

Photo-activated thin films of porphyrins for reactive oxygen species generation

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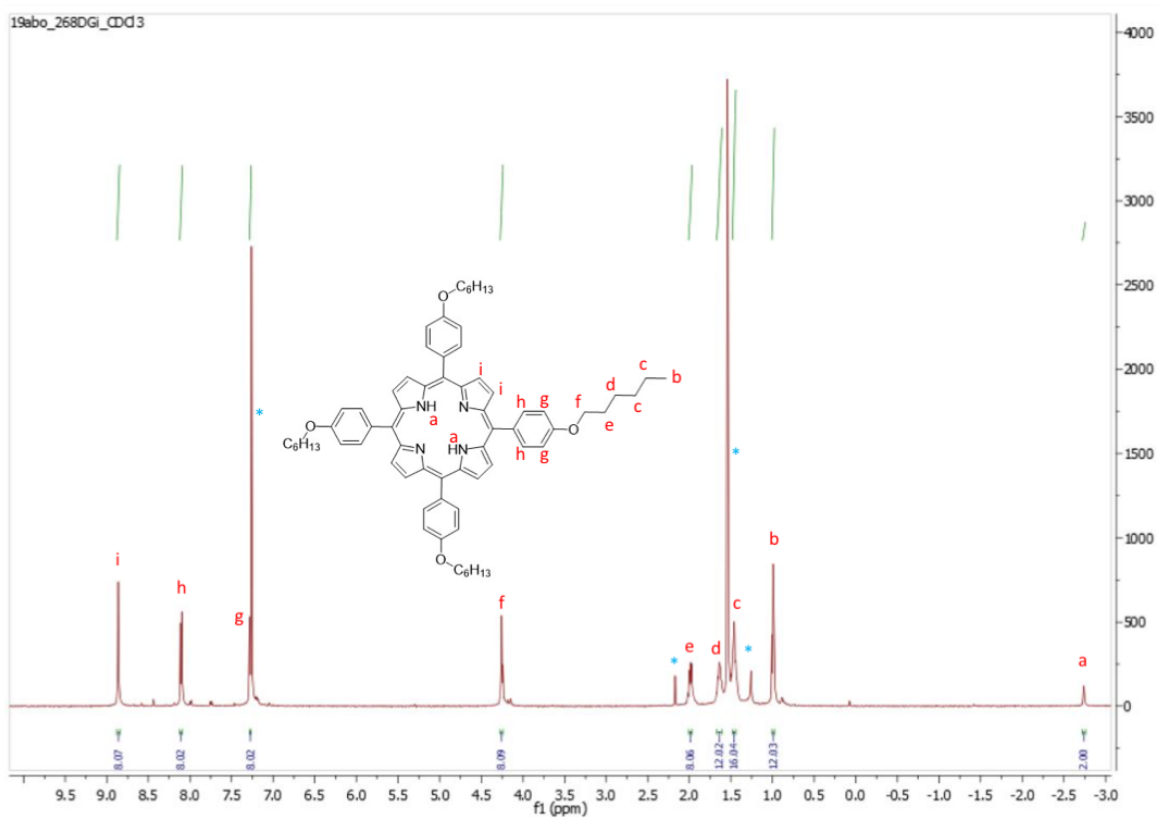


Fig. S1. ^1H NMR spectrum of **THOPP**, dissolved in deuterated chloroform (CDCl_3). This spectrum is very similar to the one in reference 22.

