

**Electronic Supplementary Material**

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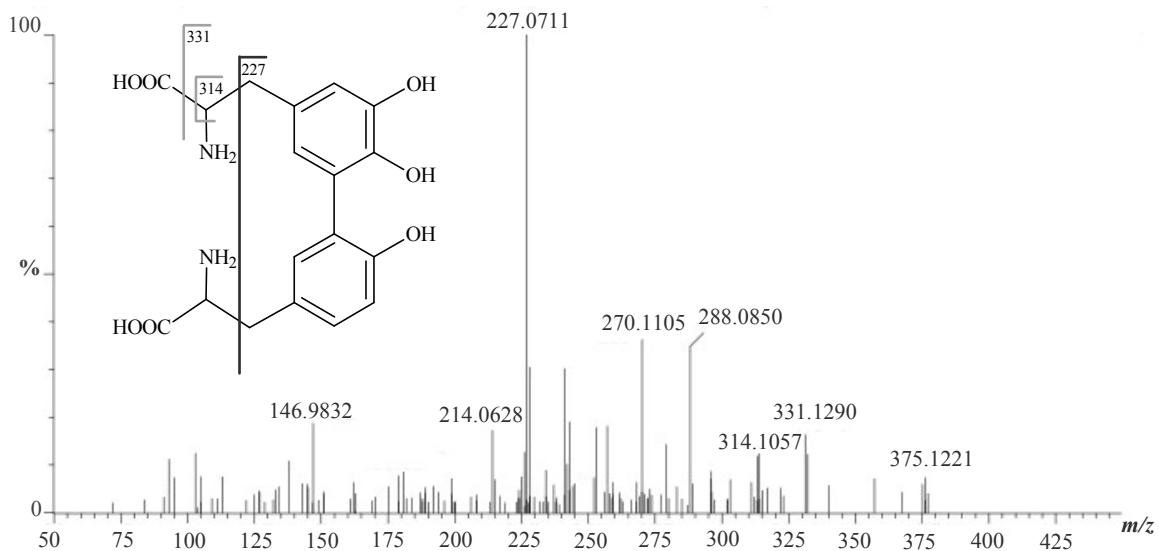
**S1. MS/MS spectrum recorded in ESI<sup>-</sup> mode of Tyr-DOPA.**

**S2. MS/MS spectrum recorded in ESI<sup>-</sup> mode of Tyr-dopaminochrome.**

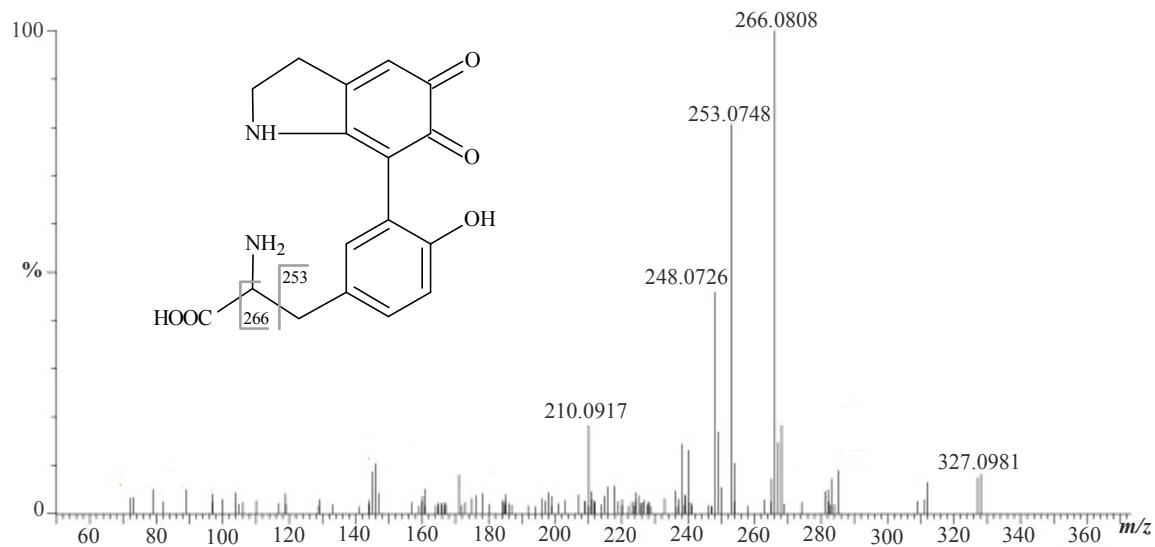
**S3. Time evolution of the absorption spectrum in alkaline air-equilibrated aqueous solution containing: a) Cyt c (Fe<sup>+3</sup>) (14 μM) as a function of irradiation time ( $\lambda_{\text{irr}} = 320$  nm). b) Cyt c (Fe<sup>+3</sup>) (14 μM) and Tyr<sub>2</sub> (14 μM) in dark conditions as a function of time.**

