Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

How protein structure affects redox reactivity: example of Human centrin 2.

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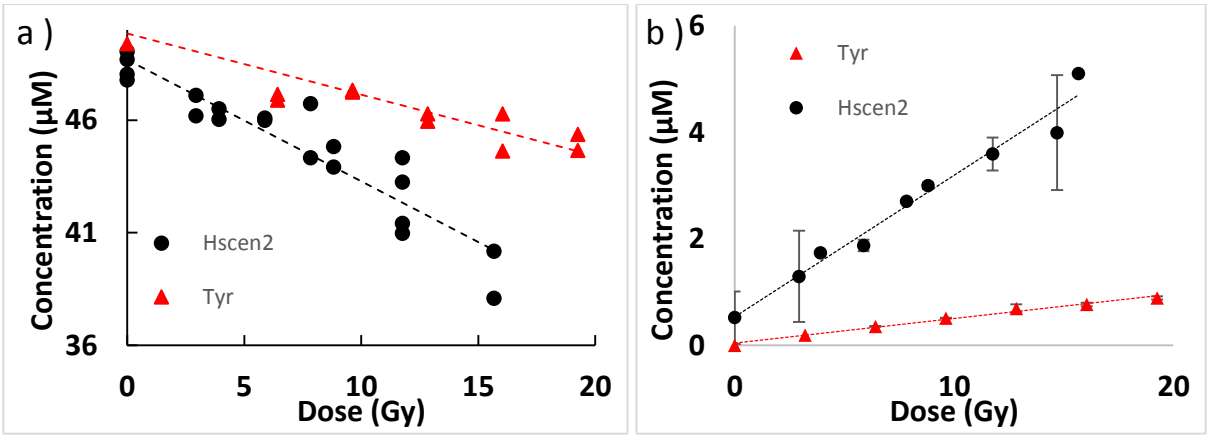
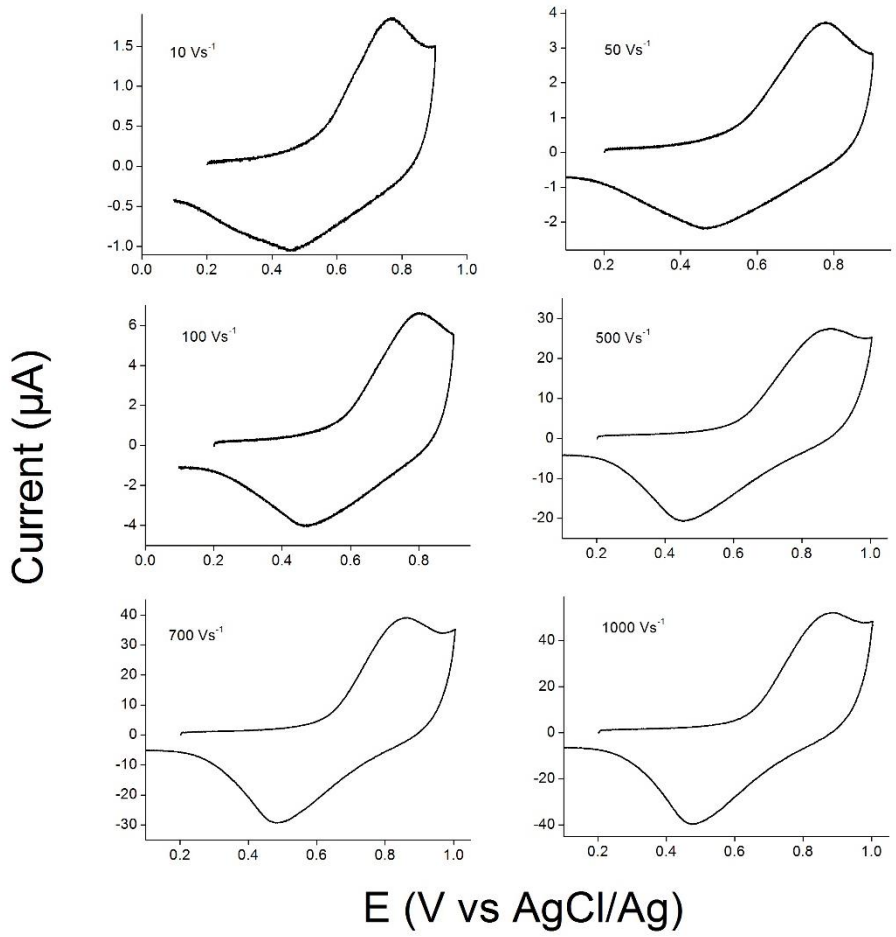


Figure S1. a) Hscen 2 and Tyrosine concentration evolution as a function of the irradiation dose determined by liquid chromatography. Yield determined: $G(_{\text{-Hscen2}}) = 0.57 \pm 0.05 \mu mol.J^{-1}$ $G(_{\text{-Tyr}}) = 0.27 \pm 0.04\ \mu molJ^{-1}$. b) Dimer concentration evolution as a function of the irradiation dose determined by liquid chromatography. Yield determined: $G_{(\text{Hscen2Dimer})} = 0.26 \pm 0.02\ \mu molJ^{-1}$, $G_{(\text{TyrDimer})} = 0.046 \pm 0.002\ \mu molJ^{-1}$.