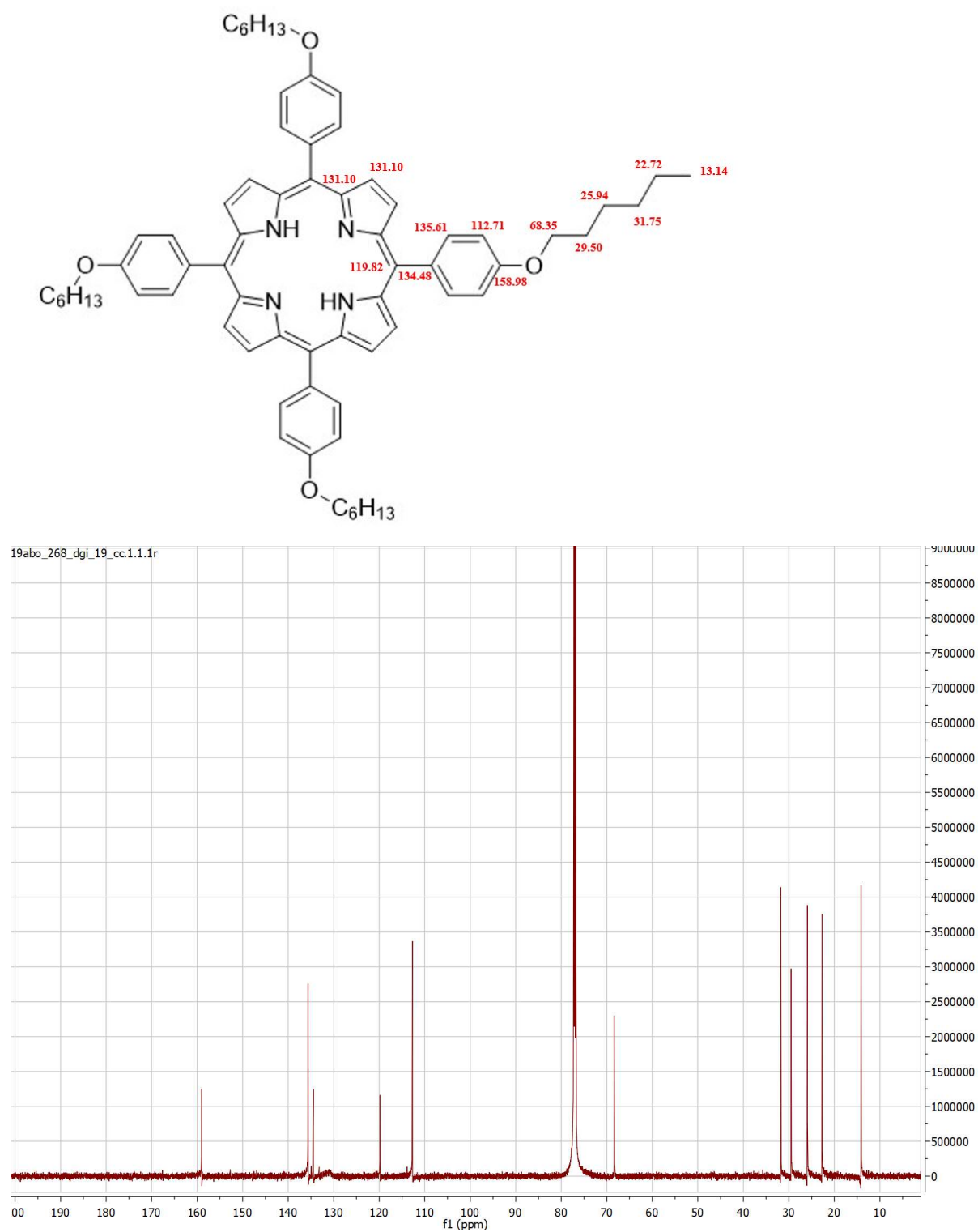


Fig. S2: ^{13}C NMR spectrum of **THOPP**, dissolved in deuterated chloroform (CDCl_3). This spectrum is very similar to the one in reference 22.

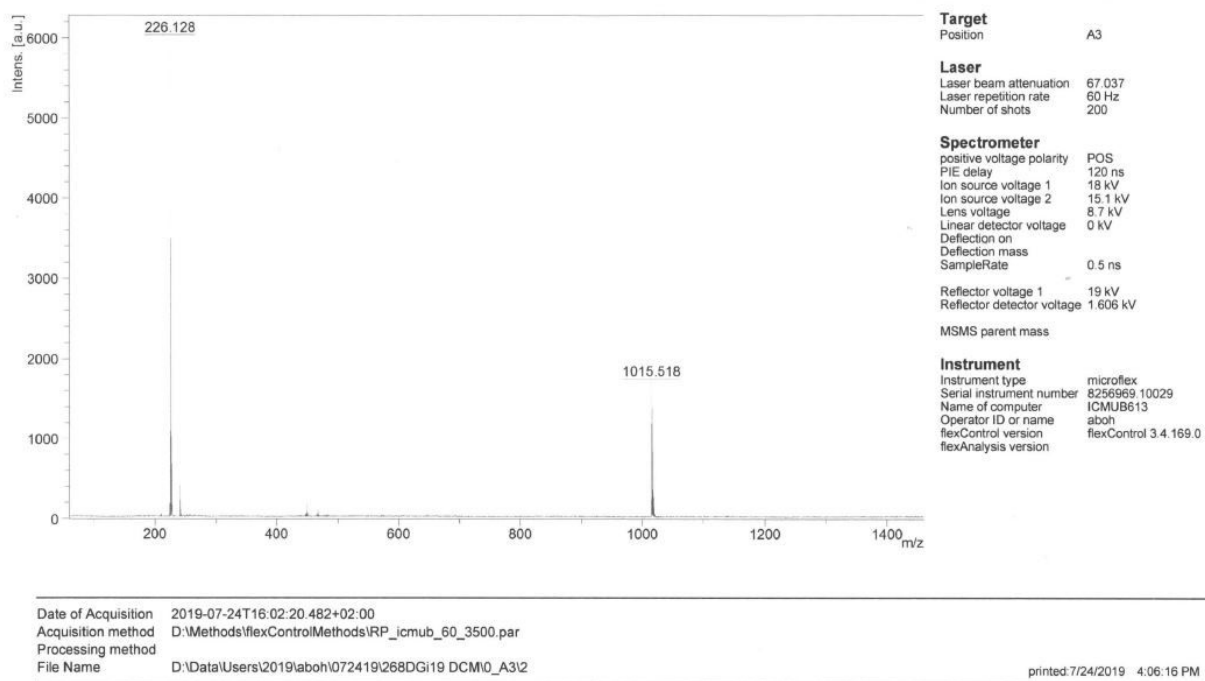


Fig. S3: Mass spectrum of *THOPP*, dissolved in dichloromethane (CH_2Cl_2 , dithranol matrix).

