Supplementary Material

Influence of the peptide bond and the presence of tryptophan on the photogenerationand photochemical properties of dityrosine

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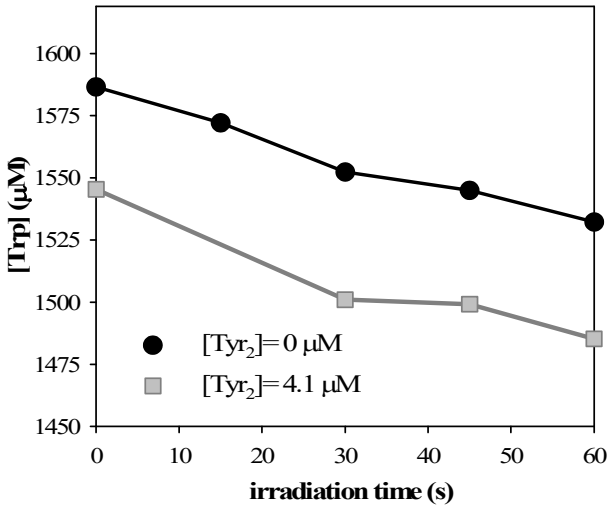
"INFLUENCE OF Trp ON THE FLUORESCENCE OF PEPTIDE Tyr_2"
Figure S5. Fluorescence area (excitation at 320 nm, emission at 405 nm) *vs.* absorbance area (λ_{an}= 320 nm) plot for the different photogenerated peptide Tyr_2.

Table S1. Slope of the fluorescence area (excitation at 320 nm, emission at 405 nm) *vs.* absorbance area (λ_{an}= 320 nm) plot for the different photogenerated peptide Tyr dimers.

Figure S6. Time evolution of peptide concentration, in air-equilibrated acid aqueous solution, as a function of irradiation time.$[Ptr]_0$ = 100µM, $[S_3GYGS_3]_0$ = 51 µM, $[S_3GWYGS_3]_0$ = 53 µM, $[GWS_6YG]_0$ = 54 µM pH = 6.0.



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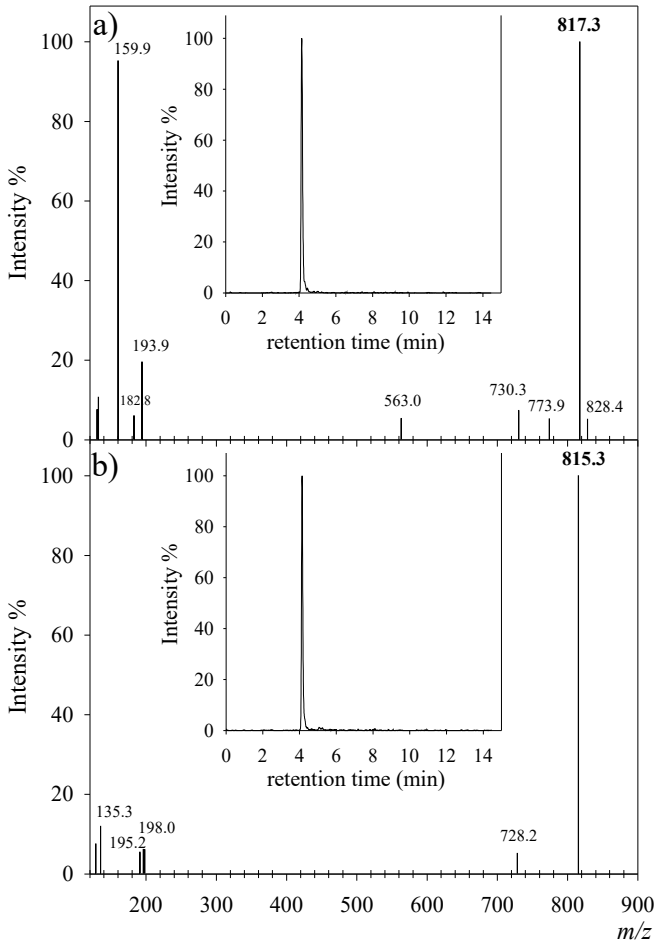

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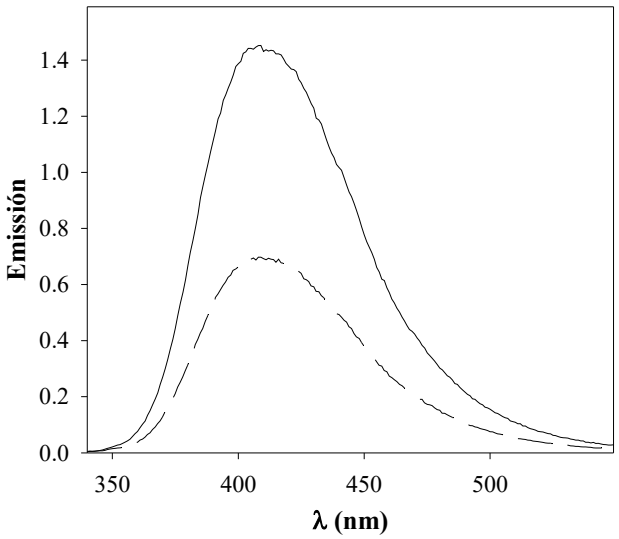

