

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

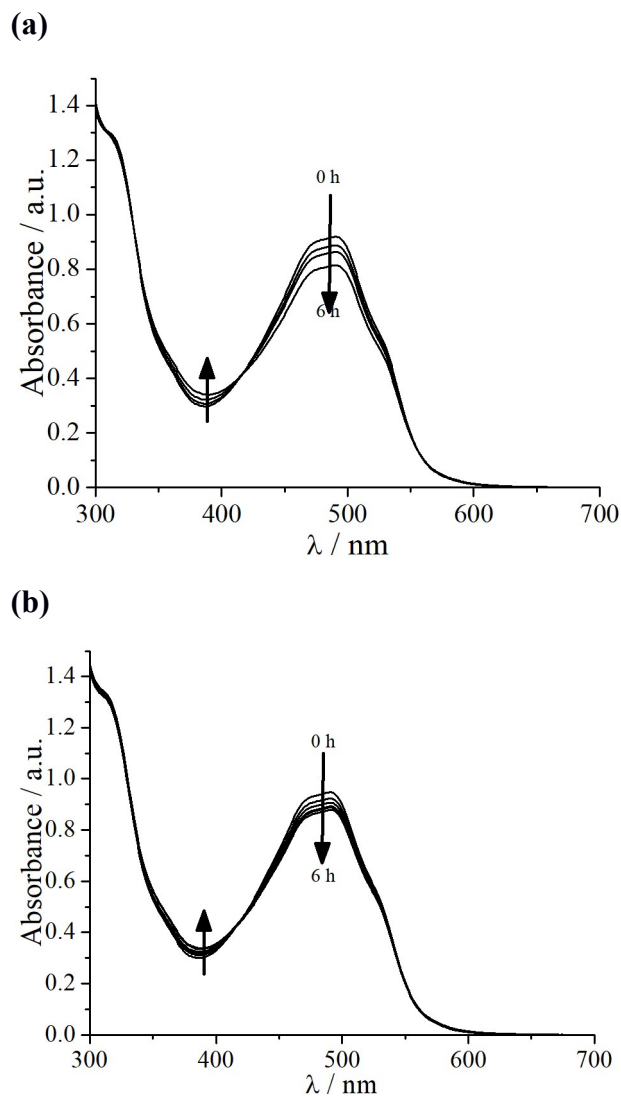


Figure SI.1. Evolution of the UV-visible absorption spectra of air-equilibrated CA aqueous solution ($[CA]_0 = 340 \mu\text{M}$) when subject to irradiation: **(a)** $h\nu = 350 \text{ nm}$, and **(b)** $h\nu = 366 \text{ nm}$.