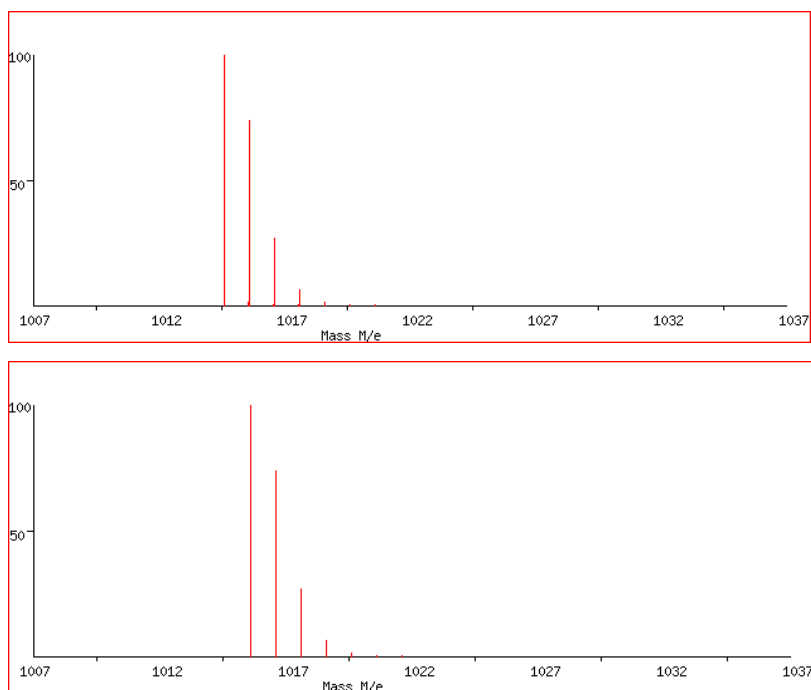
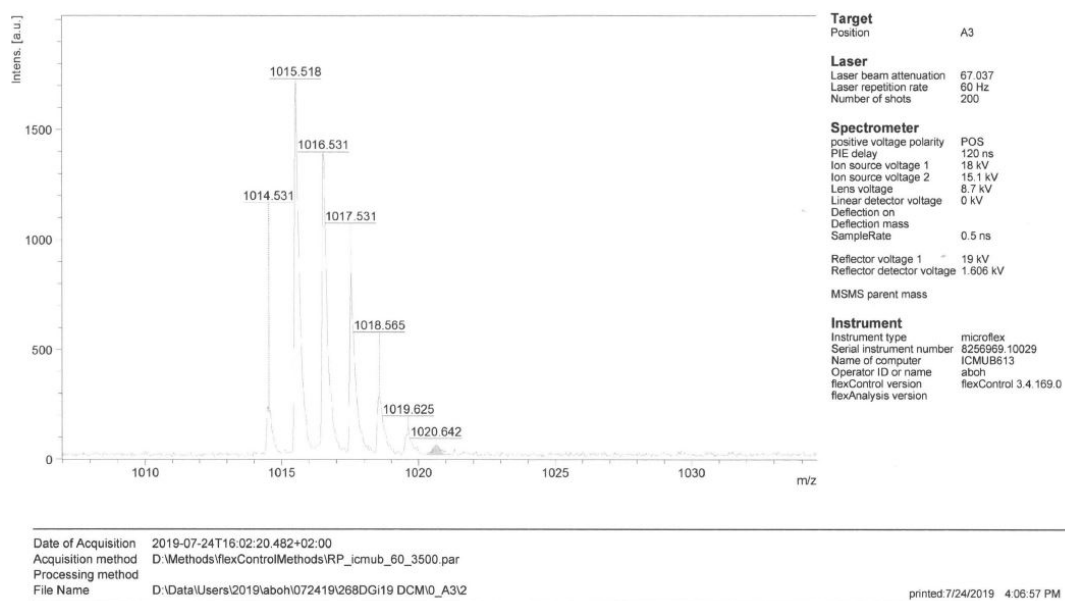


Fig. S4: Mass spectrum zoom (top), displaying the isotope pattern of **THOPP**, dissolved in dichloromethane (CH_2Cl_2 , dithranol matrix) together with calculated isotope patterns for the MS of **THOPP**. $[\text{M}]^+ = \text{C}_{68}\text{H}_{78}\text{N}_4\text{O}_4$ for upper simulation. $[\text{M}+\text{H}]^+ = \text{C}_{68}\text{H}_{79}\text{N}_4\text{O}_4$, lower simulation.