Figures S2. Cyclic voltammograms of Hscen2 (0.2 mM) in 0.2 M NaCl aqueous solution at different scan rates onto a 125 µm diameter gold electrode.

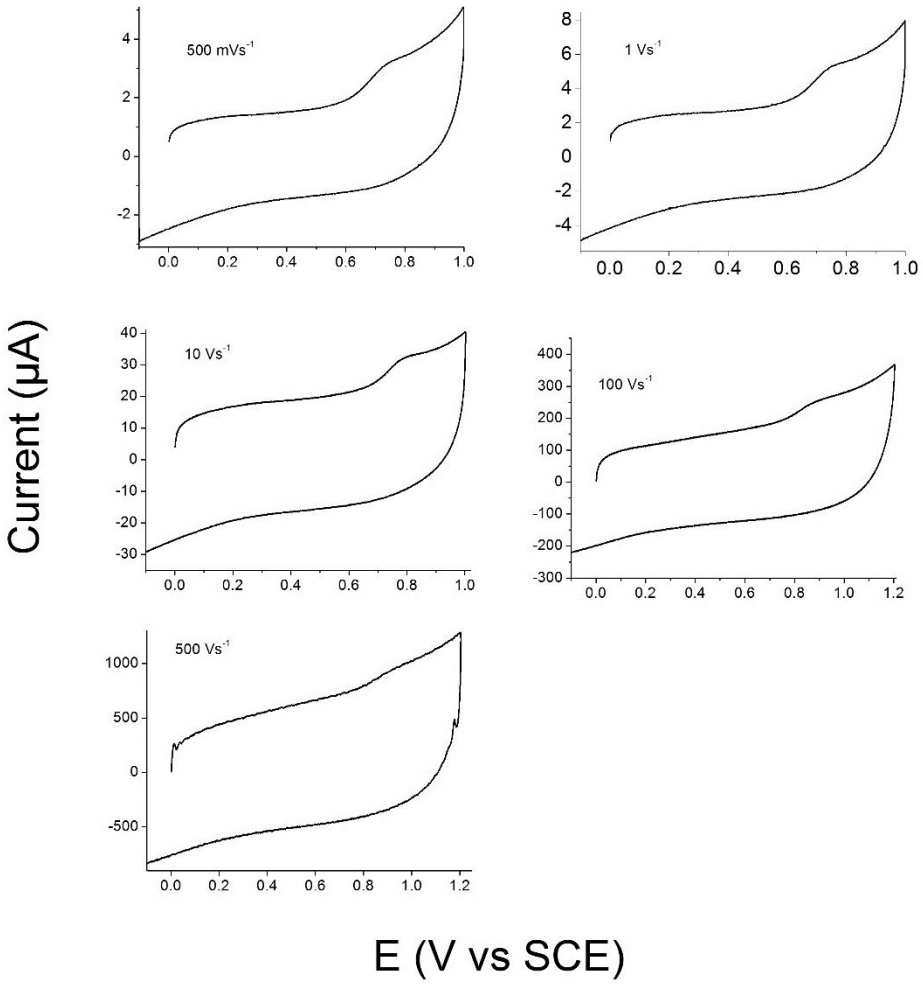


Figure S3. Cyclic voltammograms of 0.2 mM tyrosine in 0.5 M $LiNO_3$ aqueous solution on a 1 mm diameter glassy carbon electrode at different scan rates.

