Supplementary information for the paper:

Controlling Interfacial Electron Transfer and Electrocatalysis by pH- or Ion-Switchable DNA Monolayer-Modified Electrodes

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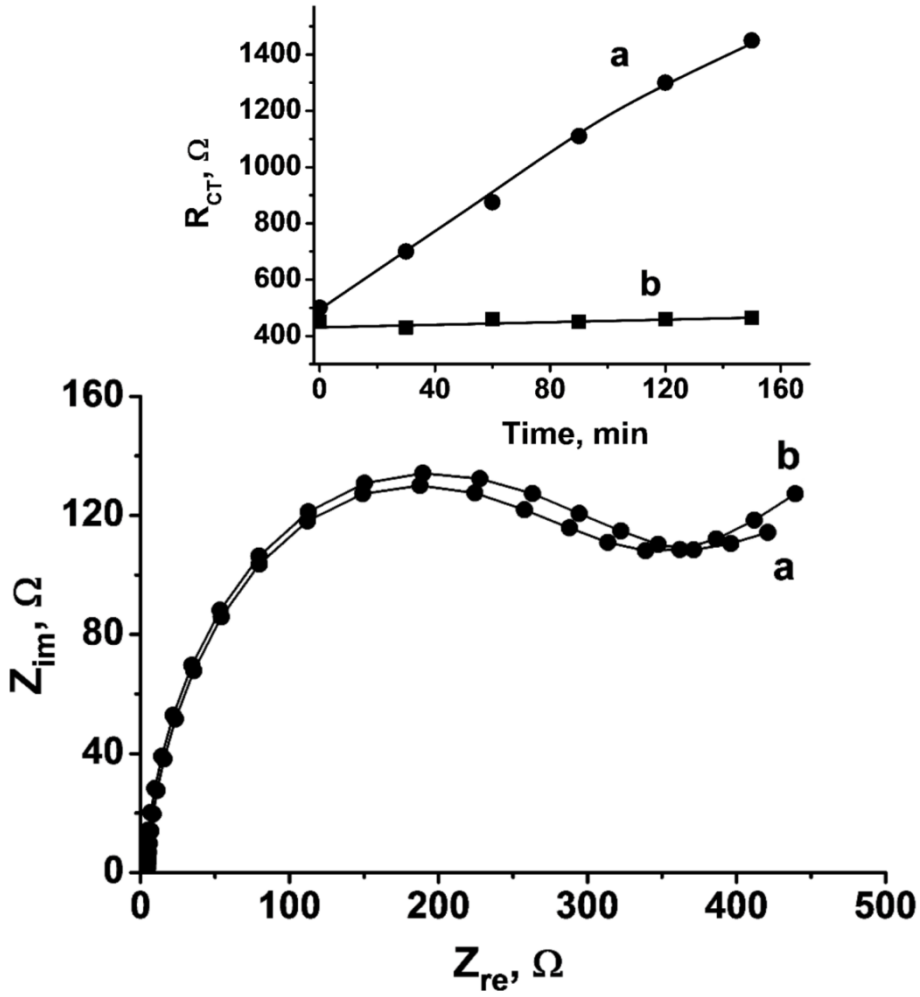

Figure S1. Faradaic impedance spectra (in the form of Nyquist plots) recorded during the RCA polymerization of the (**2**)-modified Au electrode in the presence of a thermally-denaturated (60°C, 15 minutes) Phi29 DNApolymerase: (a) Before polymerization, and, (b) After 150 minutes polymerization. Inset: Interfacial electron transfer resistances recorded during the RCA polymerization of the (**2**)-modified Au electrode, in the presence of: (a) Phi29 DNApolymerase, and (b) Thermally-denaturated Phi29 DNApolymerase. Measurements were performed in MES buffer, 0.1 M, that included $Fe(CN)_6^{3-/4-}$, 1 mM. Data was recorded in the frequency range of 10 kHz to 100 mHz at E=0.17 V vs. SCE, using an alternate perturbation potential of ±10 mV.

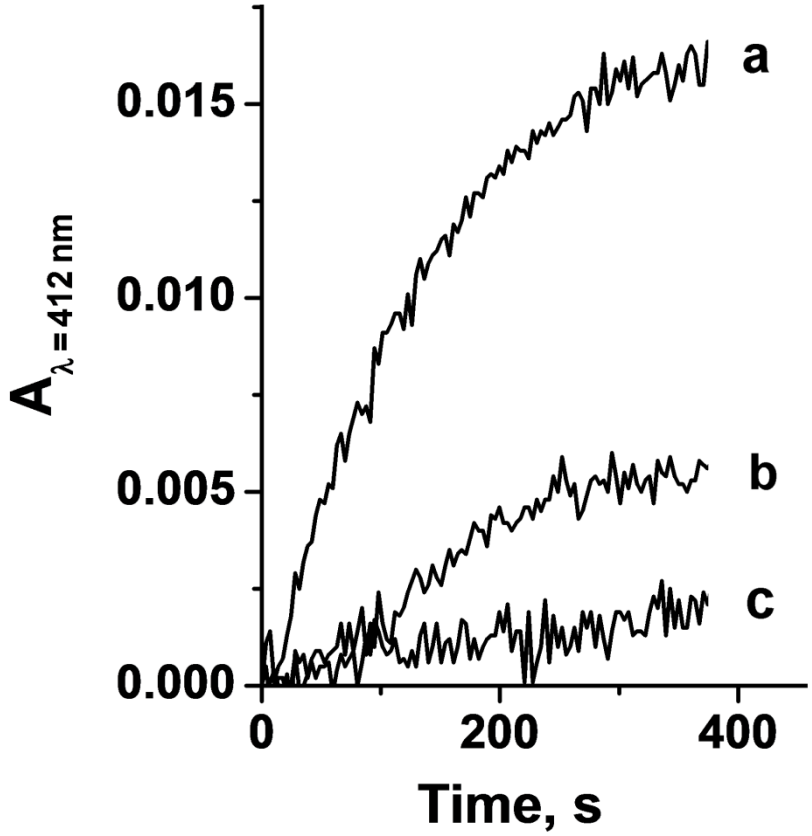

Figure S2. Time-dependant $ABTS^{\cdot-}$ absorption (at λ=412 nm), recorded for a 200 μL tris acetate buffer solution (0.1 M, pH 7.0) containing 200 μM $ABTS^{2-}$, 200 μM H_2O_2 and 0.5 μM hemin, and interacted with: (a) The (**4**)-modified Au electrode, in the presence of 0.1 M KCl; (b) The (**4**)-modified Au electrode, in the absence of KCl; (c) The (**1a**)-modified Au electrode, in the presence of 0.1 M KCl.