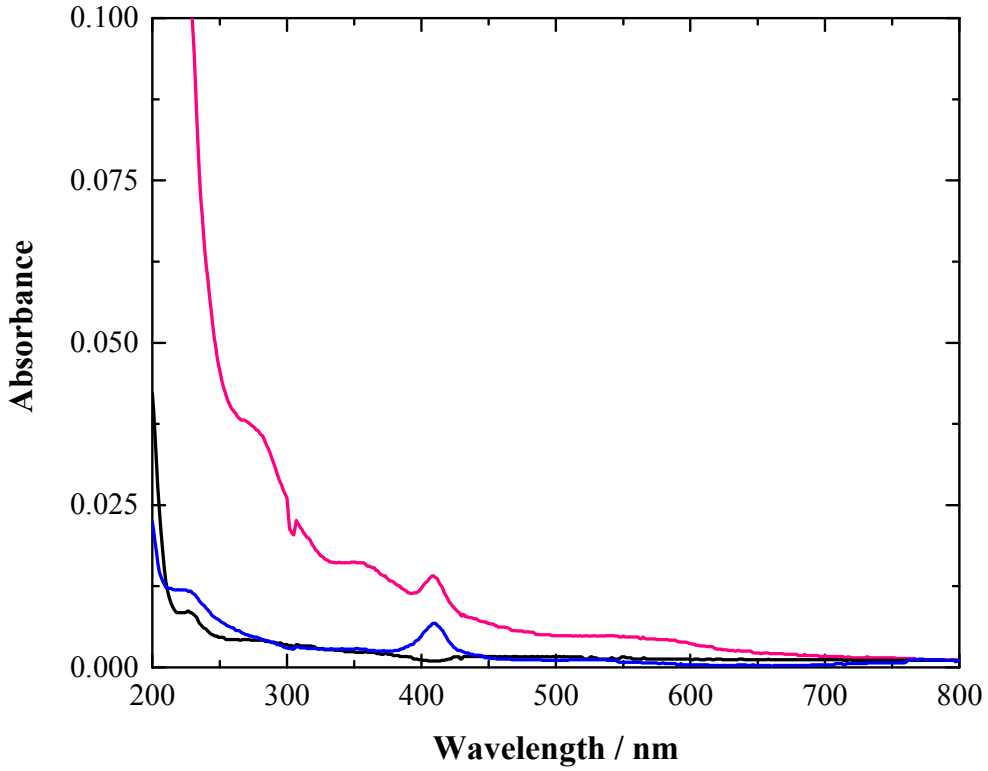

Figure S8. UV-visible absorption spectra of:

Blue line: a cytochrome *c* solution diluted to 25 nM.

Black line: the washing solution from glassy carbon electrodes modified by the grafted catechol and the lipid deposit of 75% DOPC/25 % CL.

Pink line: the washing solution from glassy carbon electrodes modified by grafted catechol, lipid deposit and immobilized cytochrome *c*.

The artefact located at 300 nm corresponds to the spectrophotometer lamp change.

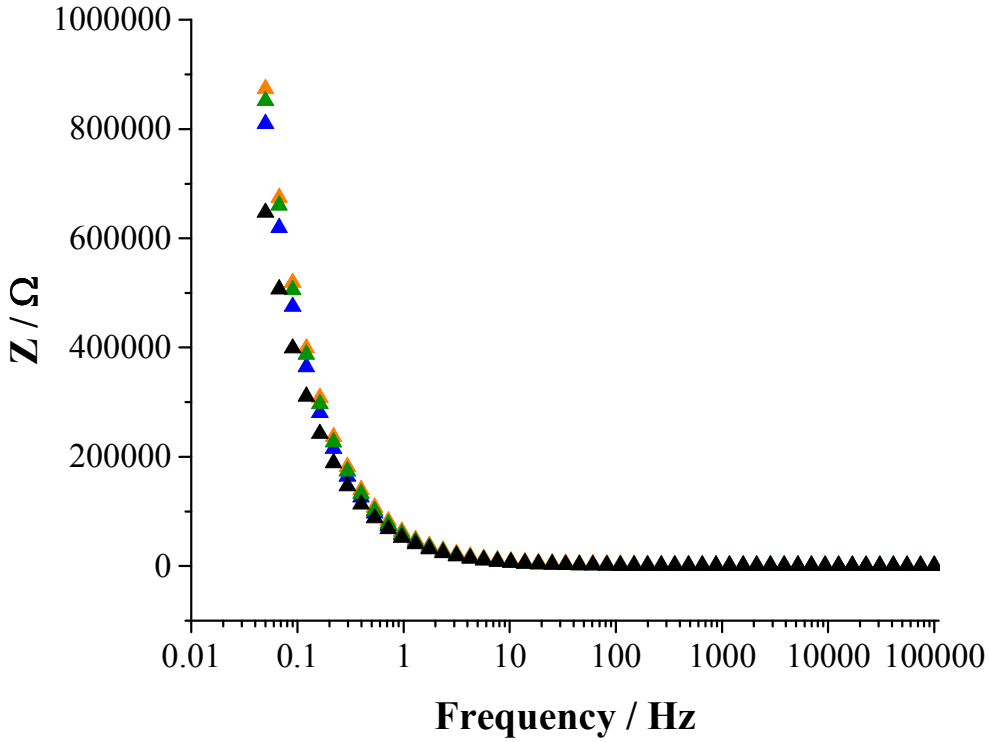

Figure S9. Bode plots from electrochemical impedance spectroscopy measurements successively recorded at Open Circuit Potential on glassy carbon electrodes unmodified (black) and modified by grafted catechol (green), grafted catechol and 75% DOPC/25% CL lipid deposit (blue) and catechol/lipid deposit/cytochrome *c* (orange) in 10 mM phosphate buffer aqueous electrolyte at pH 7.2 under inert atmosphere (Ar).