Peaks detected at: 1014.5, 1015.5, 1016.5, 1017.5, 1018.6, 1019.6, 1020.6.

Calculated at: $[\text{M}]^+$: 1014.6, 1015.6, 1016.6, 1017.6, 1018.6, 1019.6, 1020.6;

for $[\text{M}+\text{H}]^+$: 1015.6, 1016.6, 1017.6, 1018.6, 1019.6, 1020.6, 1021.6.

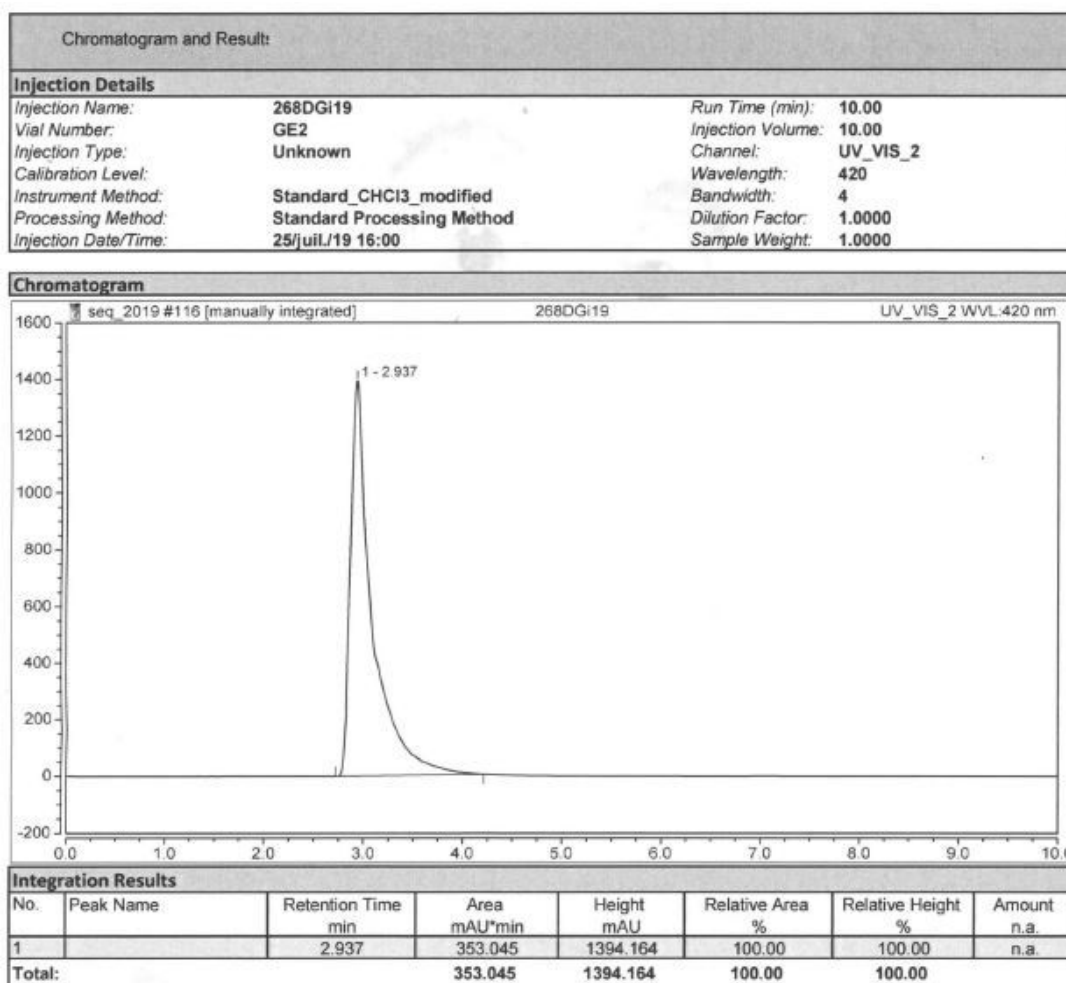


Fig. S5: HPLC analysis of *THOPP*, eluens is CHCl_3 .

