# Electronic Supplementary information (ESI)

# Photosensitized reactions initiated by 6-carboxypterin: singlet and triplet reactivity

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1. **Experimental setup.**

**Laser Flash Photolysis.**

The laser output passed through a partially closed iris and went then through the aperture in the short axis (4 mm path length) of a fully masked quartz flow cell, mounted at 13 cm of the laser output. The solution containing the photosensitizer was introduced in the flow cell of 450 µL by means of a peristaltic pump, with a flow of 1.6 mL/min, ensuring a complete purge of the exposed volume every 17 s. This limited the exposition of the introduced solution to 3–4 laser shots and maintained a constant temperature in the flow cell. All connections where made from either glass or PTFE tubing, ensuring a clean liquid flow. Typically, 32 measurements were averaged on the oscilloscope at each wavelength to obtain a transient absorption spectrum, with an accuracy of 3%. The full transient absorption spectrum was then reconstructed from the steady and transient signals.

**Chemical analysis.**

For each experiment, solvent and PFBHA impurities were checked diluting 500 µL of water in 500 µL of a 1:1, v:v, water:acetonitrile mixture and 200 µL of water in 800 µL of the daily PFBHA solution. Signal stability over time was checked using two standard solutions of adipic acid (2 µM) and levulinic acid (20 µM), this latter being daily diluted by a factor 5 in a 1mg mL$^{-1}$ PFBHA solution and left at room temperature for 24 hours for carbonyl group derivatization.

2. **Contribution of the dianionic (basic) form to the emission spectrum at pH 7.2:**

At pH 7.2, CPT is for 18.8% under its dissociated dianionic form. Taking into account the reported fluorescence quantum yield of the acid and basic form, 0.26 and 0.18 respectively, the contribution

of the acid and basic form to the total fluorescence emission spectrum would be 13.8% and 86.2% respectively[1]. But the dianionic form has a higher molar absorption coefficient, $\varepsilon_{\lambda 350nm}$, than the monoanionic form, which compensates almost for the lower quantum yield. Indeed the molar absorption coefficient measured at pH 4.6 ($\varepsilon_{350nm} = 472.28$ M$^{-1}$ cm$^{-1}$) is about 30% lower than the one obtained at pH 10.8 ($\varepsilon_{350nm} = 663.98$ M$^{-1}$ cm$^{-1}$), while the quantum yield of the acid form is 44% higher. So the contribution of the basic dianionic form to the fluorescence emission spectrum will be around 16% of the total emission. Since our solutions have pH in the 7-7.3 range, containing 10-33.5% of dianionic CPT, the contribution of this form to the total fluorescent emission spectrum will be in the range of 9-28.5%.

1   A. H. Thomas, C. Lorente, A. L. Capparelli, M. R. Pokhrel, A. M. Braun and E. Oliveros, Photochem. Photobiol. Sci., 2002, 1, 421-426.

### 3.   Comparison of the oxidation of I$^-$ by ozone and by photochemical reaction with CPT.

To calculate the I$^-$ loss through these two pathways, we assumed a concentration of 20 ppb of ozone[1] in the gas phase and an estimated concentration of 1 x 10$^{-9}$ M of CPT with as quantum yield of 0.28[2].This concentration was based on an rough estimation of the concentration of pterins in the seawater[3], since, to the best of our knowledge, no concentrations for pterins in the SML or in the aerosols have been reported. The parameters used are resumed in the Table S2.

In this case, the loss of I$^-$ through the photochemical pathway (singlet and triplet CPT) represents approximately 50% of the total loss rate. That a major part of the I$^-$ loss could be explained by this type of photochemical reactions, illustrates the importance of such pathways. This example is of course limited, since it assumes concentrations for CPT and does not take into account the lifetime

of the excited state, the quantum yield for the triplet state, other competing reactions with $I^-$… More work would be needed to evaluate the exact impact of such processes in the marine environment.

1. R. R. Dickerson, K. P. Rhoads, T. P. Carsey, S. J. Oltmans, J. P. Burrows and P. J. Crutzen, *Journal of Geophysical Research*, 1999, **104**, 21385-21396.

