ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

Chemical repair mechanisms of protein by the superoxide radical anion

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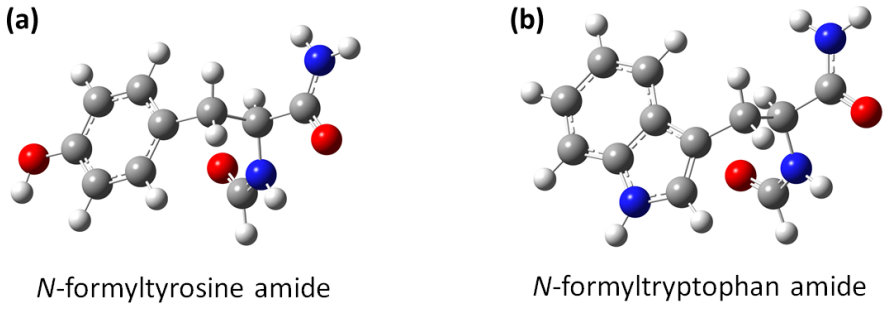

Figure S1. Molecular models of (a) tyrosine and (b) tryptophan residues.

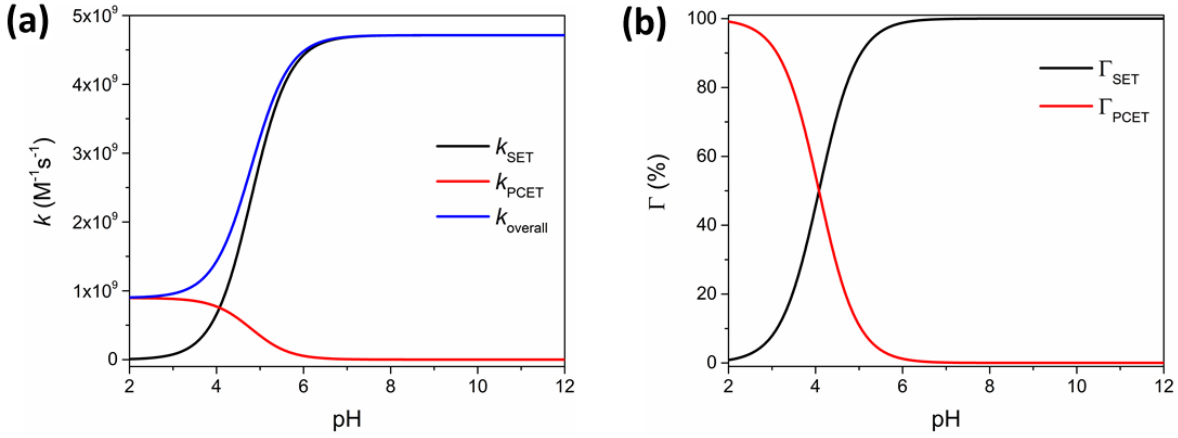

Figure S2. Influence of the pH on overall rate constant ($k_{overall}$) and the two components (single electron transfer, k_{SET}, and proton coupled-electron transfer, k_{PCET}), in the repair of TyrO$^{\bullet}$ by the two fraction of superoxide radical anion ($O_2^{\bullet-}$ and $HO_2^{\bullet}$) at 298.15 K. (a) Rate constants (k, $M^{-1}s^{-1}$) and (b) branching ratios (Γ, %).

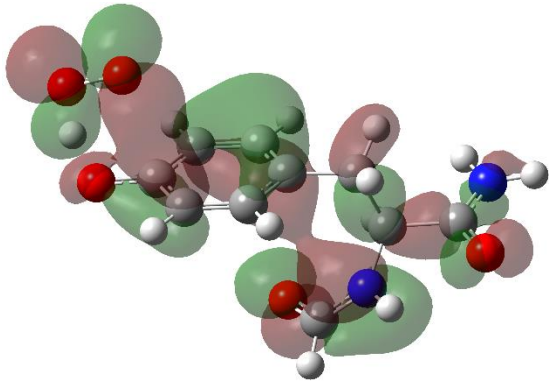

Figure S3. Non-covalent π-π stacking interactions for the highest doubly occupied molecular orbital at triplet transition state geometry for reaction between TyrO$^{\bullet}$ and $HO_2^{\bullet}$.

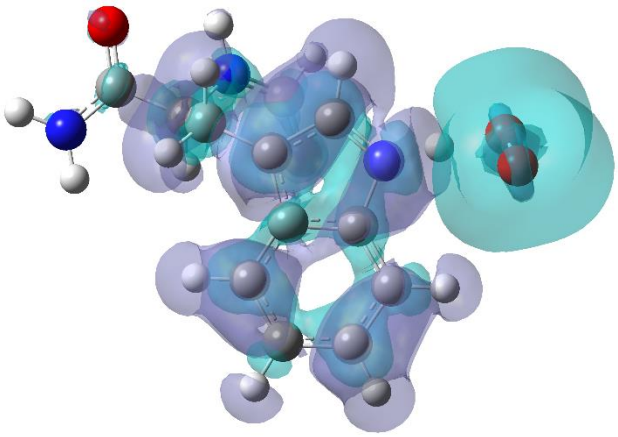

Figure S4. Total electron densities difference for the complexes for the vertical electron transfer in the hydrogen bond complex [$Trp^{\bullet+}$□$O_2^{\bullet-}$]. Purple and blue zones are related to the electron density rise and decrease, respectively.