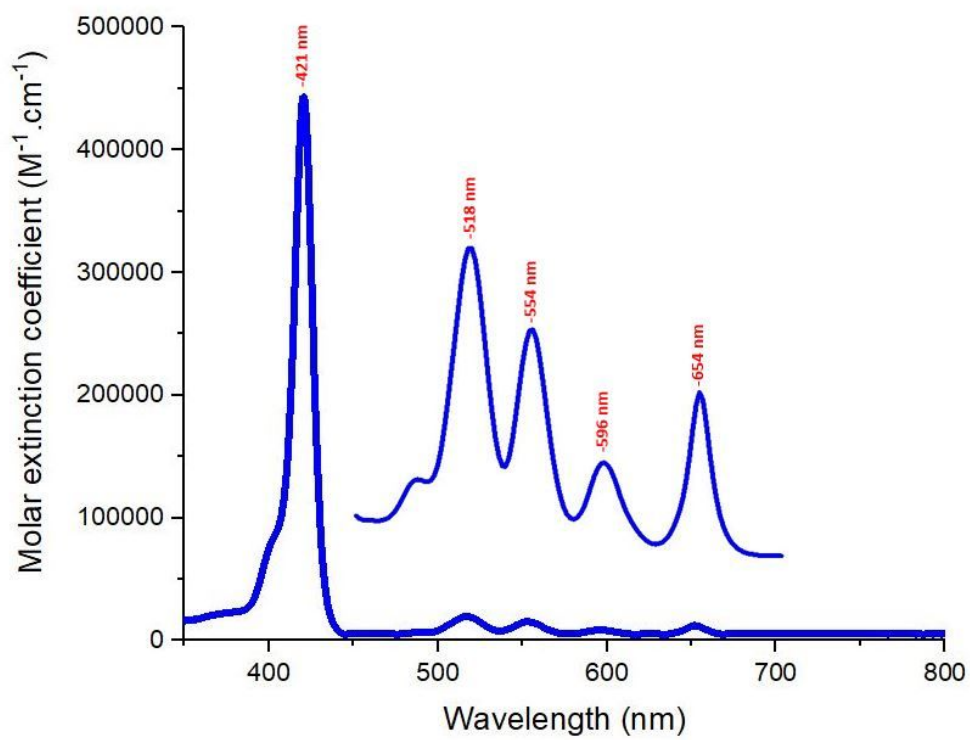


Fig. S6: UV-Visible absorption spectrum of **THOPP**, dissolved in THF. The concentration of **THOPP** in the THF solution was 2.2 μ M.

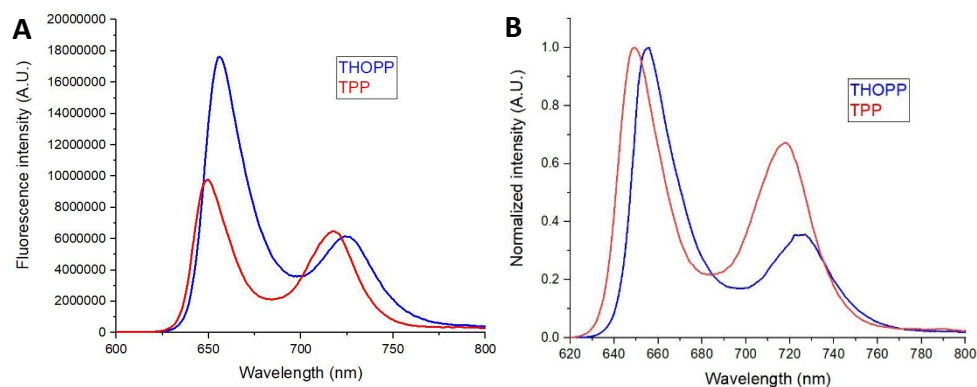


Fig. S7. (A): Fluorescence spectra of **THOPP** (blue) and **TPP** (red) in CHCl_3 using **TPP** in toluene (0.11) as a reference (Excitation wavelength = 518 nm and absorbance of both samples at this wavelength was 0.1) [25]. The fluorescence quantum yield obtained for **THOPP** was 0.22. **(B):** Normalized fluorescence emission spectra of **THOPP** (blue) and **TPP** (red) in CHCl_3 . $[\text{THOPP}] = 4 \mu\text{M}$ and $[\text{TPP}] = 4.5 \mu\text{M}$.