2. M. P. Serrano, C. Lorente, F. E. M. Vieyra, C. D. Borsarelli and A. H. Thomas, *Phys. Chem. Chem. Phys.*, 2012**, 14**, 11657-11665

3. A. Momzikoff, R. Santus and M. Giraud, *Mar. Chem.,* 1983**, 12**, 1-14.

**Table S1: Molar absorption coefficients of 6-carboxypterin**

| pH | $\lambda_{max}$ (nm) | $\varepsilon_{max}$ ($M^{-1}$ $cm^{-1}$) | $\varepsilon_{350nm}$ ($M^{-1}$ $cm^{-1}$) |
|---|---|---|---|
| 4.6 | 300 | 489.49 | 472.28 |
| 7.4 | 347 | 548.36 | 539.28 |
| 10.8 | 364 | 808.78 | 663.98 |

**Table S2: Comparison of the oxidation of I⁻ by ozone and by photochemical reaction with CPT**

| | Oxidation by ozone | Photochemical oxidation by $^3$CPT | Photochemical oxidation by $^1$CPT |
|---|---|---|---|
| k ($M^{-1}$ $s^{-1}$) | $1.5 \times 10^9$ | $1.89 \times 10^8$ | $4.06 \times 10^9$ |
| [I-] (M) | $1 \times 10^{-8}$ | $1 \times 10^{-8}$ | $1 \times 10^{-8}$ |
| [O3] (M) | $8.172 \times 10^{-10}$ | | |
| [*CPT] (M) | | $0.28 \times 10^{-9}$ | $0.28 \times 10^{-9}$ |
| **Calculated loss rate (M s⁻¹)** | **$1.23 \times 10^{-8}$** | **$5.29 \times 10^{-10}$** | **$1.14 \times 10^{-8}$** |
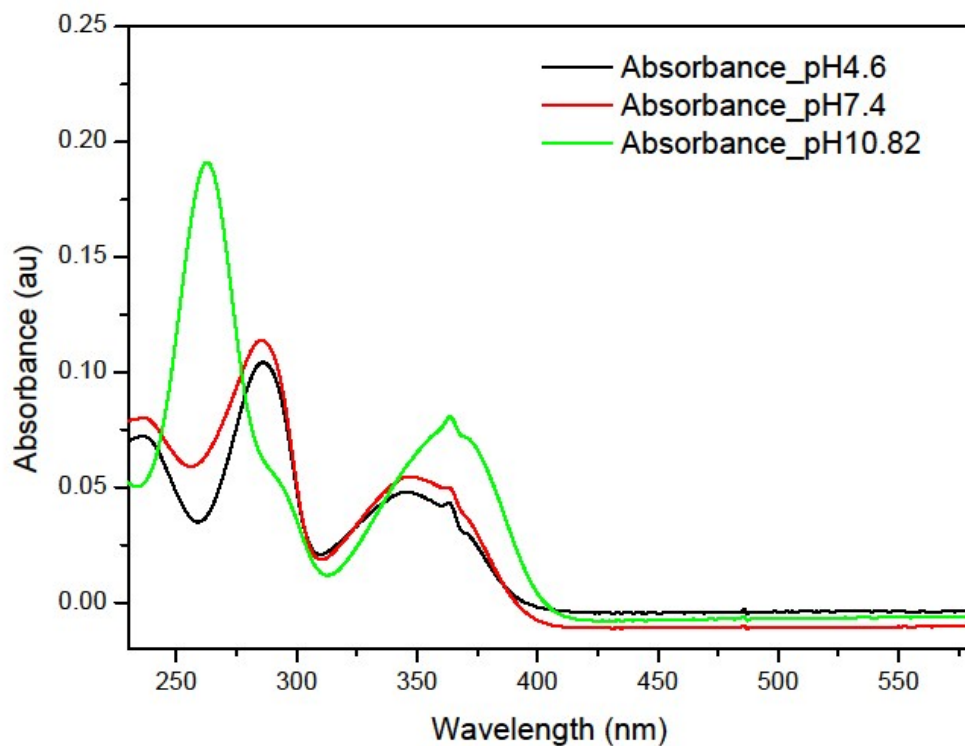
**Figure S1:**