2. EEMs of CA irradiated aqueous solution (420 nm)

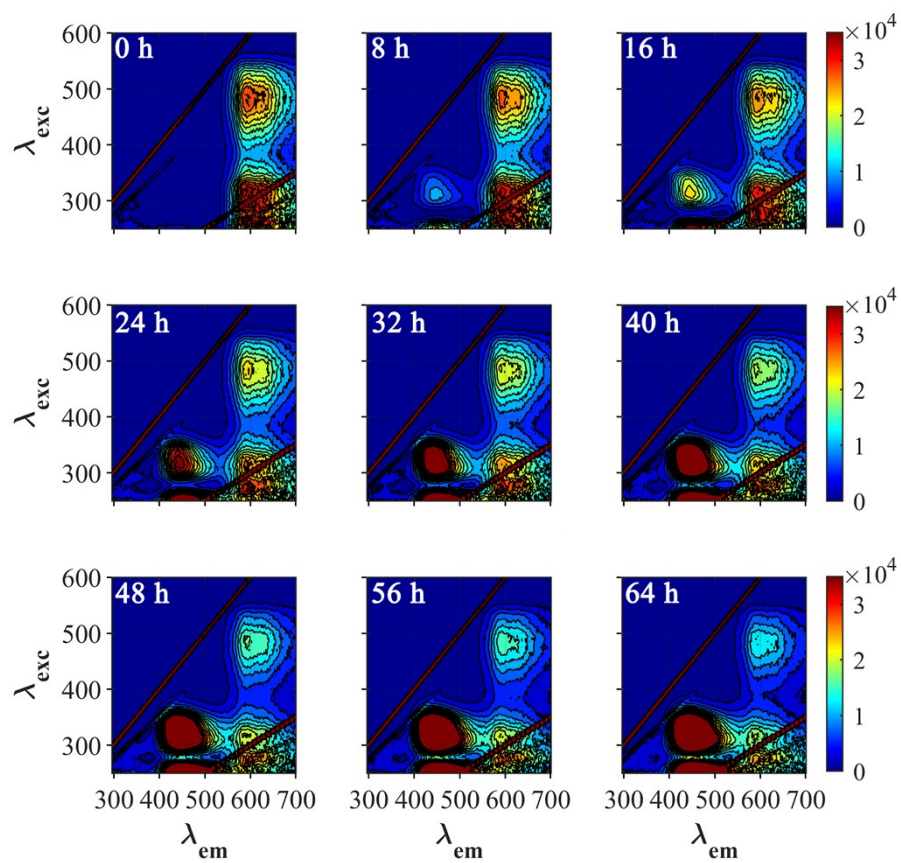


Figure SI.2. Evolution of EEMs of air-equilibrated CA aqueous solution ($[CA]_0 = 110 \mu\text{M}$) when subject to irradiation ($h\nu = 420 \text{ nm}$). Irradiation times are depicted as inset inside each EEM.

3. EEMs of CA irradiated aqueous solution (300 nm)

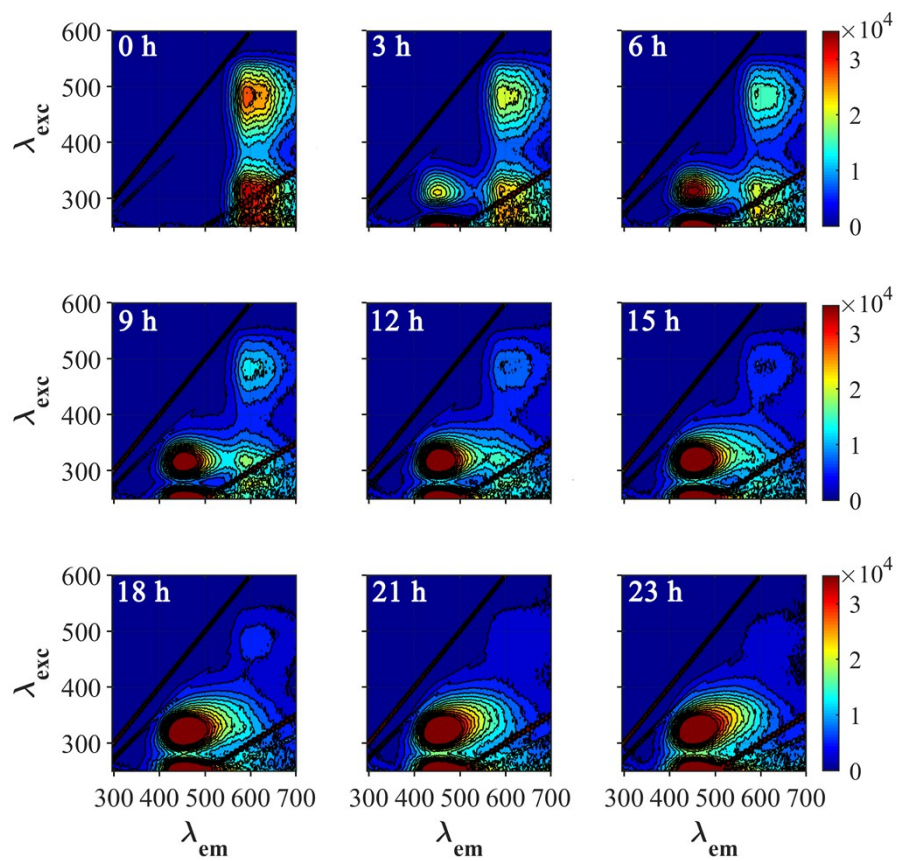


Figure SI.3. Evolution of EEMs of air-equilibrated CA aqueous solution ($[CA]_0 = 110 \mu\text{M}$) when subject to irradiation ($h\nu = 300 \text{ nm}$). Irradiation times are depicted as inset inside each EEM.

