SUPPORTING INFORMATION

Diphenyl Functional Porphyrins and their metal complexes as Visible-Light Photoinitiators for Free-Radical, Cationic and Thiol-Ene Polymerizations

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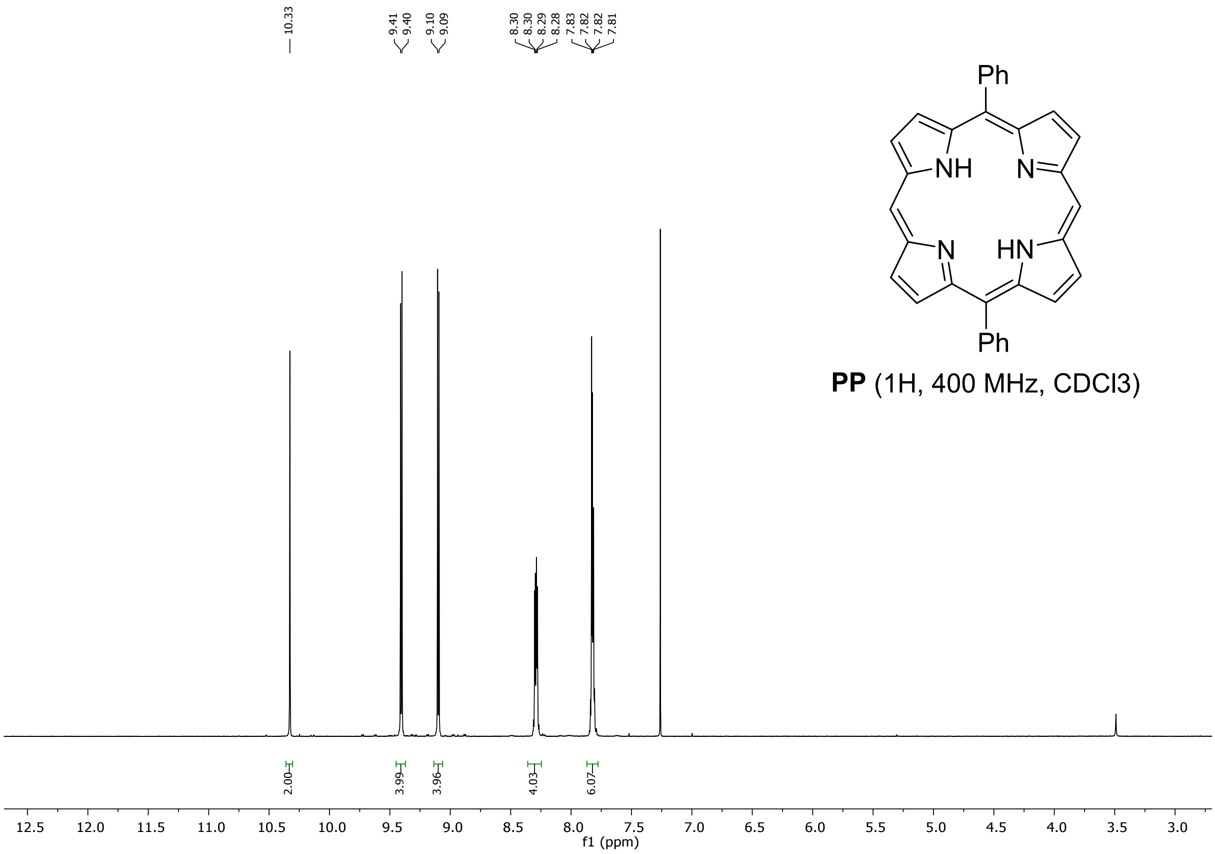


Figure S1. ^1H NMR spectrum of **PP** (in $CDCl_3$)

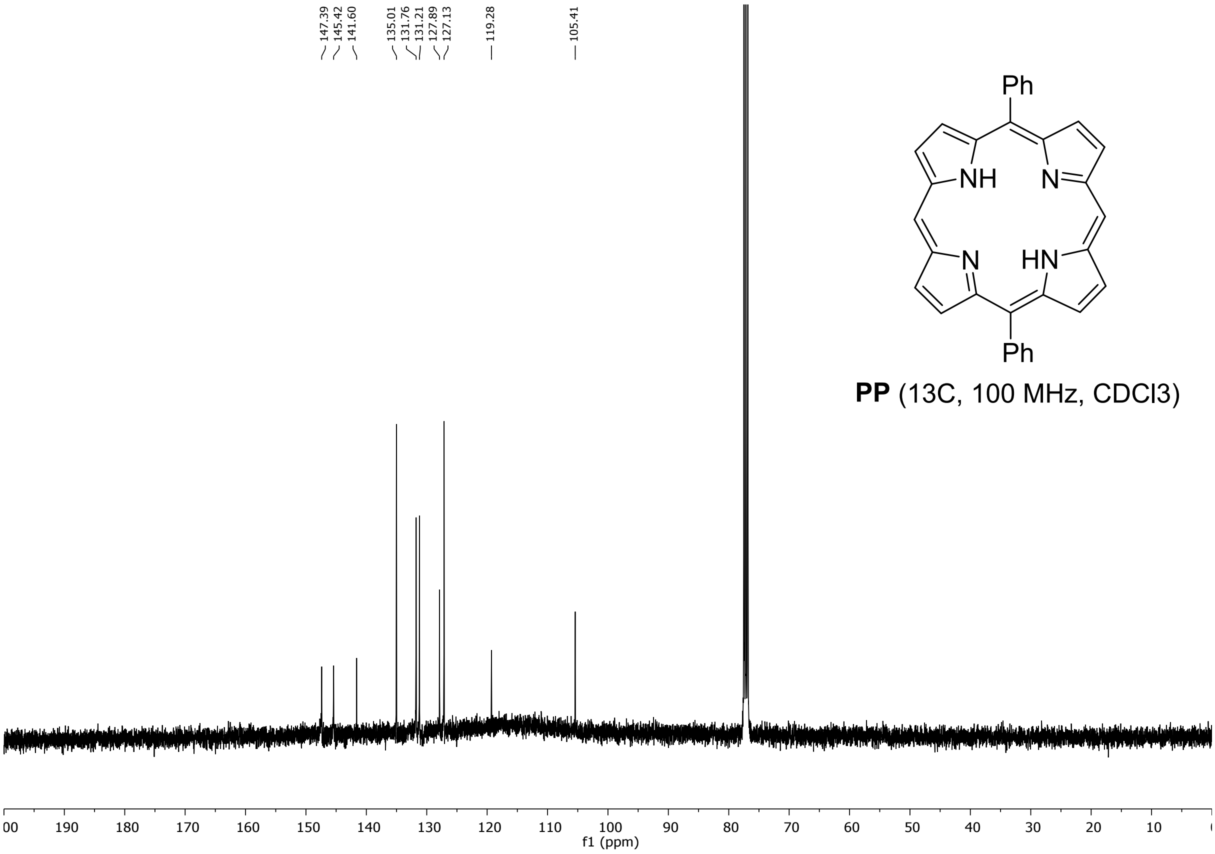
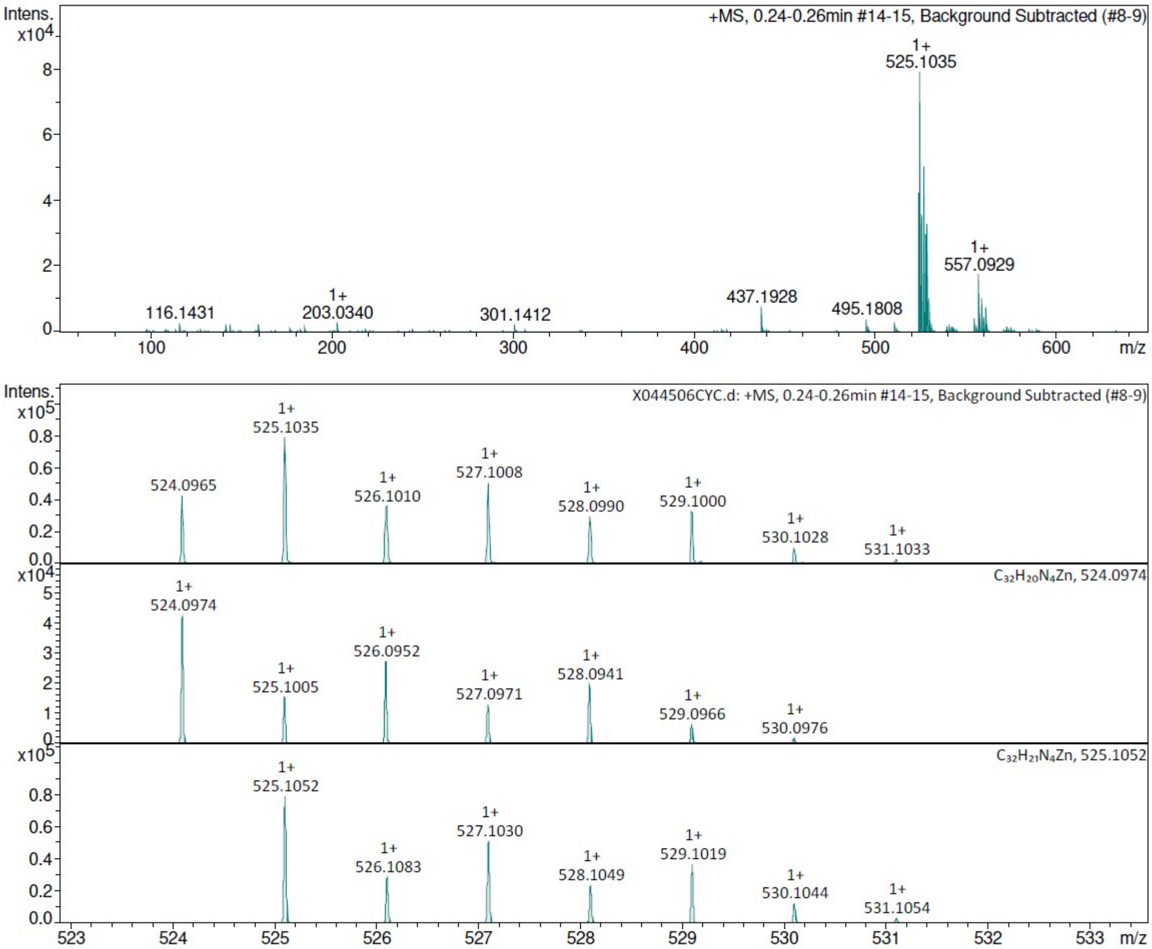