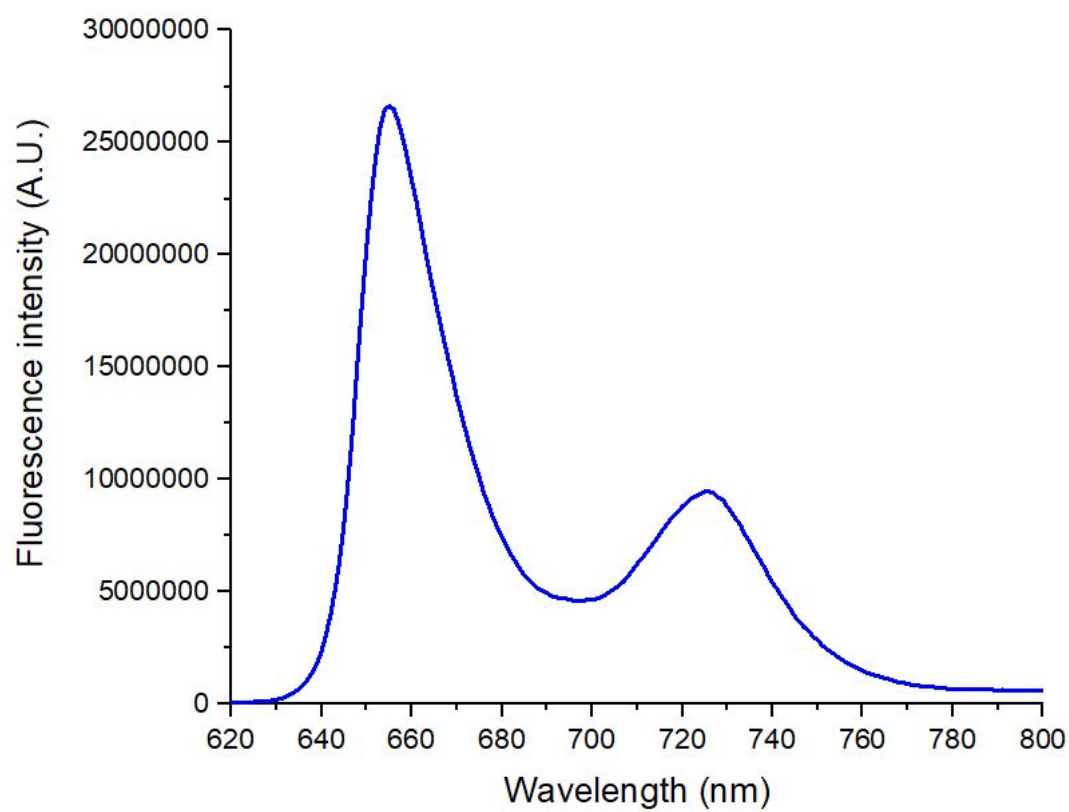


Fig. S8: Emission spectrum of **THOPP** in THF, excitation at 518 nm.

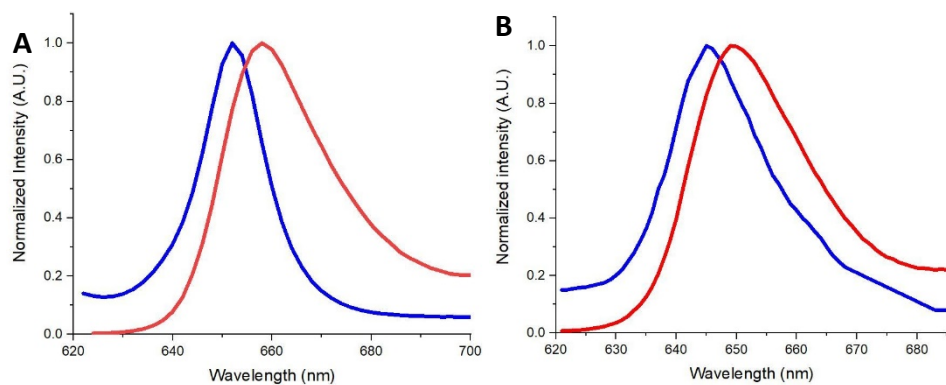


Fig. S9. (A): THOPP's normalized absorption (blue) and emission spectra (red) in CHCl_3 . $E(S_1)$ of **THOPP** = 654 nm.

(B): TPP's normalized absorption (blue) and emission spectra (red) in CHCl_3 . $E(S_1)$ of **TPP** = 648 nm.

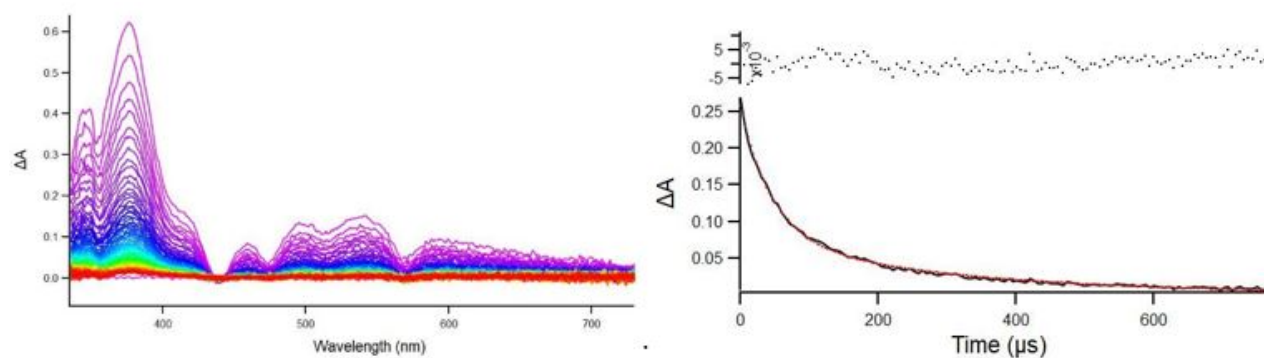


Fig. S10: (Left): Nanosecond transient absorption spectrum of **THOPP** in THF (in oxygen-free solution). Excitation wavelength = 517 nm, incremental time delay = 6 μ s. Time increases from violet to red. (Right): Decay kinetics trace at 517 nm. The decay curve was decayed bi-exponentially.