4. Difference UV-visible absorption and emission spectra of CA aqueous solution irradiated under air-equilibrated and N₂-saturated conditions

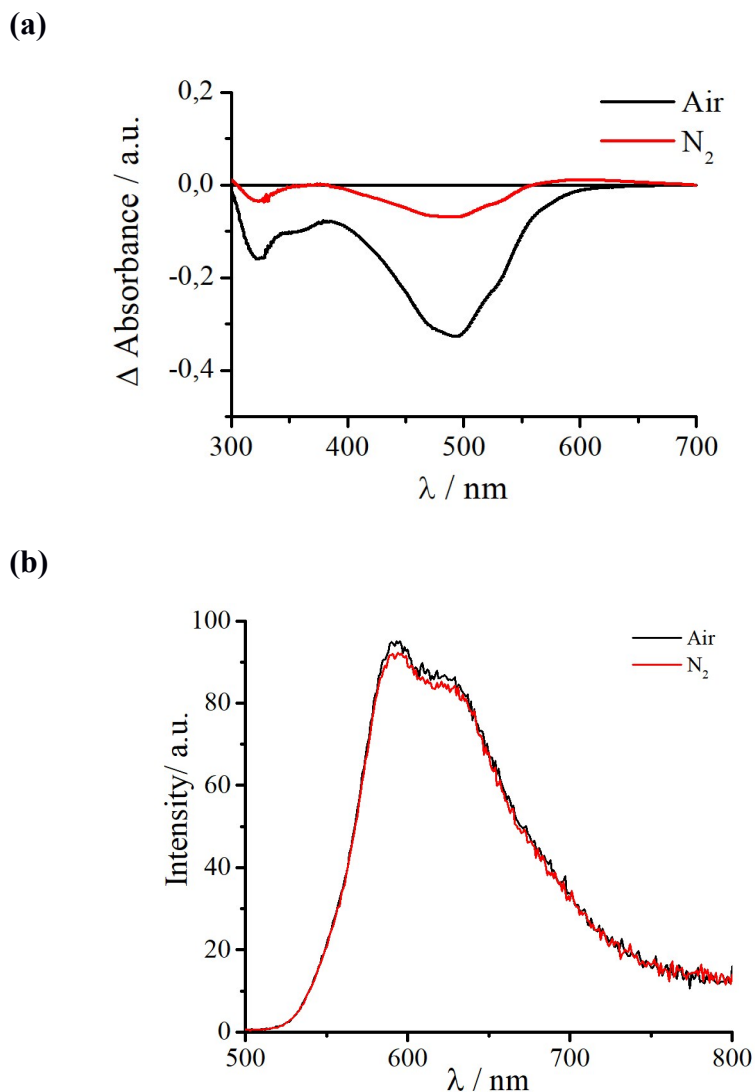


Figure SI.4. (a) Experimental difference (ED) absorption spectra of CA irradiated ($h\nu = 420$ nm; Irradiation time = 24 h) under air-equilibrated (**black**) and N₂-saturated (**red**) atmosphere. (b) Fluorescence emission spectra of CA recorded under air-equilibrated and N₂-saturated solutions.

5. Hydrogen peroxide production upon CA photoexcitation

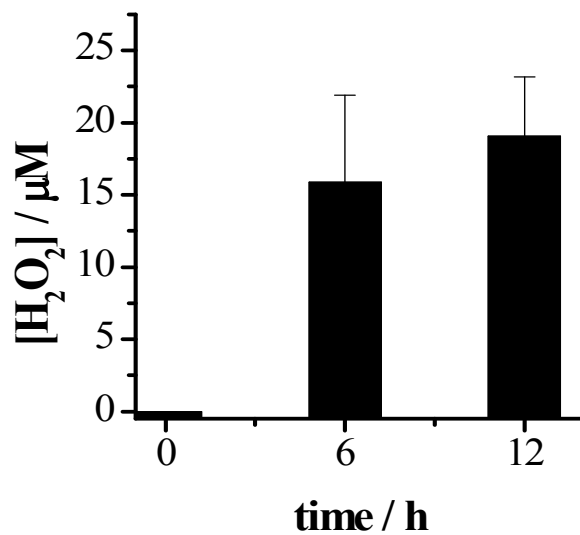


Figure SI.5. Generation of H₂O₂ upon photoexcitation ($h\nu = 420$ nm, irradiation times = 0, 6 and 12 h) of CA in air-equilibrated aqueous solution ($[CA]_0 = 110$ μM).