Figure S2. ^{13}C NMR spectrum of **PP** in $CDCl_3$

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e^- Conf
524.096516	1+	1	C32H20N4Zn	524.097390	1.7	349.2	25.5	odd
	1+	2	C31H24O4Zn	524.096053	-0.9	357.9	20.5	odd
525.103473	1+	1	C32H21N4Zn	525.105215	3.3	48.8	25.0	even
	1+	2	C31H25O4Zn	525.103878	0.8	57.3	20.0	even
557.092867	1+	1	C27H21N6O4Zn	557.091022	-3.3	25.2	21.0	even
	1+	2	C31H25O6Zn	557.093707	1.5	31.3	20.0	even
	1+	3	C32H21N4O2Zn	557.095045	3.9	35.4	25.0	even

Figure S3. HRMS analysis of **PPZn**

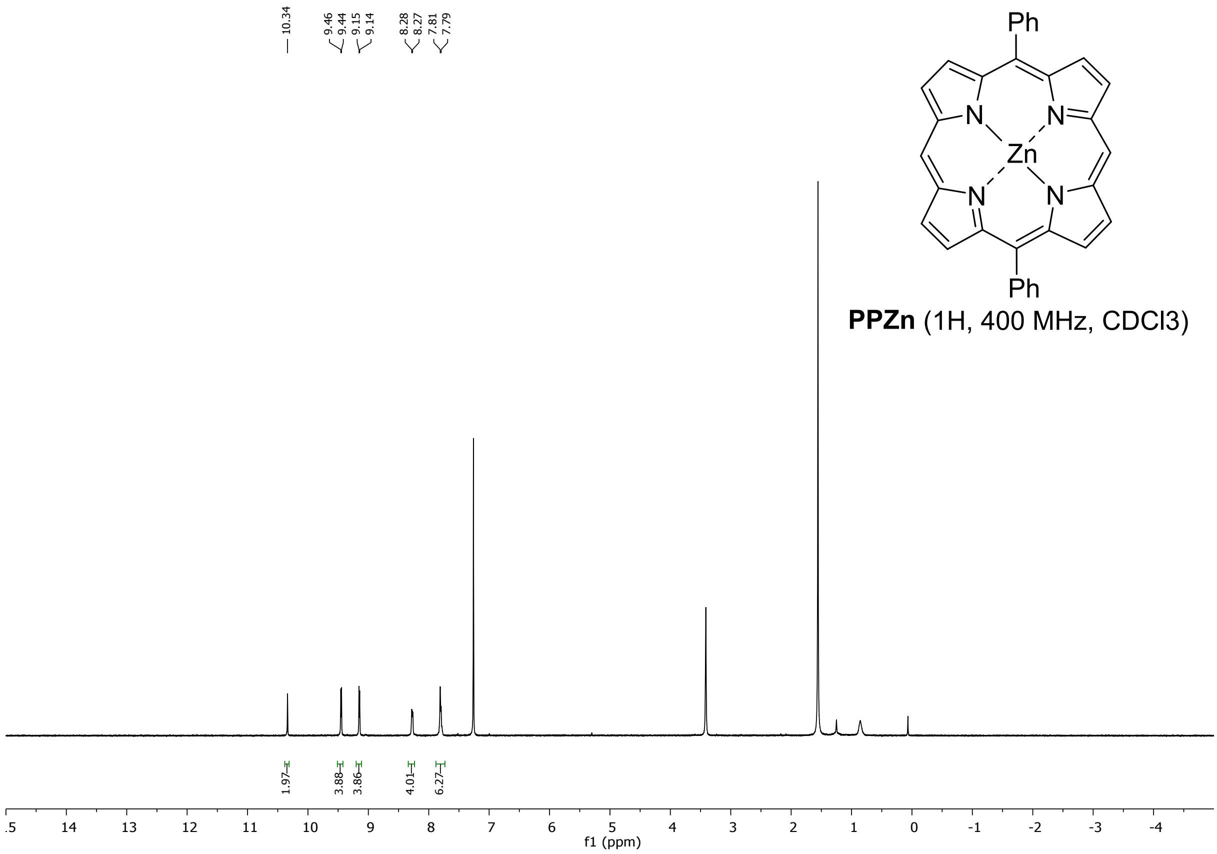


Figure S4. ^1H NMR spectrum of **PPZn** in $CDCl_3$

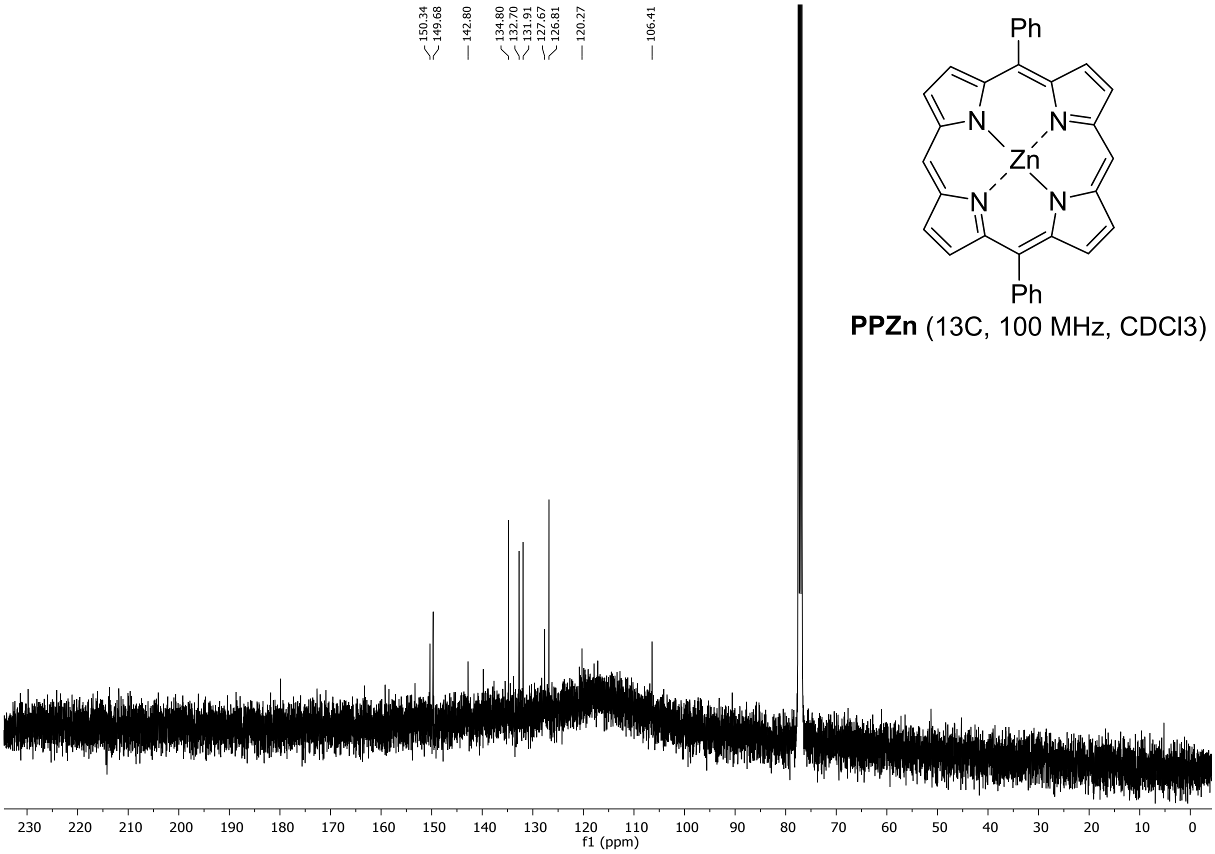


Figure S5. ^{13}C NMR spectrum of **PPZn** in $CDCl_3$.

