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: \( G_{(\text{Hscen}2)} = 0.57 \pm 0.05 \mu \text{molJ}^{-1} \), \( G_{(\text{Tyr})} = 0.27 \pm 0.04 \mu \text{molJ}^{-1} \). b) Dimer concentration evolution as a function of the irradiation dose determined by liquid chromatography. Yield determined: \( G_{(\text{Hscen}2\text{Dimer})} = 0.26 \pm 0.02 \mu \text{molJ}^{-1} \), \( G_{(\text{TyrDimer})} = 0.046 \pm 0.002 \mu \text{molJ}^{-1} \).
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 $D_{Δ25} = 8.2 \times 10^{-7}$ cm² s⁻¹, $k_{dim} = 1.45 \times 10^4$ L mol⁻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$_{\text{Os(bpy)}2/3^+}$ = 623 mV/AgCl/Ag; E$_{\text{Tyrosine}}$ = 730 mV/AgCl/Ag; D$_{\text{Os(bpy)}2/3^+}$ = 6.10$^{-6}$ cm$^2$.s$^{-1}$; D$_{\text{Tyrosine}}$ = 4.10$^{-5}$ cm$^2$.s$^{-1}$; $k_{\text{dimerization}}$ = 10$^7$ M$^{-1}$.s$^{-1}$; $K_{\text{eq}}$ = 1.5.10$^5$). Phosphate buffer concentrations of 10 (blue), 50 (green) and 100 (red) mM, $k_{\text{app}}$ 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 $D_{\text{Tyrosine}}$ of 4x10$^{-5}$ cm$^2$.s$^{-1}$ in line with Fecenko $et$ $al$. Such high value nevertheless seems overestimated in comparison with the one published recently by Wiegang $et$ $al$. Nevertheless, introducing a larger $k_{\text{app}}$ and a smaller $D_{\text{Tyrosine}}$ did not lead to a correct fit since then the system shifted to the "total catalysis" zone as described by Saveant. 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.