6. Effect of SOD on the photodegradation of CA

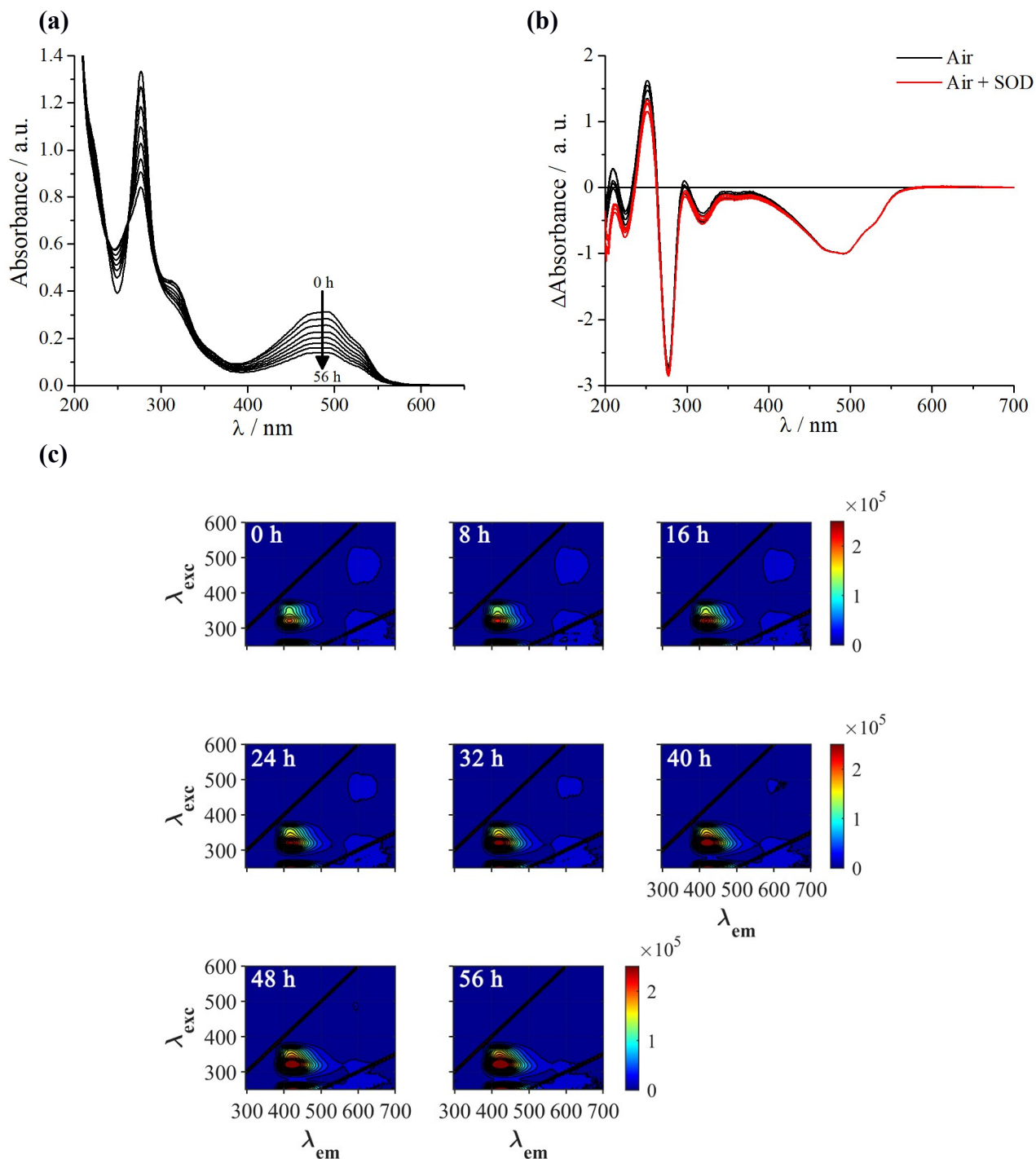


Figure SI.6. (a) UV-vis absorption and (b) Normalized Difference (ND) spectra of CA solution ($[\text{CA}]_0 = 110 \mu\text{M}$) irradiated ($h\nu = 420 \text{ nm}$) in the absence (red) and in the presence (black) of SOD (40 U/ml). (c) Evolution of EEMs of CA irradiated solutions. Irradiation times are depicted as inset inside each EEM.