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
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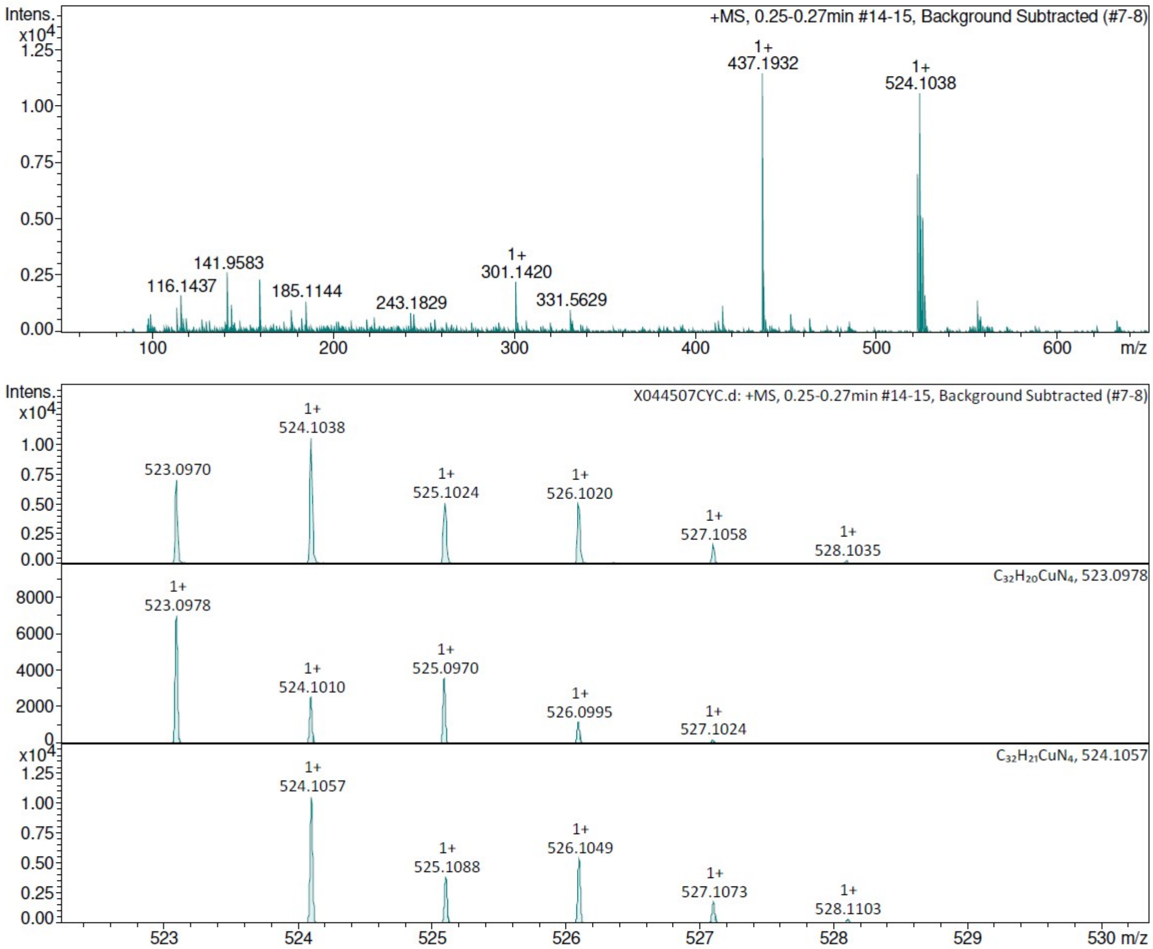
Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e⁻ Conf
523.096977	1+	1	C32H20CuN4	523.097846	1.7	355.5	25.0	even
	1+	2	C31H24CuO4	523.096508	-0.9	365.5	20.0	even
524.103760	1+	1	C32H21CuN4	524.105671	3.6	58.0	24.5	odd
	1+	2	C31H25CuO4	524.104333	1.1	67.9	19.5	odd

Figure S6. HRMS analysis of **PPCu**

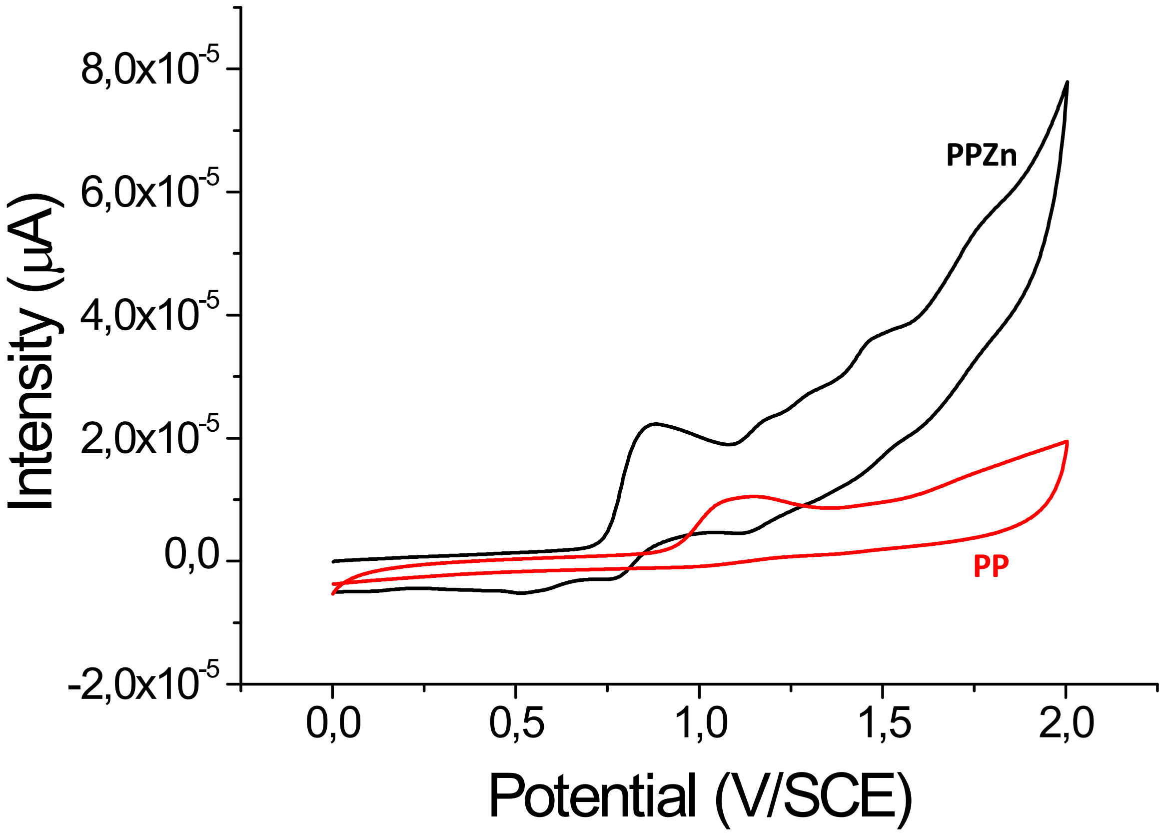


Figure S7. Cyclic voltammogram of **PP** and **PPZn** in acetonitrile + 0.05 M Bu_4NBF_4 measured at a scan rate of 50 mV.s^{-1}. [**PP**] = [**PPZn**] = 10^{-3} M.