*Fig. S1: UV-Vis absorption spectrum of ground state CPT (0.1mM) at different pH: pH 4.6 (black), pH 7.4 (red) and pH 10.8 (green)*

**Figures S2:**

Fluorescence emission spectra of CPT with different concentrations of quenchers: (a) iodide, (b) chloride, (c) propionic acid, (d) citric acid, (e) lactic acid, (f) malonic acid and (g) limonene. In figure S2(g) the specta were taken in a mixture acetonitrile-water, and the spectrum of an aqueous solution of CPT is shown for comparison.
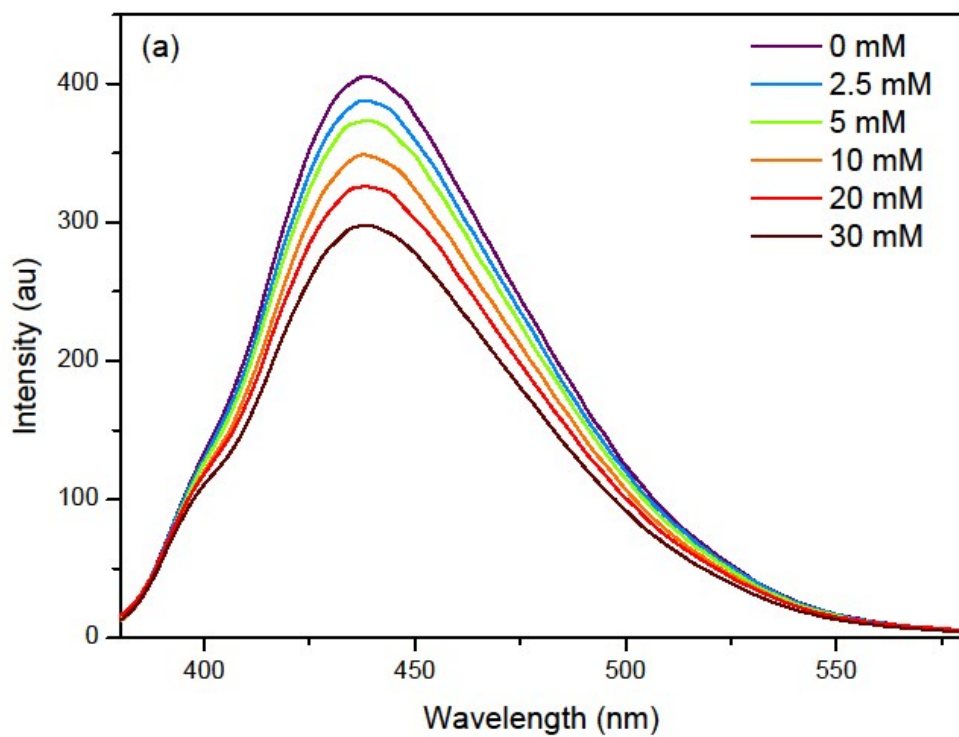
*Fig. S2 (a): iodide*
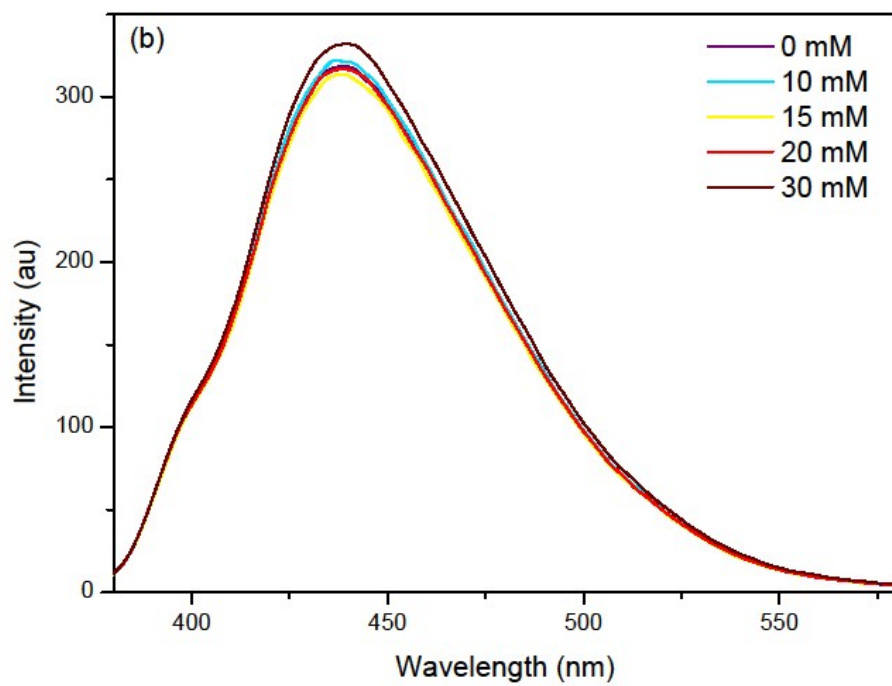
*Fig. S2 (b): chloride*
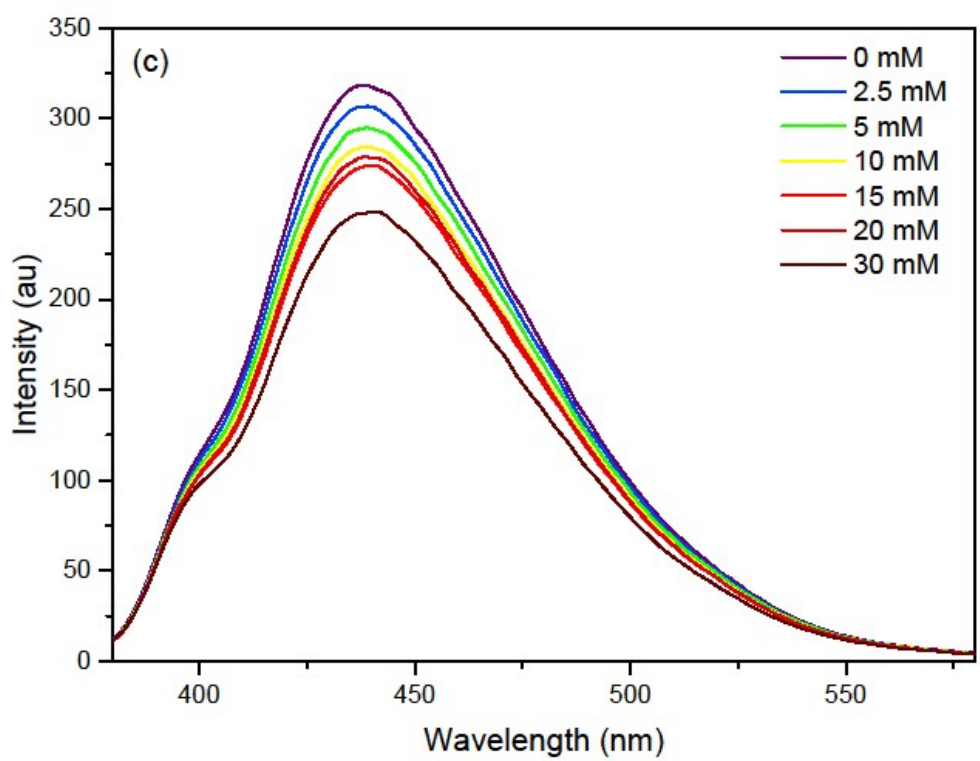
*Fig. S2 (c): propionic acid*