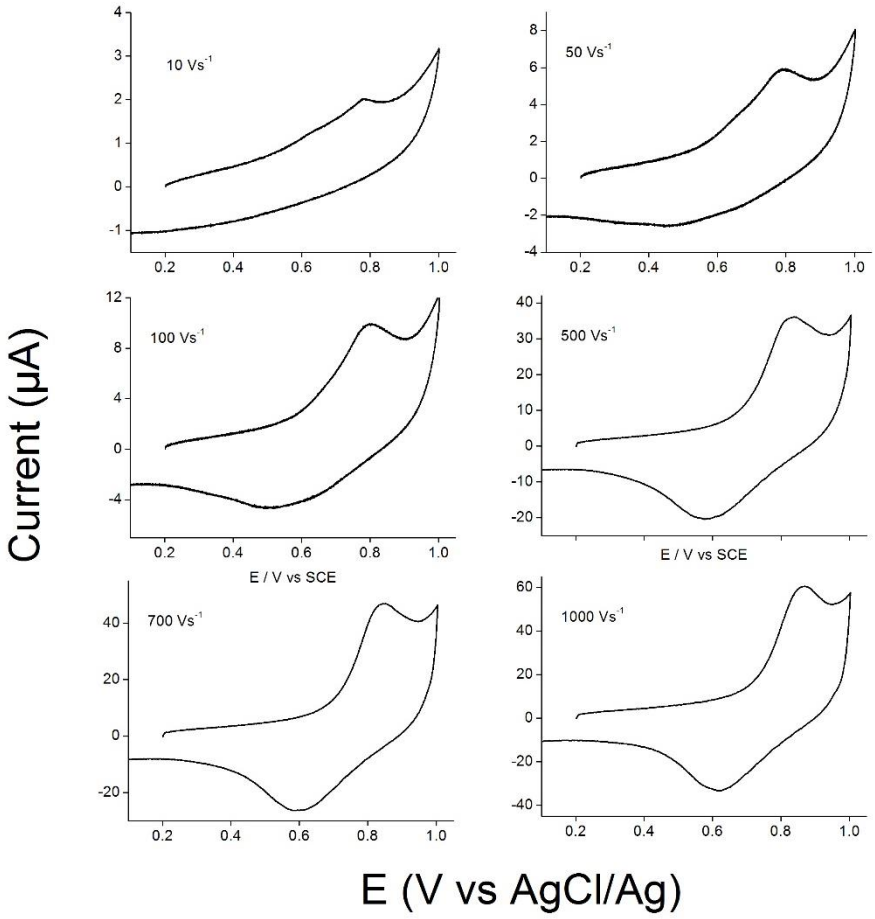


Figure S4. Cyclic voltammograms of Δ25 Human centrin 2 (0.2 mM) in 0.2 M NaCl aqueous solution at different scan rates onto a 125 µm diameter gold electrode.

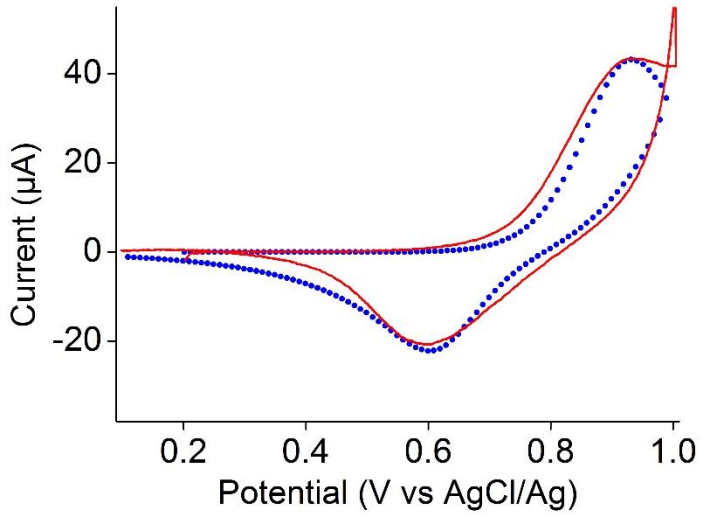


Figure S5. Experimental (solid line) and simulated cyclic voltammograms (dots) of Δ25 Human Centrin 2 (0.2 mM) in 0.2 M NaCl aqueous solution at 1000 Vs^{-1} onto a 125 µm diameter gold electrode. The background current is subtracted. Simulation parameters: E^0 = 0.765 V vs AgCl/Ag diffusion coefficient $D_{\Delta 25}$ = 8.2x10^{-7} cm^2s^{-1}, k_{dim} = 1.45x10^4 $Lmol^{-1}s^{-1}$, layer thickness = 180 nm, [Δ25] = 59 mM. pH = 7.5.