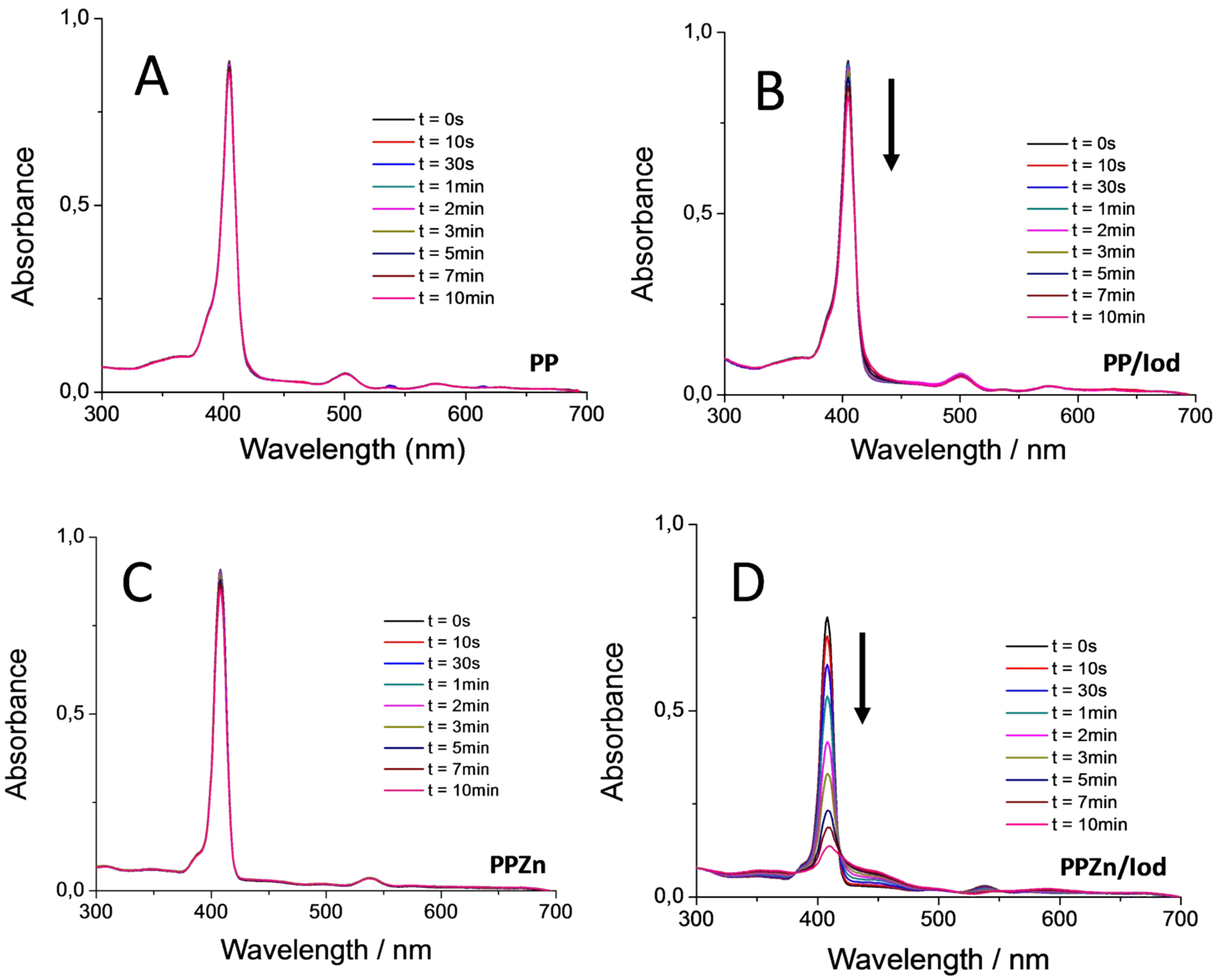


Figure S8. Steady-state photolysis of A) **PP**, B) **PP**/Iod, C) **PPZn** and D) **PPZn**/Iod in dichloromethane after LED@385 nm exposure under air. [**PP**] = 1,89 x 10^{-6} mol/L, [**PPZn**] = 1,67 x 10^{-6} mol/L; [Iod] = 3 x 10^{-5} mol/L.

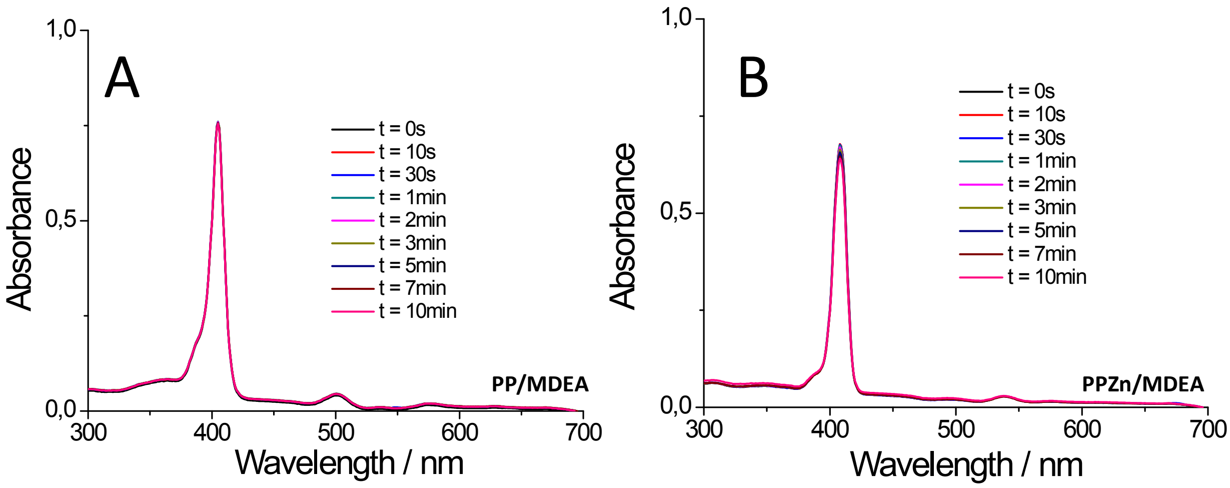


Figure S9. Steady-state photolysis of A) **PP**/MDEA and B) **PPZn**/MDEA in dichloromethane after LED@385 nm exposure under air. [**PP**] = 1,89 x 10^{-6} mol/L, [**PPZn**] = 1,67 x 10^{-6} mol/L; [MDEA] = 30 x 10^{-3} mol/L.

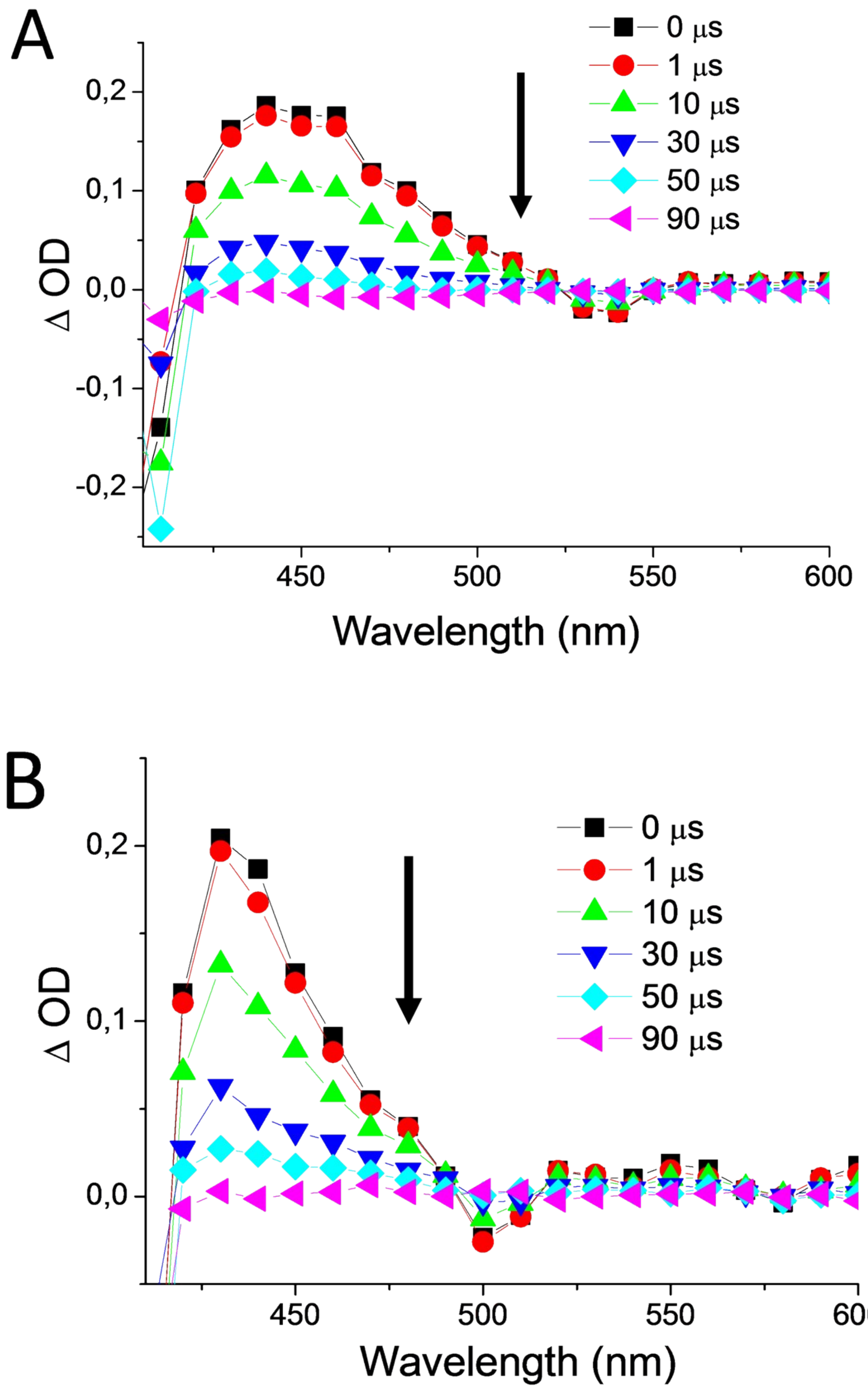


Figure S10. Transient absorption spectra of A) **PPZn** and B) **PP** in deoxygenated CH_2Cl_2 solution at 0 μs, 1 μs, 10 μs, 30 μs, 50 μs and 90 μs after the laser pulse (385 nm, 7 ns pulse width).