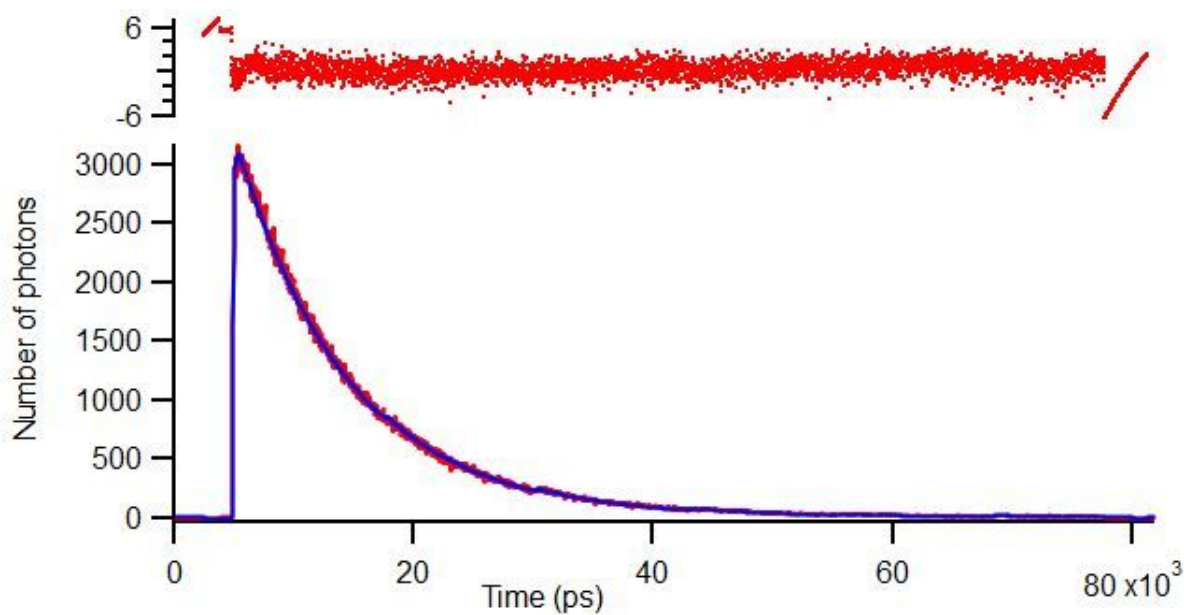


Fig. S11. Time-correlated single photon counting (TC-SPC) data of **THOPP** in THF. Excitation wavelength = 560 nm. Emission wavelength = 650 nm. The absorbance was 0.05 at the excitation wavelength. Laser power is 0.44 mW and at this power, **THOPP** data was fitted mono-exponentially, the S_1 lifetime is 9.33 ns. On the top, weighted residuals are presented. Note the longer time axis, relative to figure S12 and S13.

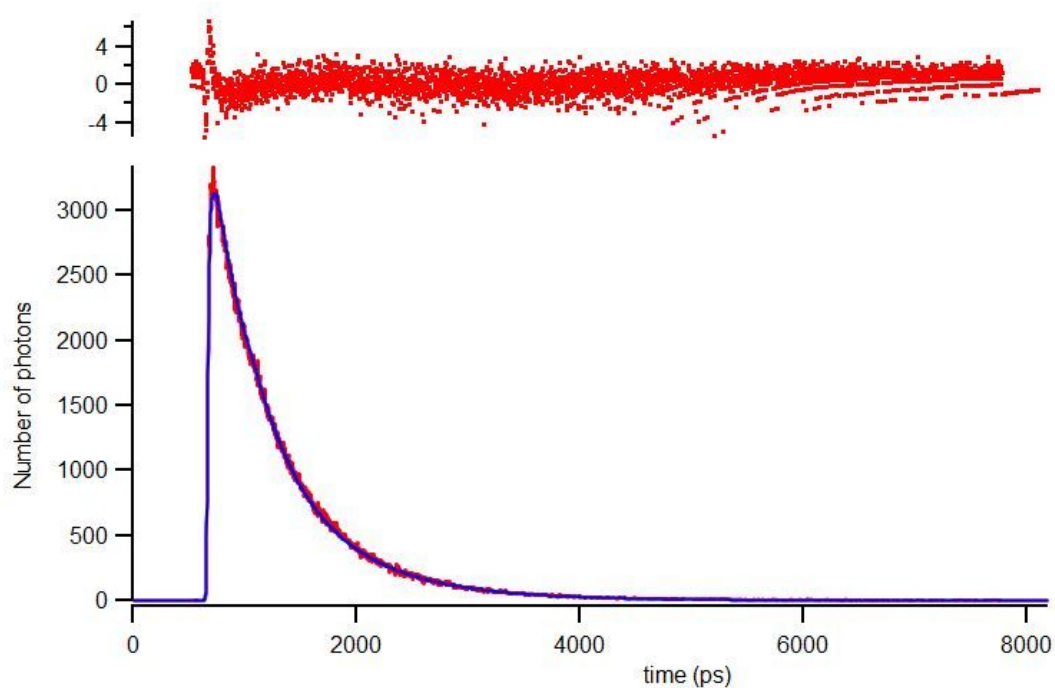


Fig. S12: Time-correlated single photon counting of **THOPP** in a SC thin film (at full laser power). Excitation wavelength = 560 nm. Emission wavelength = 650 nm. The optical density was 0.05 at the excitation wavelength (560 nm). Laser power is 0.44 mW. **THOPP** decays bi-exponentially in this film at this laser power. Weighted residuals are shown on top of the graph.