7. Effect of sodium azide (NaN_3) on the photodegradation of CA

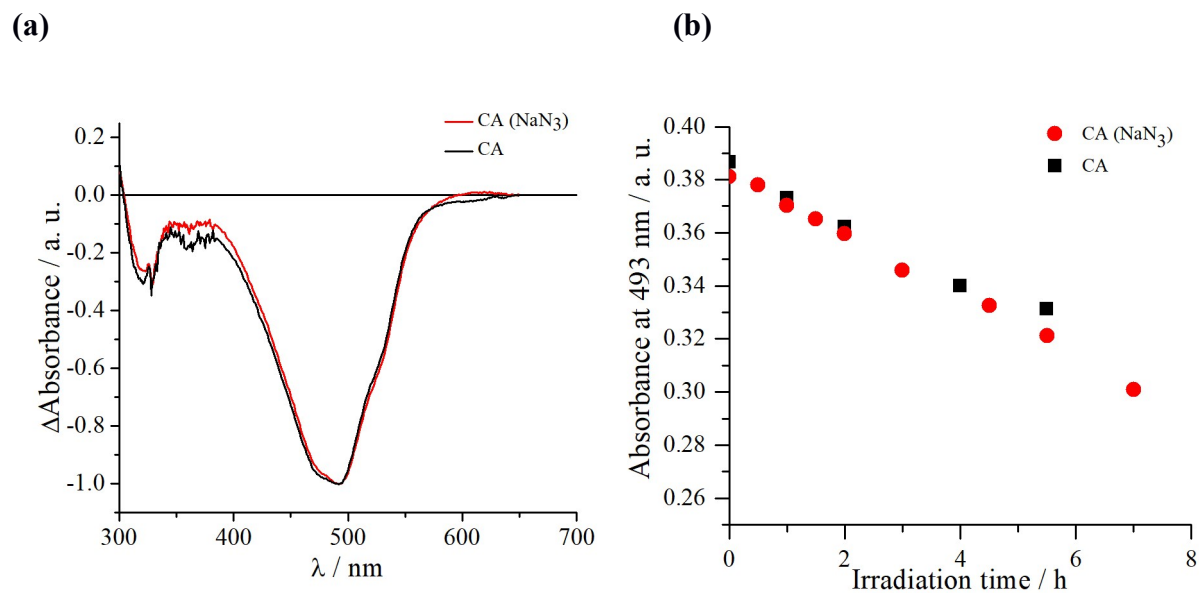


Figure SI.7. (a) Normalized Difference (ND) UV-vis absorption spectra of CA solution ($[\text{CA}]_0 = 110 \mu\text{M}$) irradiated ($h\nu = 420 \text{ nm}$, irradiation time = 7 h) in the absence (**black**) and in the presence (**red**) of sodium azide ($[\text{NaN}_3]_0 = 11 \text{ mM}$). (b) Evolution 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

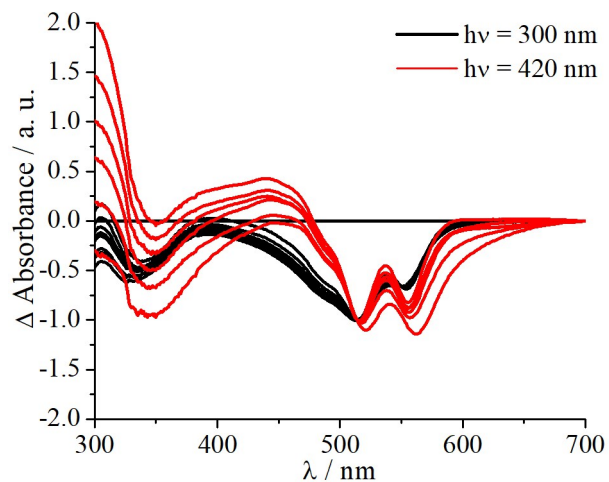


Figure SI.8. Normalized Difference (ND) absorption spectra of Lake aqueous solutions irradiated at $h\nu = 420$ nm (**red**) and 300 nm (**black**). Total irradiation time = 24 h.