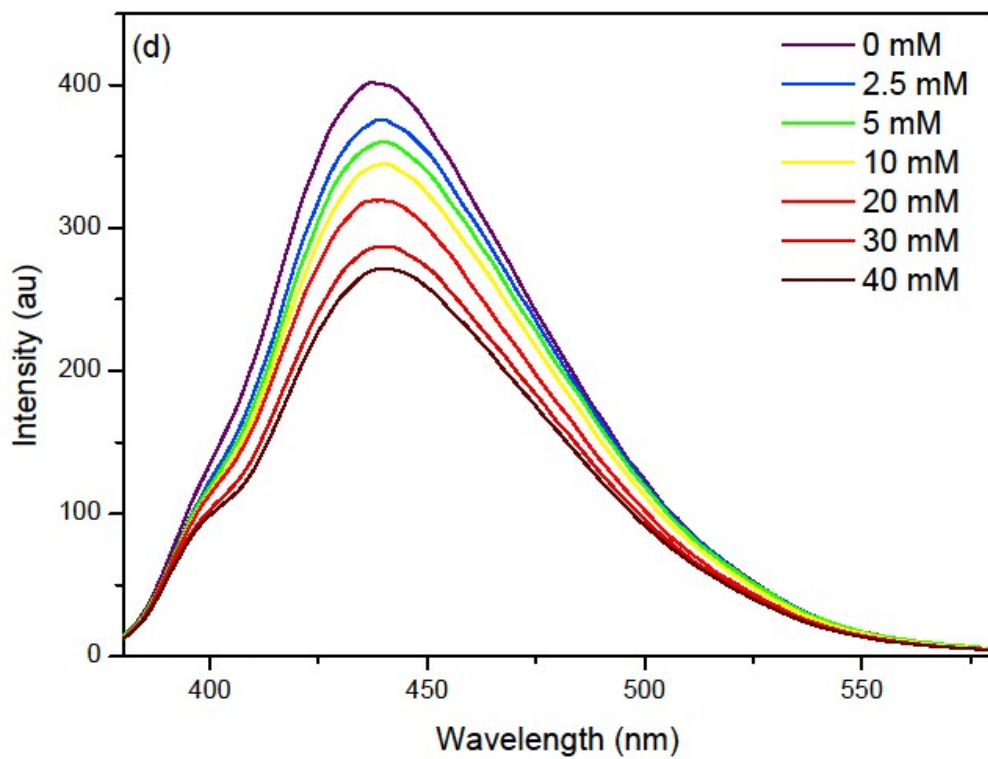
*Fig. S2 (d): citric acid*
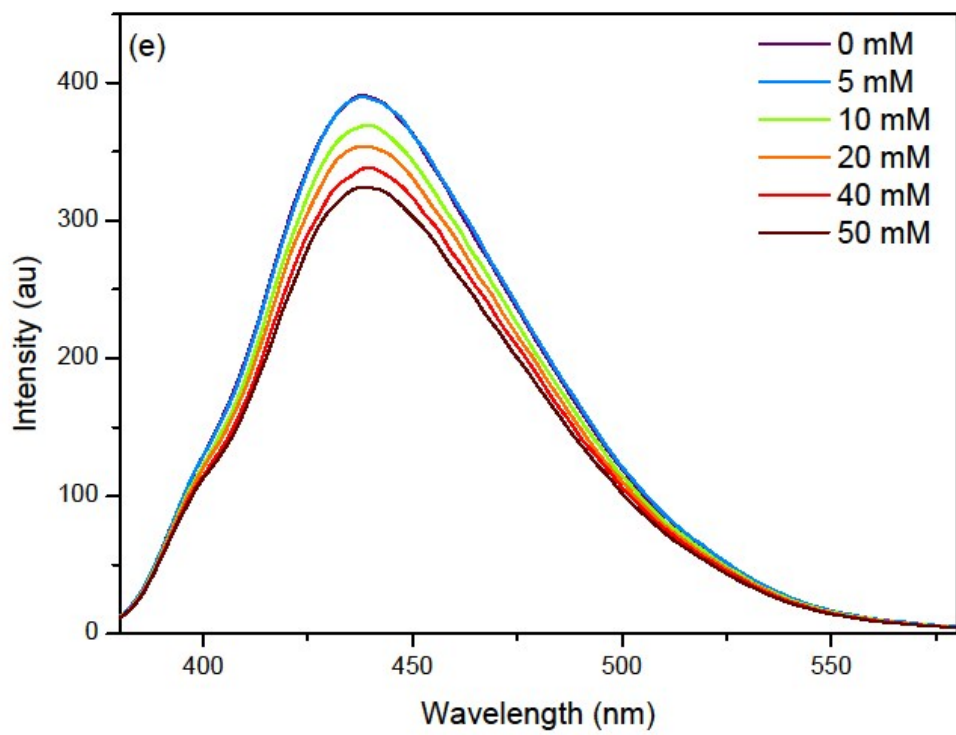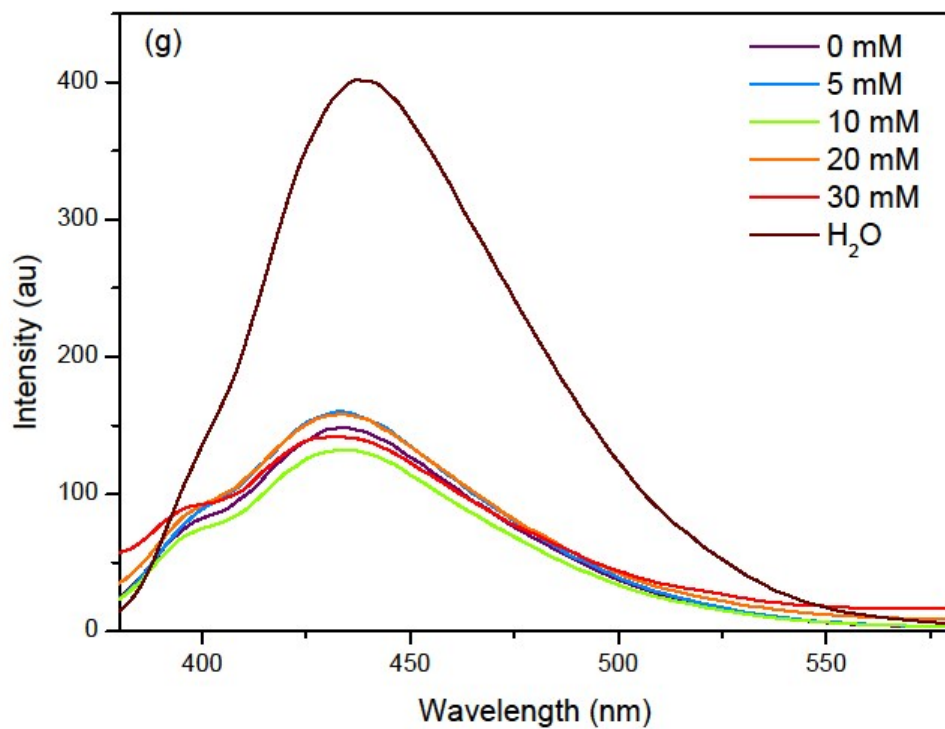
*Fig. S2 (e): lactic acid*
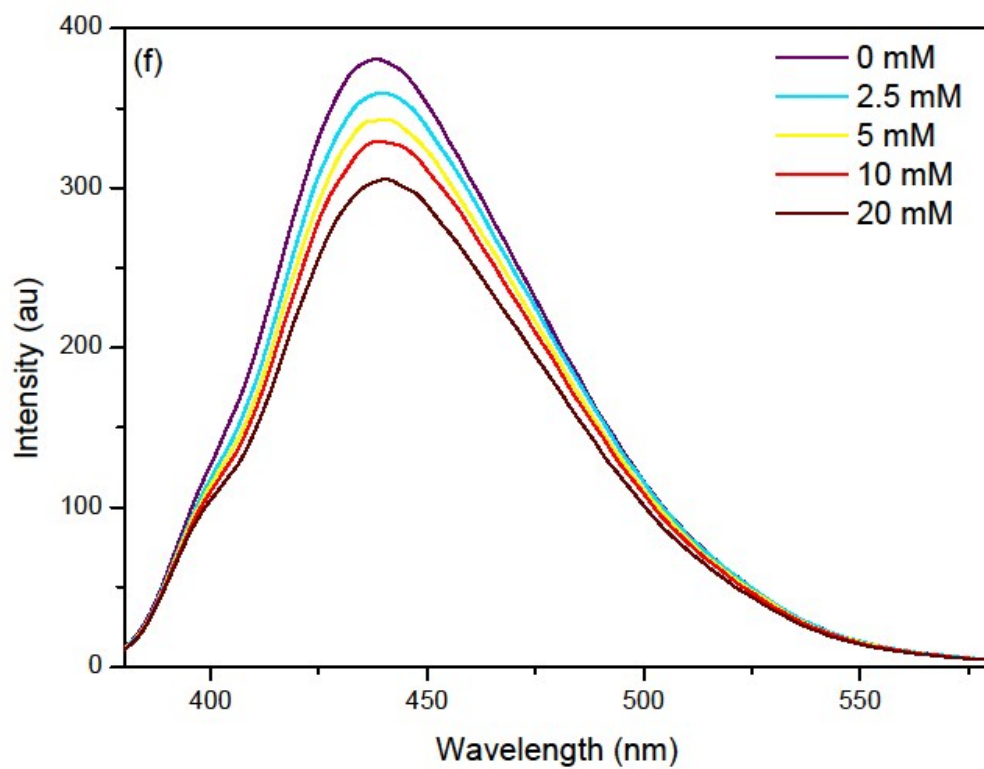
*Fig. S2 (f): malonic acid*