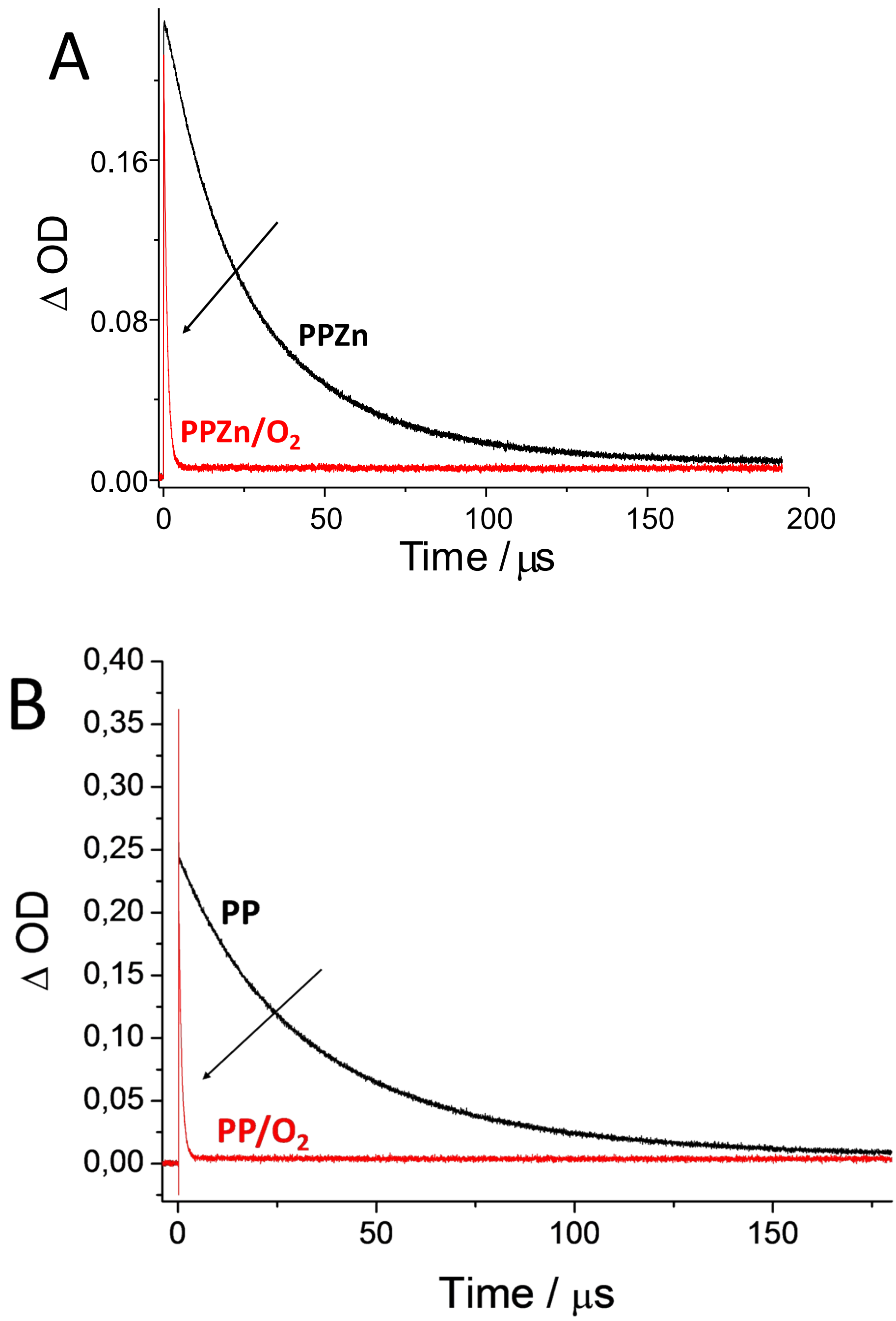


Figure S11. Decay traces of A) **PPZn** and B) **PP** triplet state after a laser pulse (λ_{ex} = 385 nm) with and without oxygen.

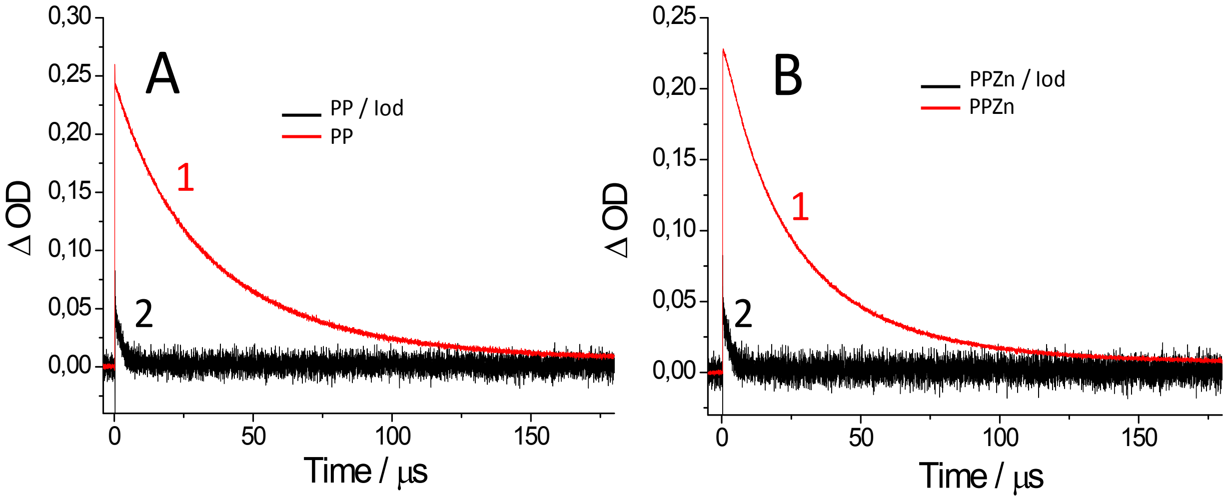


Figure S12. Decay traces of A) **PP** and B) **PPZn** triplet state after a laser pulse (λ_{ex} = 385 nm) without Iod (trace 1) and with Iod (trace 2). [**PP**] = 1.3 x 10^{-6} mol/L and [**PPZn**] = 1.67 x 10^{-6} mol/L.

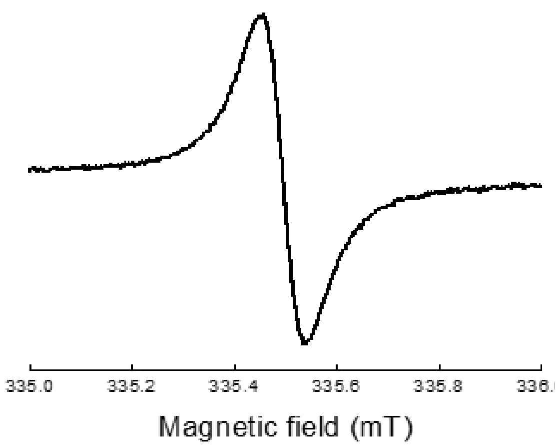


Figure S13. Experimental EPR spectra obtained upon LED@385nm exposure at 295 K of a **PPZn**/Iod solution under argon. Solvent = benzene. Lorentzian EPR signal (g = 2.0045; ΔBpp = 0.08 mT).

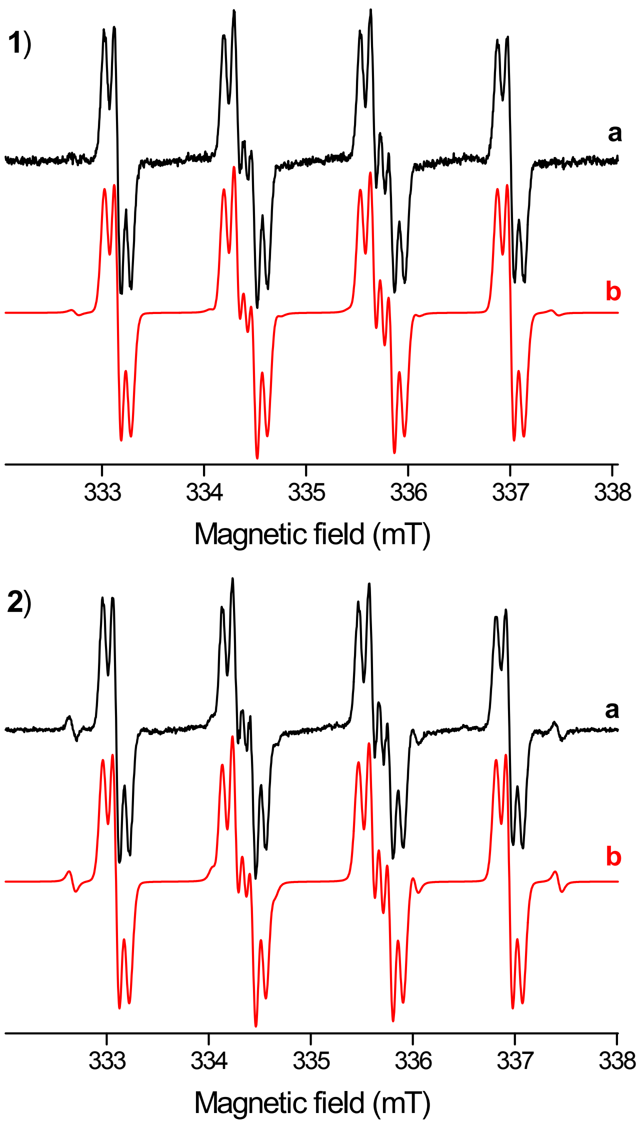


Figure S14. Experimental EPR spectra (a) measured during 900-s *in situ* exposure (LED@385 nm) of 1) **PP**/Iod/TT/DMPO and 2) **PPZn**/Iod/TT/DMPO in benzene solutions under argon along with their simulations (b). EMX EPR spectrometer settings: microwave frequency, ~ 9.443–9.453 GHz; microwave power, 1.003 mW; center field, ~335.2 mT; sweep width, 7 mT; gain, 2.00×10^5; modulation amplitude, 0.025 mT; sweep time, 90 s; time constant, 20.48 ms; number of scans, 10.