**S4. Time evolution of the Tyr concentration in alkaline aqueous solutions under UV-A irradiation in the absence (●) and in the presence of Tyr<sub>2</sub> (▼). Inset: time evolution of the Tyr<sub>2</sub> concentrations in alkaline aqueous solutions under UV irradiation in the presence of Tyr.  $\lambda_{\text{exc}}=320$  nm, [Tyr]= 8.0 μM, [Tyr<sub>2</sub>]= 63 μM, pH=9.5.**

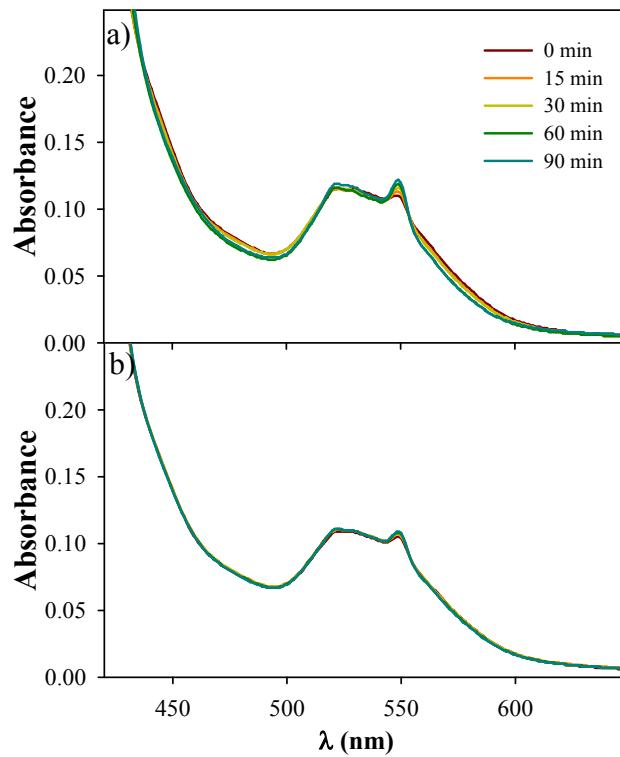
### S1. MS/MS spectrum recorded in ESI<sup>-</sup> mode of Tyr-DOPA



### S2. MS/MS spectrum recorded in ESI<sup>-</sup> mode of Tyr-dopaminochrome



**S3. Time evolution of the absorption spectrum in alkaline air-equilibrated aqueous solution containing: a) Cyt c ( $\text{Fe}^{+3}$ ) (14  $\mu\text{M}$ ) as a function of irradiation time ( $\lambda_{\text{irr}} = 320$  nm). b) Cyt c ( $\text{Fe}^{+3}$ ) (14  $\mu\text{M}$ ) and  $\text{Tyr}_2$  (14  $\mu\text{M}$ ) in dark conditions as a function of time.**



**S4. Time evolution of the Tyr concentration in alkaline aqueous solutions under UV-A irradiation in the absence (●) and in the presence of  $\text{Tyr}_2$  (▼). Inset: time evolution of the  $\text{Tyr}_2$  concentrations in alkaline aqueous solutions under UV irradiation in the presence of Tyr.  $\lambda_{\text{exc}}=320 \text{ nm}$ ,  $[\text{Tyr}]= 8.0 \mu\text{M}$ ,  $[\text{Tyr}_2]= 63 \mu\text{M}$ , pH=9.5**