9. EEMs of CA Lake irradiated aqueous solution (420 nm)

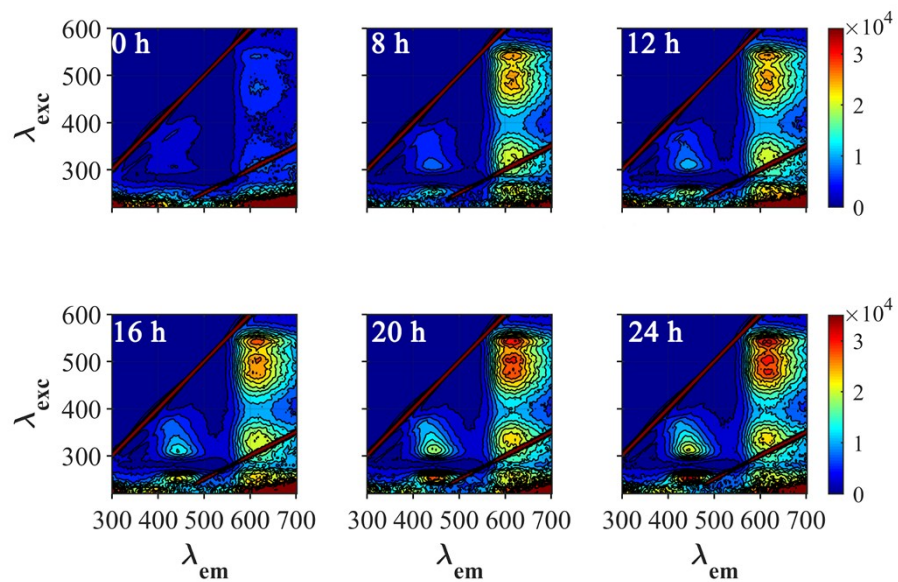


Figure SI.9. Evolution of EEMs of air-equilibrated Lake aqueous solution when subject to irradiation ($h\nu = 420$ nm). Irradiation times are depicted as inset inside each EEM.

10. EEMs of CA Lake irradiated aqueous solution (300 nm)

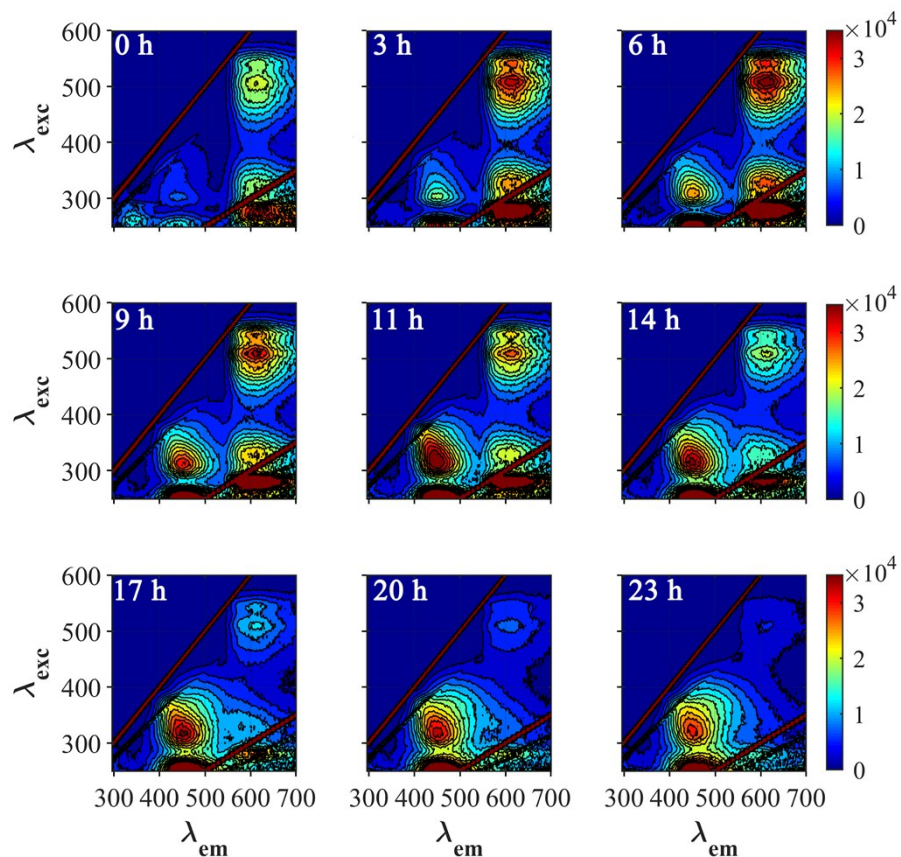


Figure SI.10. Evolution of EEMs of air-equilibrated Lake aqueous solution when subject to irradiation ($h\nu = 300$ nm). Irradiation times are depicted as inset inside each EEM.

