SUPPLEMENTARY INFORMATION

Photophysics and photochemistry of carminic acid and related natural pigments

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1. UV-visible absorption spectra of air-equilibrated CA aqueous solution irradiated at 350 nm and 366 nm

Figure S1.1. Evolution of the UV-visible absorption spectra of air-equilibrated CA aqueous solution ([CA]₀ = 340 μM) when subject to irradiation: (a) hν = 350 nm, and (b) hν = 366 nm.
2. **EEMs of CA irradiated aqueous solution (420 nm)**

![EEMs of CA irradiated aqueous solution](image)

**Figure S1.2.** Evolution of EEMs of air-equilibrated CA aqueous solution ([CA]₀ = 110 μM) when subject to irradiation (hv = 420 nm). Irradiation times are depicted as inset inside each EEM.
Figure S1.3. Evolution of EEMs of air-equilibrated CA aqueous solution ([CA]₀ = 110 μM) when subject to irradiation (hv = 300 nm). Irradiation times are depicted as inset inside each EEM.
4. Difference UV-visible absorption and emission spectra of CA aqueous solution irradiated under air-equilibrated and N$_2$-saturated conditions

(a)

Figure SI.4. (a) Experimental difference (ED) absorption spectra of CA irradiated ($h\nu = 420$ nm; Irradiation time = 24 h) under air-equilibrated (black) and N$_2$-saturated (red) atmosphere. (b) Fluorescence emission spectra of CA recorded under air-equilibrated and N$_2$-saturated solutions.
5. Hydrogen peroxide production upon CA photoexcitation

Figure S1.5. Generation of H$_2$O$_2$ upon photoexcitation ($h\nu = 420$ nm, irradiation times = 0, 6 and 12 h) of CA in air-equilibrated aqueous solution ([CA]$_0$ = 110 μM).
6. Effect of SOD on the photodegradation of CA

![Figure SI.6.](image)

**Figure SI.6.** (a) UV-vis absorption and (b) Normalized Difference (ND) spectra of CA solution ([CA]₀ = 110 μM) irradiated (hv = 420 nm) in the absence (red) and in the presence (black) of SOD (40 U/ml). (c) Evolution of EEMs of CA irradiated solutions. Irradiation times are depicted as inset inside each EEM.
7. Effect of sodium azide (NaN₃) on the photodegradation of CA

(a) Normalized Difference (ND) UV-vis absorption spectra of CA solution ([CA]₀ = 110 μM) irradiated (hv = 420 nm, irradiation time = 7 h) in the absence (black) and in the presence (red) of sodium azide ([NaN₃]₀ = 11 mM).

(b) Evolution of absorbance at 495 nm as a function of the irradiation time.

Figure SI.7. (a) Normalized Difference (ND) UV-vis absorption spectra of CA solution ([CA]₀ = 110 μM) irradiated (hv = 420 nm, irradiation time = 7 h) in the absence (black) and in the presence (red) of sodium azide ([NaN₃]₀ = 11 mM). (b) Evolution of absorbance at 495 nm as a function of the irradiation time.
8. Normalized Difference spectra of CA Lake air-equilibrated aqueous solution irradiated at 300 nm and 420 nm

![Normalized Difference (ND) absorption spectra of Lake aqueous solutions irradiated at $h\nu = 420$ nm (red) and 300 nm (black). Total irradiation time = 24 h.](image)

**Figure S1.8.** Normalized Difference (ND) absorption spectra of Lake aqueous solutions irradiated at $h\nu = 420$ nm (red) and 300 nm (black). Total irradiation time = 24 h.
9. EEMs of CA Lake irradiated aqueous solution (420 nm)

Figure S1.9. Evolution of EEMs of air-equilibrated Lake aqueous solution when subject to irradiation ($h\nu$ = 420 nm. Irradiation times are depicted as inset inside each EEM.)
10. **EEMs of CA Lake irradiated aqueous solution (300 nm)**

![Figure SI.10](image)

**Figure SI.10.** Evolution of EEMs of air-equilibrated Lake aqueous solution when subject to irradiation ($hν = 300$ nm). Irradiation times are depicted as inset inside each EEM.
11. Comparative analysis of CA, Lake and the photoproducts fluorescence emission spectra

(a) (b)

Figure SI.11. (a) Normalized fluorescence emission spectra of CA (red) and CA-like chromophore (black) produced upon irradiation (ν = 300 nm) of Lake. (b) Evolution of the total emission intensity of CA-like chromophore (calculated as the integral below the entire emission spectra) as a function of the irradiation time (ν = 300 and 420 nm). (c) and (d) Normalized excitation (dashed lines, λ<sub>exc</sub> = 495 nm) and emission (solid lines, λ<sub>em</sub> = 340 nm) spectra of photoproducts F#3 and F#4, respectively, obtained during the irradiation (24 h) of CA (red) and Lake (black).