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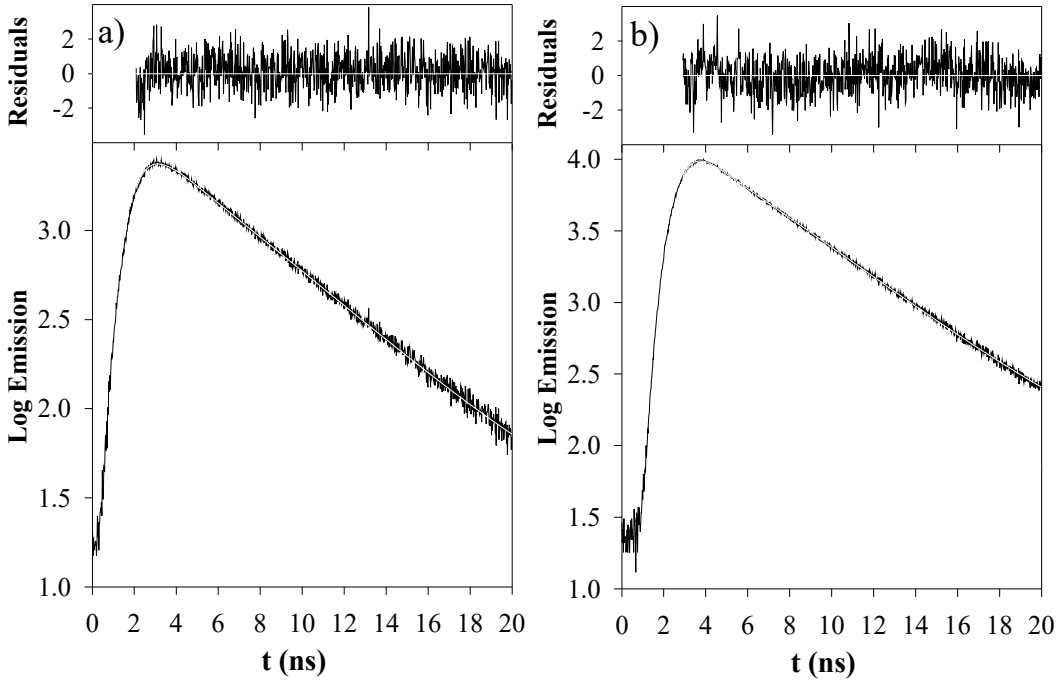

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"INFLUENCE OF Trp ON THE FLUORESCENCE OF PEPTIDE Tyr_2"

It was evaluated if the same calibration curve obtained for $(S_3GYGS_3)_2$using the fluorescence detector (HPLC-FL) could be applied to all peptide Tyr_2generated ($(S_3GWYGS_3)_2$,and $(GWS_6YG)_2$). To this end, fluorescence area curves—obtained by integrating the peptide Tyr_2 peak—were compared with the area obtained by integrating the same peak using the PDA detector (Figure S5). This methodology was used because the low concentration of the different peptide Tyr_2 generated make their isolation and purification difficult for analysis, as was done for $(S_3GYGS_3)_2$. As shown in Figure S5 and Table S1, the slopes of the resulting curves are the same, within experimental error, confirming that the presence of Trp in the same chain does not affect the fluorescence quantum yield of the peptide Tyr_2.

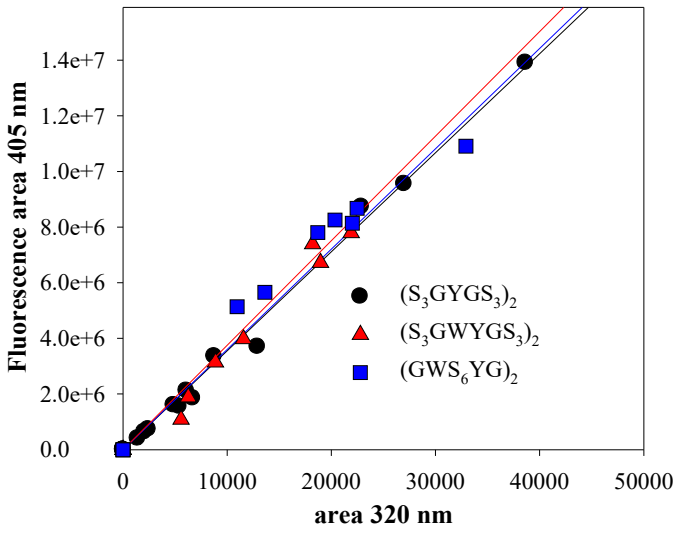

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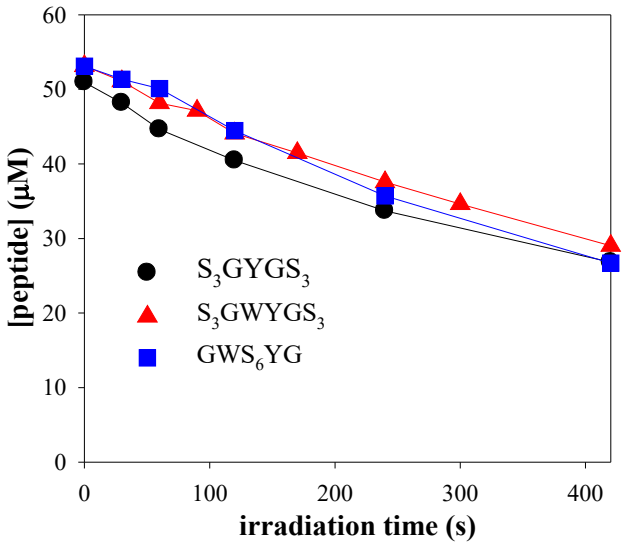
Table S1. Slope of the fluorescence area (excitation at 320 nm, emission at 405 nm)*vs.* absorbance area (λ_{an}= 320 nm) plot for the different photogenerated peptide Tyr dimmers.

Peptide dimer	Slope
$(S_3GYGS_3)_2$	$(3.5 \pm 0.3) \times 10^2$
$(S_3GWYGS_3)_2$	$(3.3 \pm 0.2) \times 10^2$
$(GWS_6YG)_2$	$(3.6 \pm 0.2) \times 10^2$



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