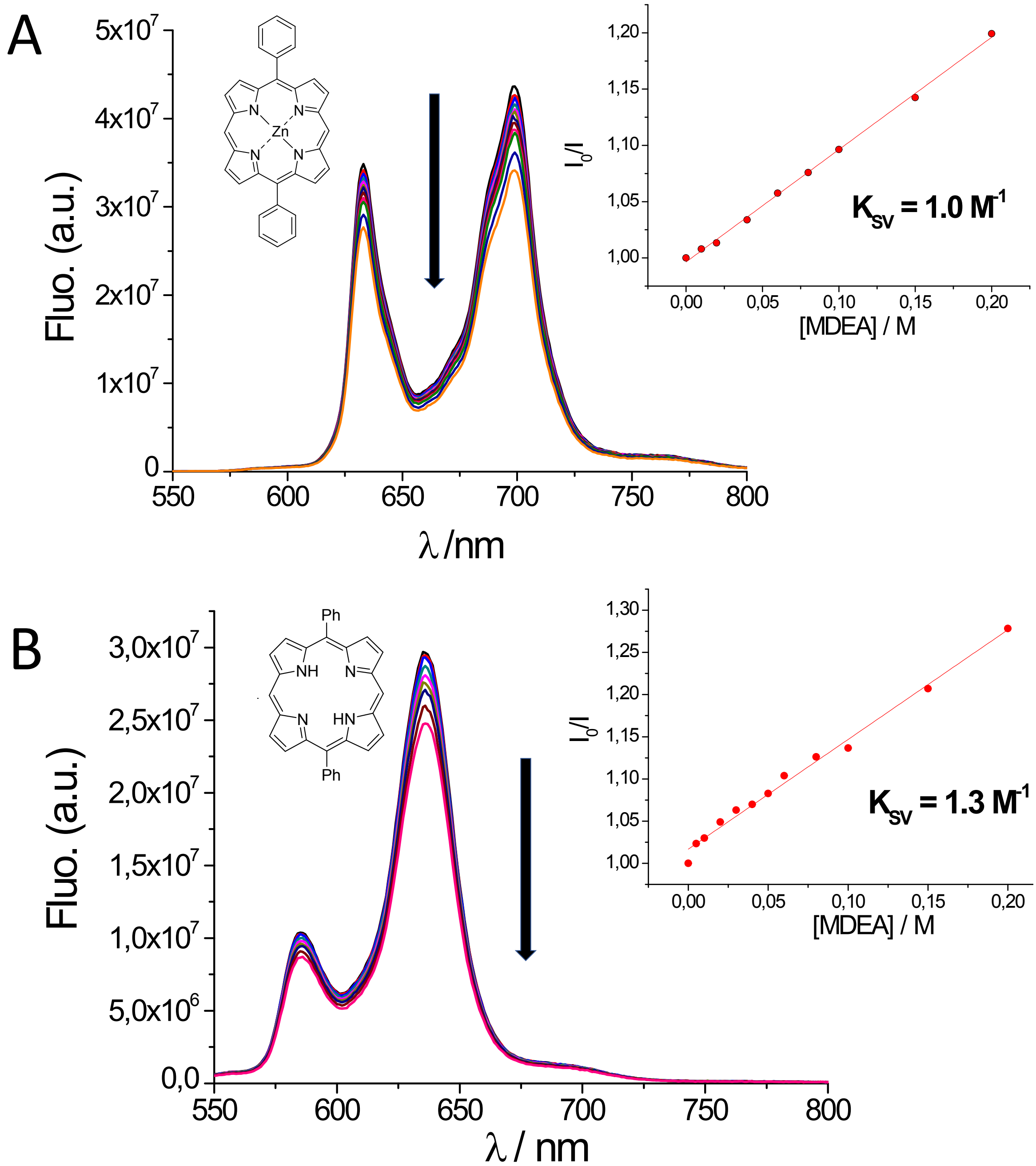


Figure S15. Progressive quenching of the fluorescence of porphyrin-based derivatives upon the addition of MDEA: A) **PPZn**/MDEA and B) **PP**/MDEA. Insets: corresponding Stern-Volmer plots (solvent: THF).

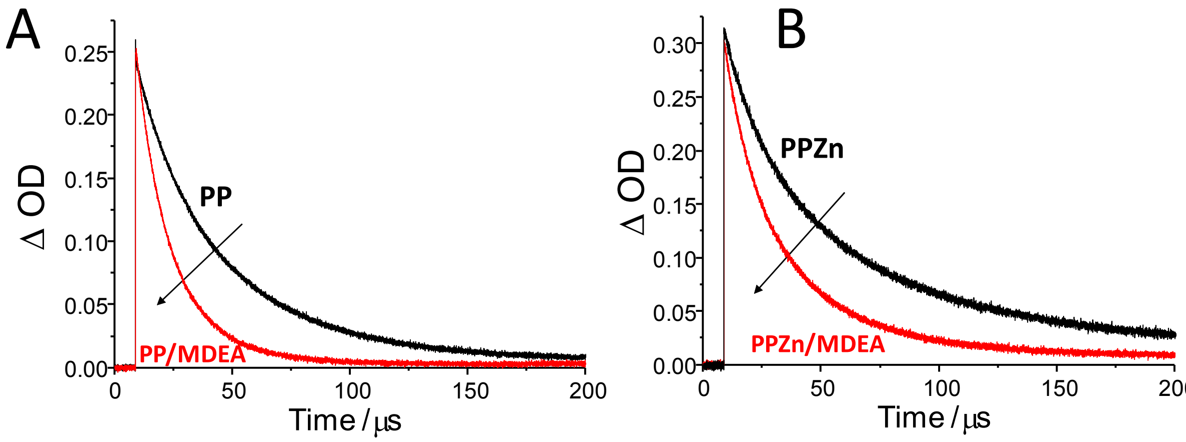


Figure S16. Decay traces of A) **PP** and B) **PPZn** triplet state after a laser pulse (λ_{ex} = 385 nm) with and without MDEA. 1,89 x 10^{-6} mol/L, [**PPZn**] = 1,67 x 10^{-6} mol/L.

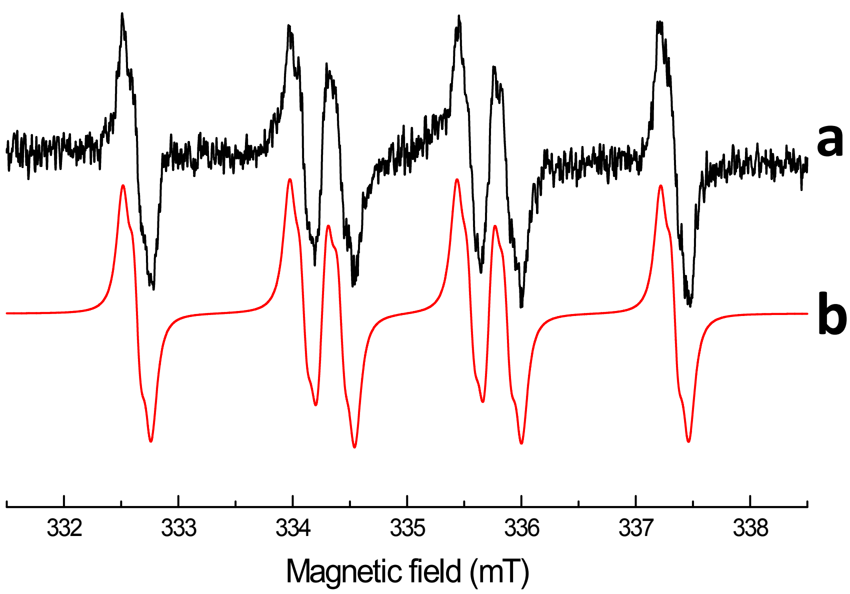


Figure S17. Experimental (a) and simulated (b) EPR spectra of a solution of **PPZn**/MDEA in the presence of the DMPO spin-trap and obtained after LED@385nm exposure in benzene and under argon. EPR signals correspond to the α-aminoalkyl spin-adduct with spin-Hamiltonian parameters: a_N = 1.469 mT, $a_H\beta$ = 1.794 mT, $a_H\gamma$ = 0.106 mT, $a_H\gamma$ = 0.072 mT; g = 2.0057.