*Fig. S2 (g): limonene*

**Figure S3:**
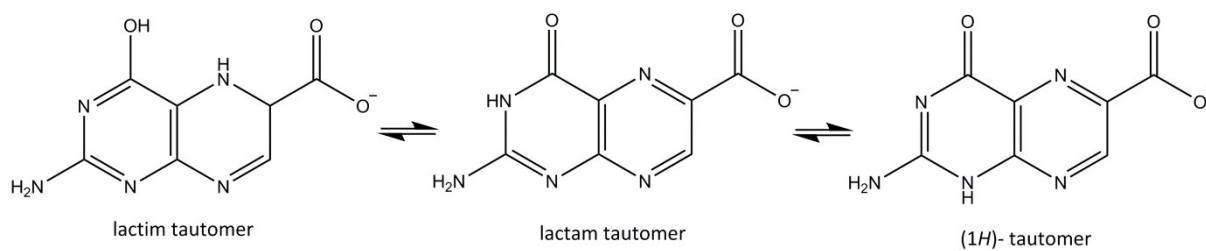


lactim tautomer       lactam tautomer       (1*H*)- tautomer

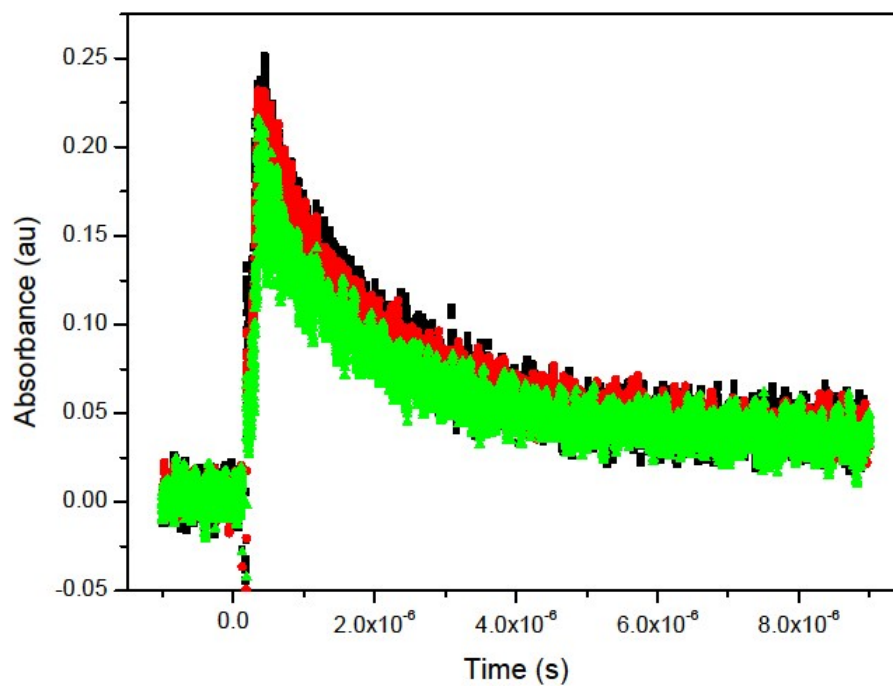*Fig. S3: Configuration of the most stable tautomers for CPT*

*Fig. S4: Transient signal of absorption of triplet CPT (0.2 mM) in water-actonitrile at 425 nm without limonene ( ■) and in presence of 50 mM ( ●) and 100 mM ( ◆) limonene registered 450ns after the laser pulse*