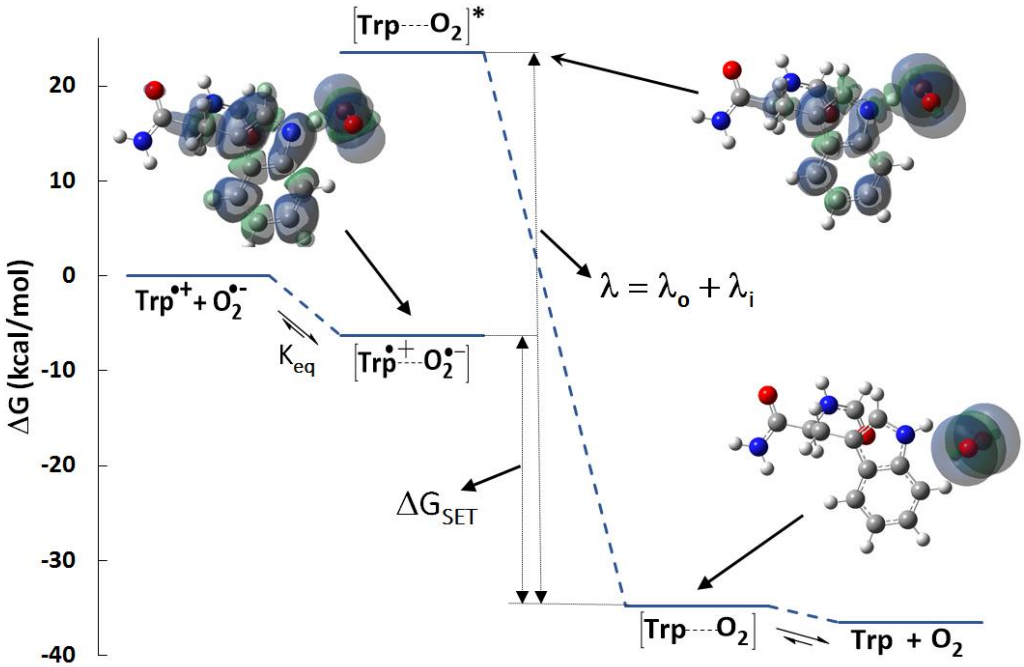

Figure S5. Pre-equilibrium reaction and parameters used in the kinetic analyses of the SPGET mechanism between $Trp^{\bullet+}$ and $O_2^{\bullet-}$. Structures and spin densities are shown. The first elementary (SPGET-1) corresponding to the protonation of $Trp_{(-H)}^{\bullet}$ is not included.

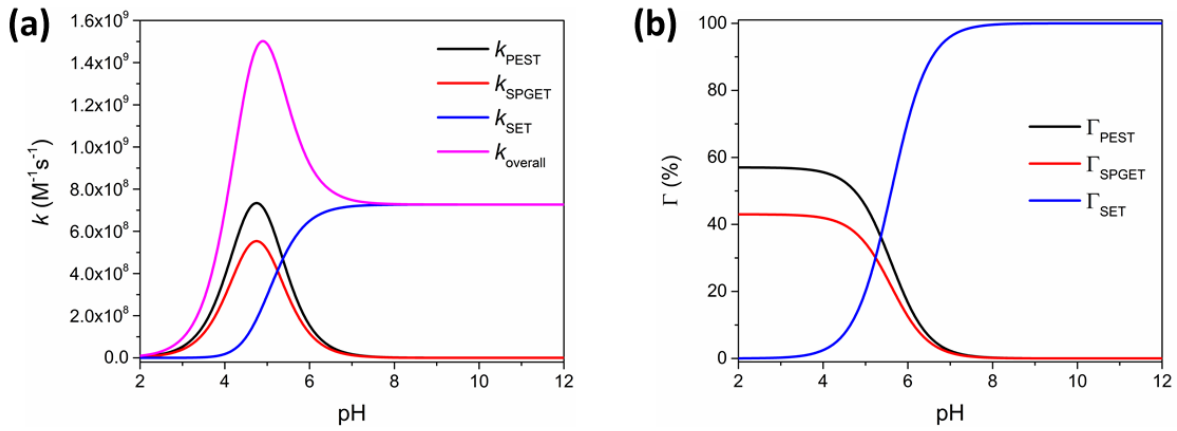

Figure S6. Influence of the pH on overall rate constant ($k_{overall}$) and the three components (single electron transfer, k_{SET}, proton coupled-electron transfer, k_{PCET}, and sequential proton gain-electron transfer, k_{SPGET}), in the repair of the $Trp^{\bullet}$ and $Trp^{\bullet+}$ radicals by the two fraction of superoxide radical anion ($O_2^{\bullet-}$ and $HO_2^{\bullet}$) at 298.15 K. (a) Rate constants (k, $M^{-1}s^{-1}$) and (b) branching ratios (Γ, %).