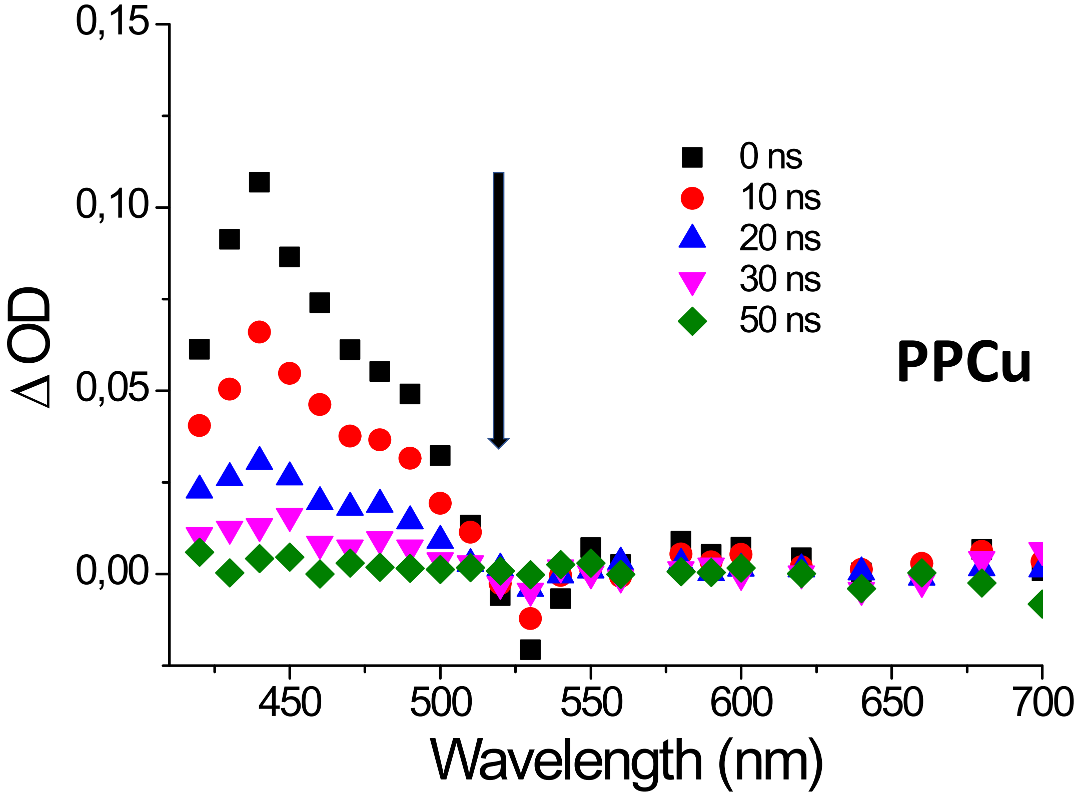


Figure S18. Transient absorption spectra of **PPCu** in deoxygenated dichloromethane solution at 0 to 50 ns after the laser pulse (385 nm, 7 ns pulse width). [**PPCu**] = 2,85 x 10^{-5} mol. L^{-1}.

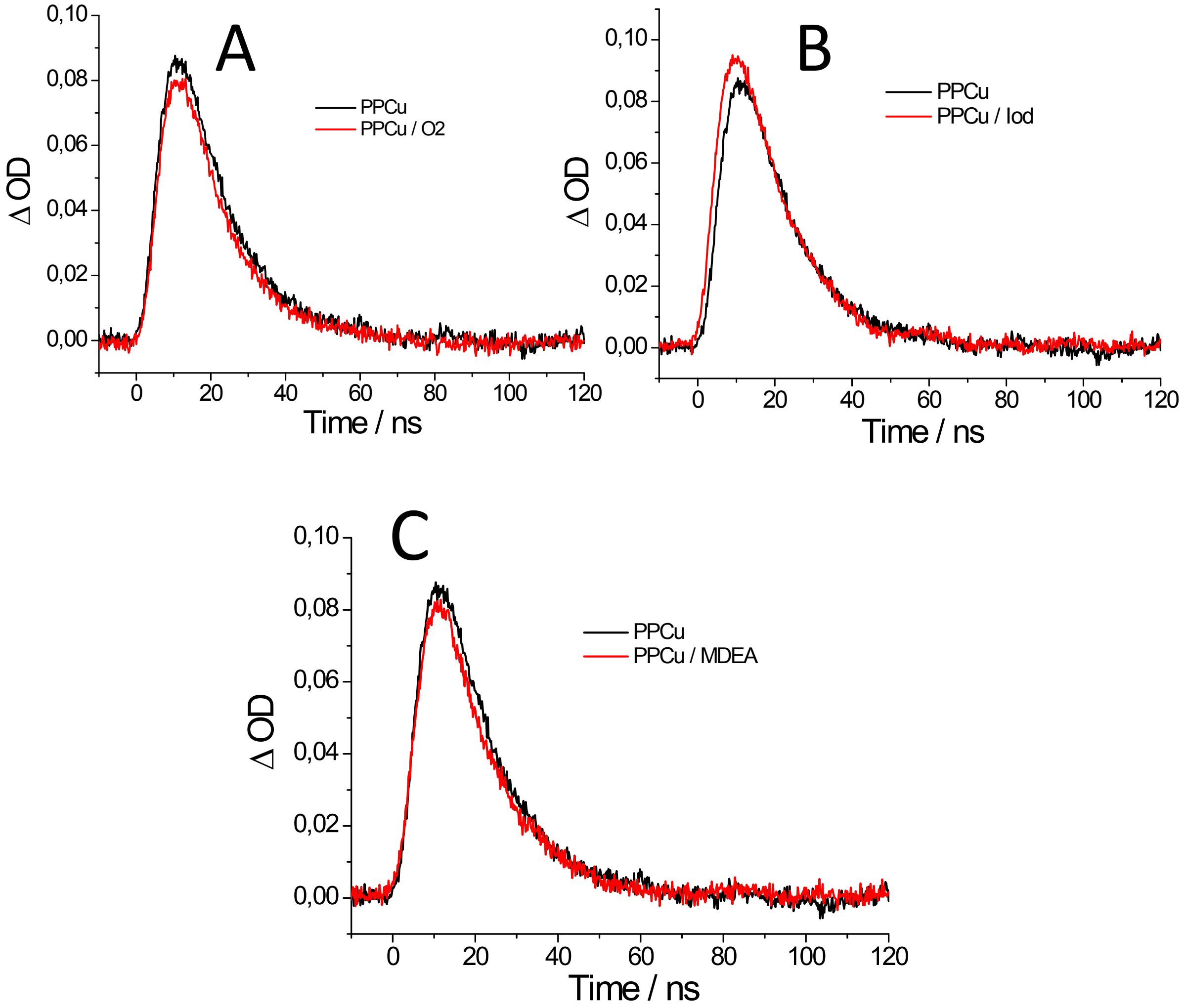


Figure S19. Decay traces of the triplet state of **PPCu** with A) O_2, B) Iod and C) MDEA after a laser pulse (λ_{ex} = 385 nm). [O_2] = 1.9 x 10^{-3} mol. L^{-1}, [Iod] = 2.5 x 10^{-4} mol. L^{-1}, [MDEA] = 1.1 x 10^{-3} mol. L^{-1} and [**PPCu**] = 2,85 x 10^{-5} mol. L^{-1}.

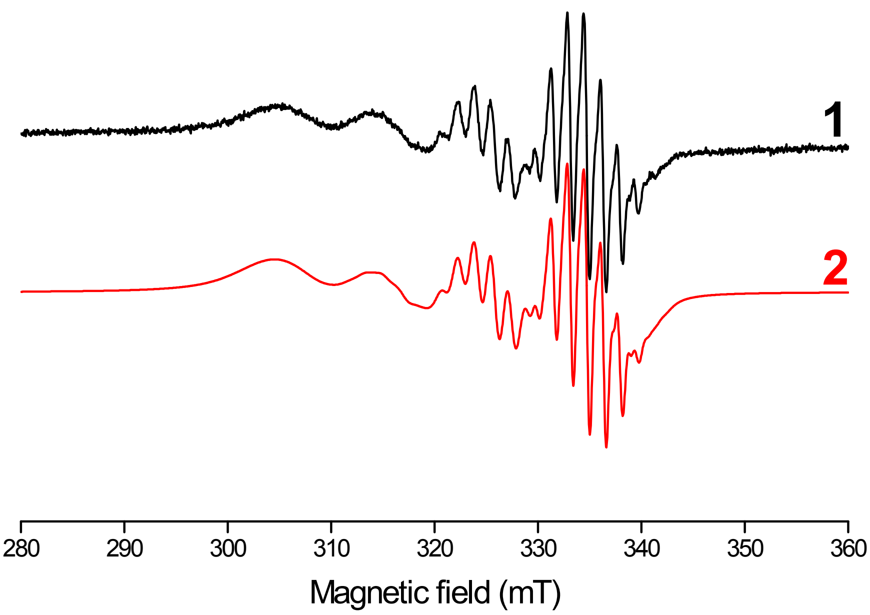


Figure S20. Experimental (1) and simulated (2) EPR spectra of **PPCu** in benzene under argon measured at 295 K. Spin-Hamiltonian parameters elucidated from the simulation of experimental spectrum (hyperfine coupling constants in mT): $g_x = 2.0950$, $g_y = 2.0977$, $g_z = 2.0950$, $g_{av} = 2.0959$; $A_{\mathrm{Cu},x} = 8.951$, $A_{\mathrm{Cu},y} = 9.264$, $A_{\mathrm{Cu},z} = 9.189$, $A_{\mathrm{Cu},av} = 9.1355$; $A_{\mathrm{N1},x} = 1.696$, $A_{\mathrm{N1},y} = 1.675$, $A_{\mathrm{N1},z} = 1.643$, $A_{\mathrm{N1},av} = 1.671$; $A_{\mathrm{N2},x} = 1.644$, $A_{\mathrm{N2},y} = 1.643$, $A_{\mathrm{N2},z} = 1.689$, $A_{\mathrm{N2},av} = 1.659$; $A_{\mathrm{N3},x} = 1.712$, $A_{\mathrm{N3},y} = 1.742$, $A_{\mathrm{N3},z} = 1.540$, $A_{\mathrm{N3},av} = 1.665$; $A_{\mathrm{N4},x} = 1.621$, $A_{\mathrm{N4},y} = 1.632$, $A_{\mathrm{N4},z} = 1.818$, $A_{\mathrm{N4},av} = 1.690$; $log(t_{\mathrm{corr}}) = -6.50$