11. Comparative analysis of CA, Lake and the photoproducts fluorescence emission spectra

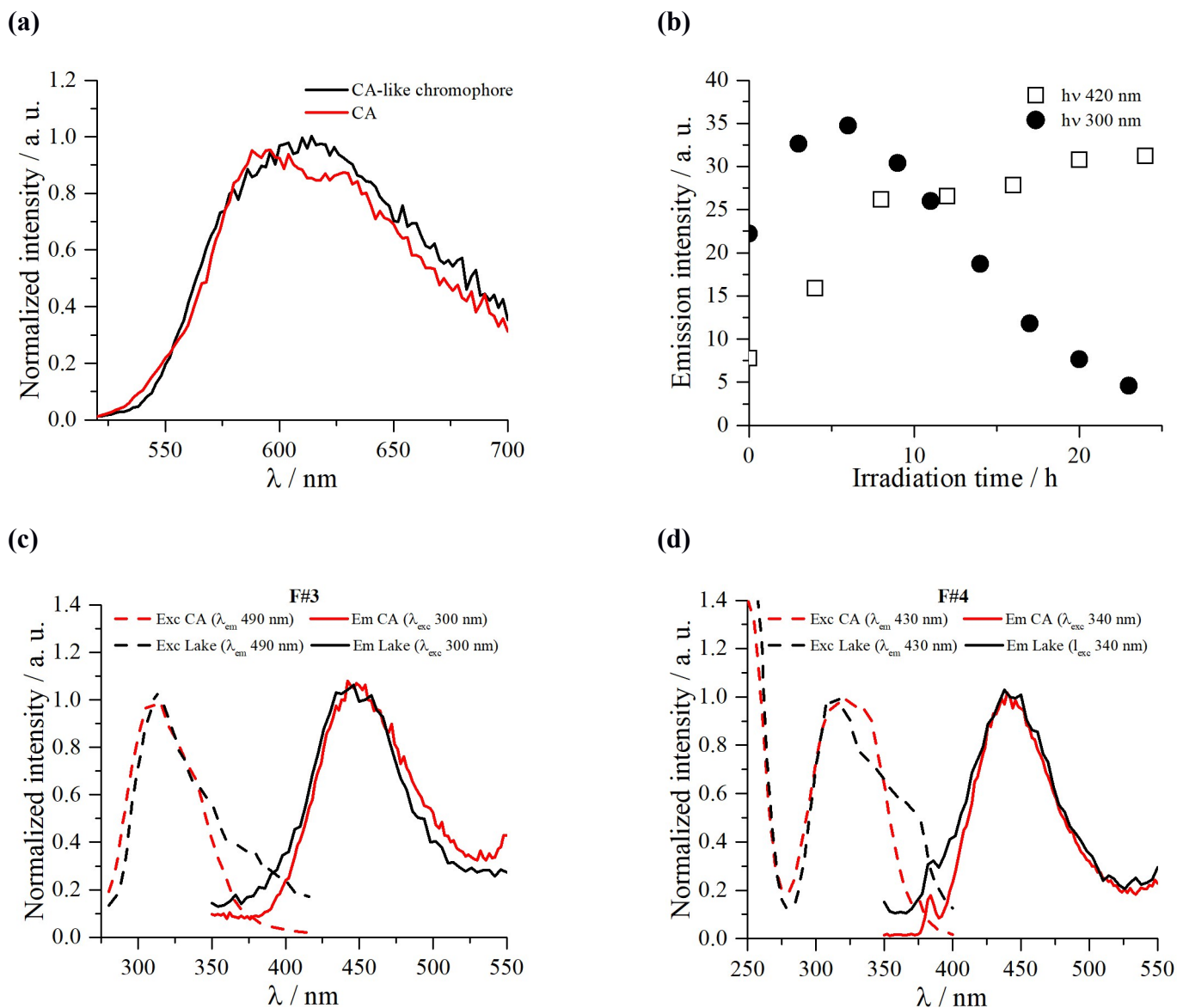


Figure SI.11. (a) Normalized fluorescence emission spectra of CA (red) and CA-like chromophore (black) produced upon irradiation ($h\nu = 300$ nm) of Lake. (b) Evolution of the total emission intensity of CA-like chromophore (calculated as the integral below the entire emission spectra) as a function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