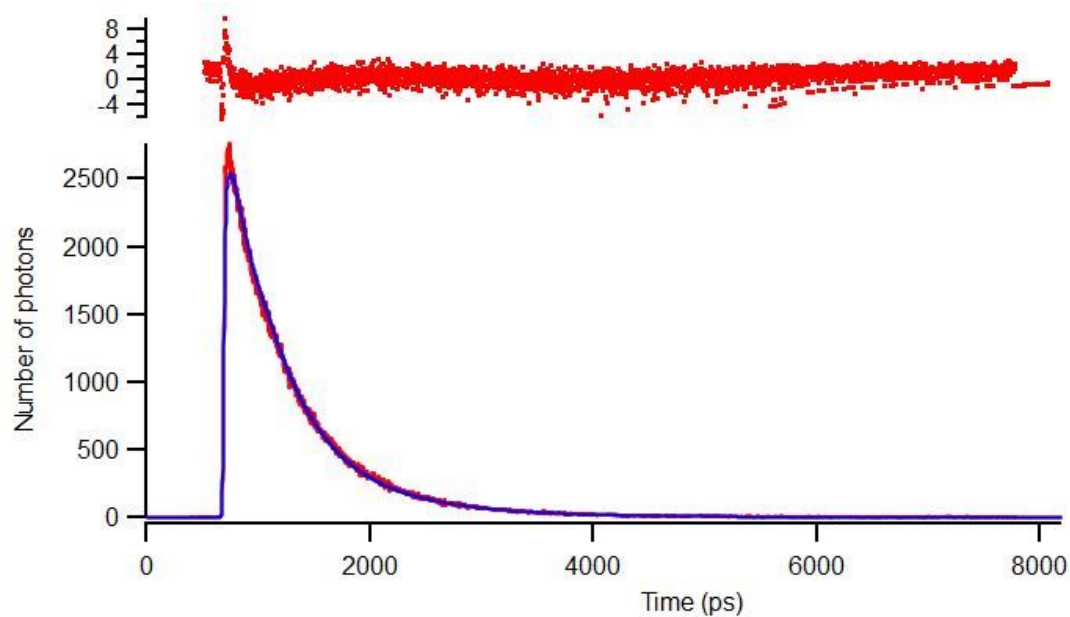


Fig. S13: Time-correlated single photon counting spectrum of **THOPP** in a thin film (at half laser power). Excitation wavelength = 560 nm. Emission wavelength = 650 nm. The optical density was 0.05 at the excitation wavelength (560 nm). Laser power is 0.22 mW and **THOPP** decays were fitted bi-exponentially in this film at this laser power. Weighted residuals are shown on top of the graph.

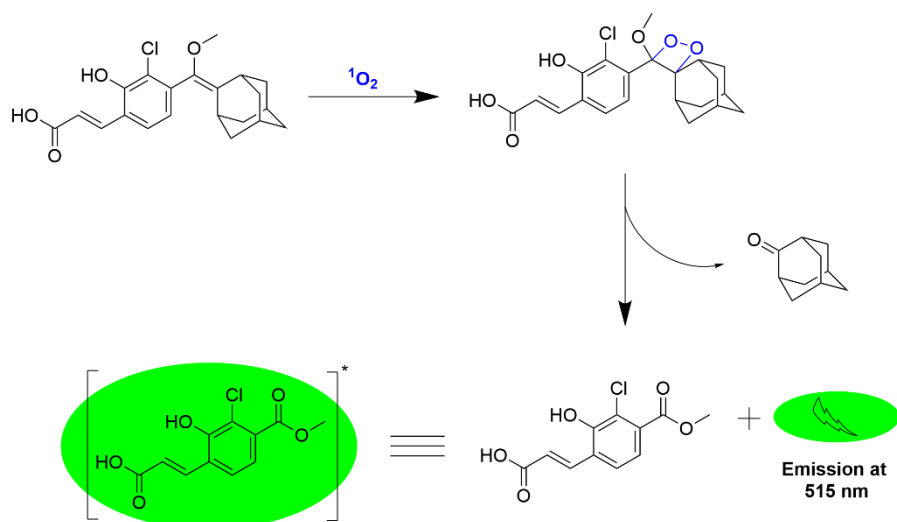


Fig. S14. Mechanism of AquaSpark probe (SOCL) reacting with singlet oxygen to give emission at 515 nm by a chemiluminescent reaction.