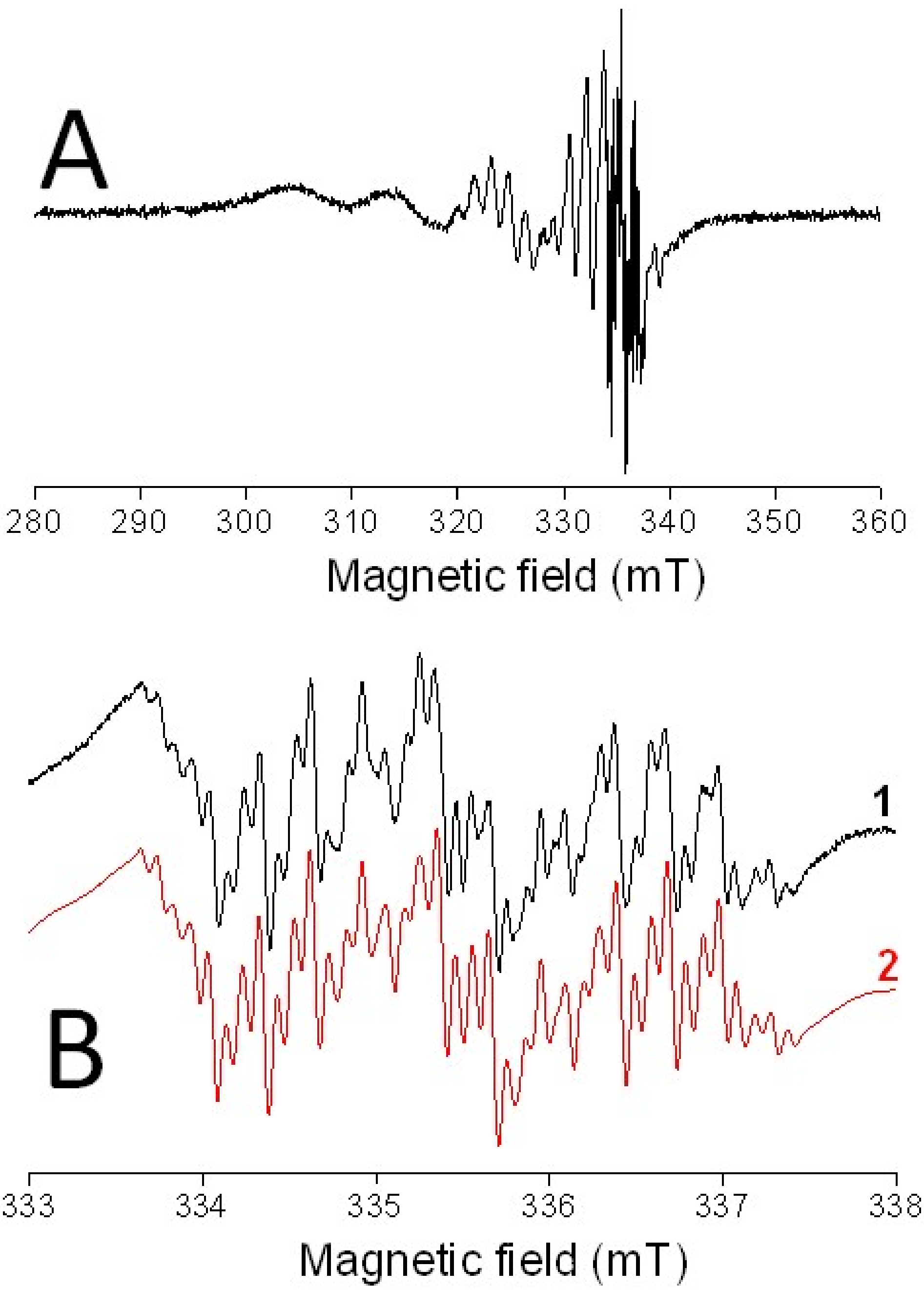


Figure S21. A) Experimental EPR spectrum measured after 900-s *in situ* 400 nm irradiation of **PPCu**/Iod/benzene/argon in the presence of ND spin trapping agent and B) Detail of the EPR experimental spectrum in **A** with (1) EPR spectrum measured after 900-s *in situ* 400 nm irradiation of **PPCu**/Iod/benzene/argon in the presence of ND spin trapping agent along with its simulation (2).

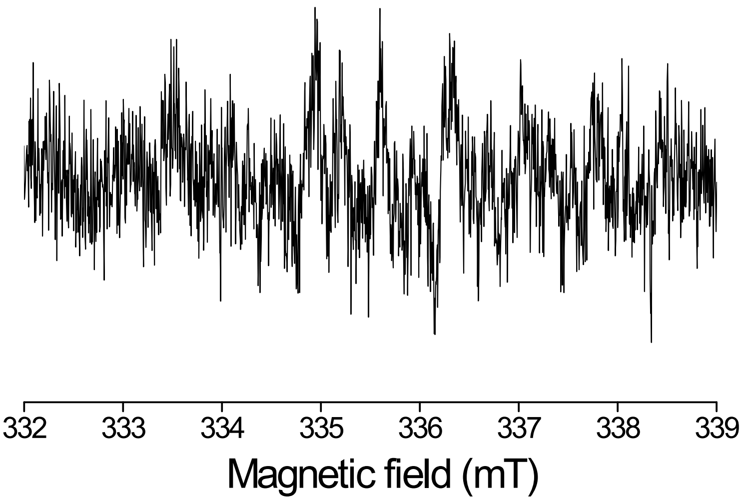


Figure S22. Difference EPR spectrum obtained by the abstraction of EPR spectra measured after 2700-s exposure (400 nm) and before exposure of **PPCu**/MDEA/DMPO/benzene/argon EPR spectra.

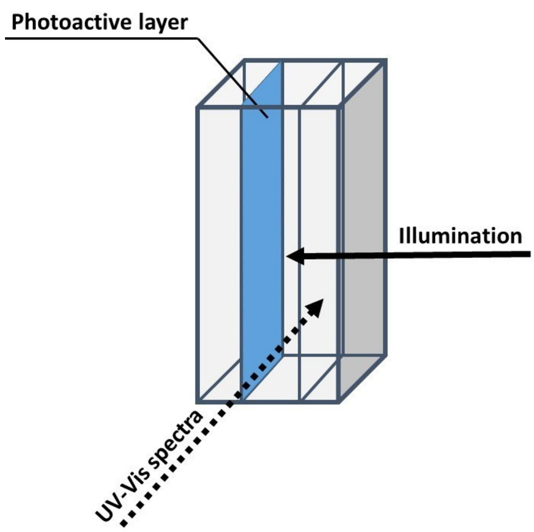


Figure S23. Schematic representation of the evaluation of the singlet oxygen generation from the porphyrin-derived coatings with a 1,3-diphenylisobenzofuran (DPBF).

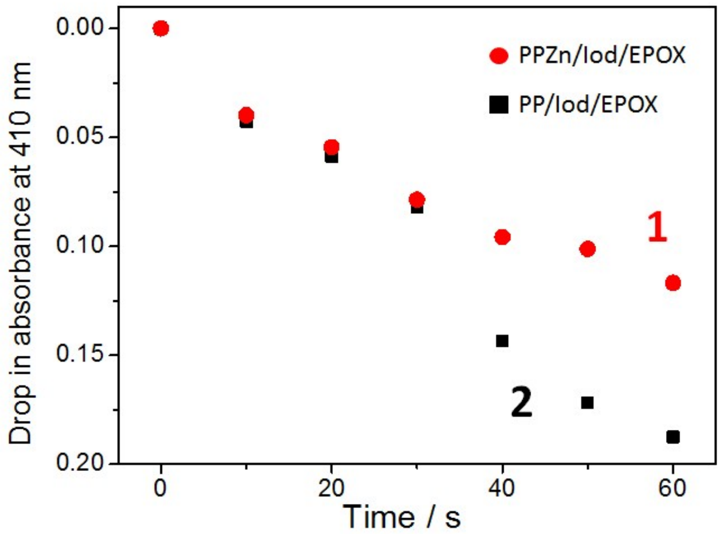


Figure S24. Evolution of $^{1}O_2$ at the surface of the porphyrin-derived films according to the oxidation of a methanolic solution of DPBF (λ = 410 nm) with the 1) **PPZn**/Iod/EPOX and 2) **PP**/Iod/EPOX systems after 60 s of laser irradiation.