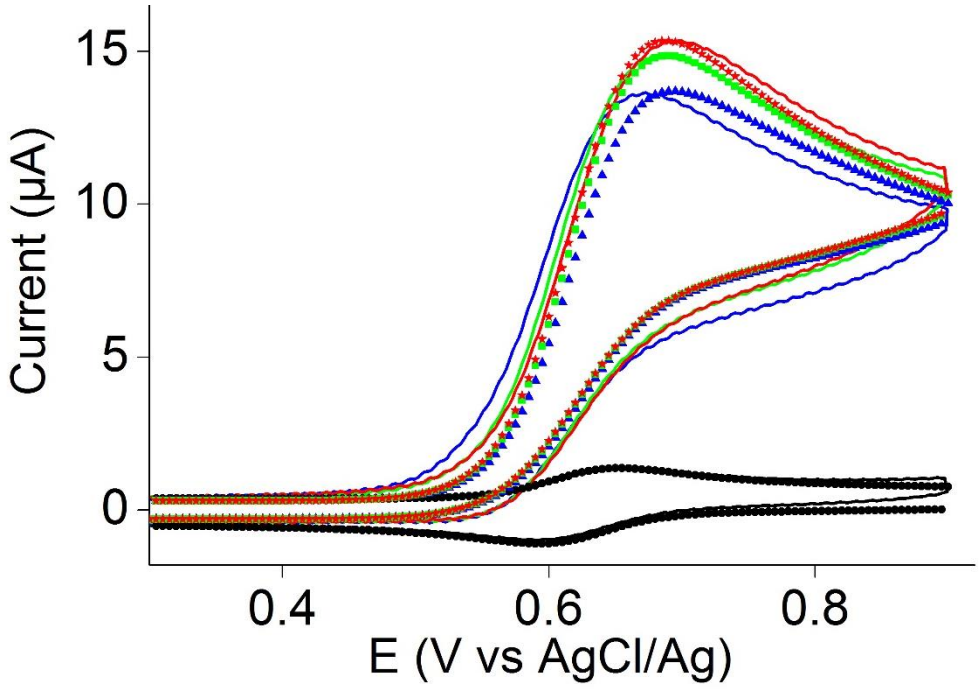


Figure S6. Redox catalysis of 0.1 mM tyrosine in the presence of 11 µM $Os(bpy)^{2+}$ ($E°_{Os(bpy)2/3+}$ = 623 mV/AgCl/Ag; $E°_{Tyrosine}$ = 730 mV/AgCl/Ag; $D_{Os(bpy)2/3+} = 6.10^{-6}$ cm².s^{-1}; $D_{Tyrosine} = 4.10^{-5}$ cm².s^{-1}; $k_{dimerization} = 10^7$ M^{-1}.s^{-1}; $K_{eq} = 1.5.10^5$). Phosphate buffer concentrations of 10 (blue), 50 (green) and 100 (red) mM, k_{app} were found to be $3.5x10^6$, $4.5x10^6$ and $5.1x10^6$ M^{-1}.s^{-1}, respectively. The fits are performed taking a diffusion coefficient $D_{Tyrosine}$ of $4x10^{-5}$ cm^{2}s^{-1} in line with Fecenko *et al.*[1] Such high value nevertheless seems overestimated in comparison with the one published recently by Wiegang *et al.*[2] Nevertheless, introducing a larger k_{app} and a smaller $D_{tyrosine}$ did not lead to a correct fit since then the system shifted to the "total catalysis" zone as described by Saveant.[3] Revisiting the model of Fecenko et al. was however beyond the scope of this study.

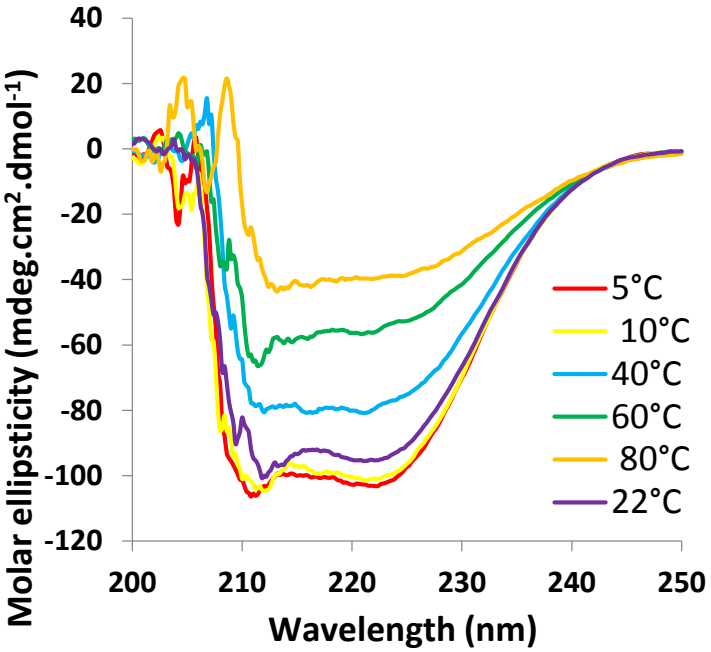


Figure S7. Hscen2 circular dichroism signal evolution as a function of the temperature.

References.

1. C. J. Fecenko, T. J. Meyer and H. H. Thorp, *J. Am. Chem. Soc.*, 2006, 128, 11020-11021.
2. Z. L. Wang, H. Kriegs and S. Wiegand, *J. Phys. Chem. B*, 2012, 116, 7463-7469.
3. J.-M. Saveant, *Elements Molecular and Biomolecular Electrochemistry*, John Wiley and Son, 2002.