Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Porphyrin-based photosensitizers for visible-light polymerization and antibacterial applications

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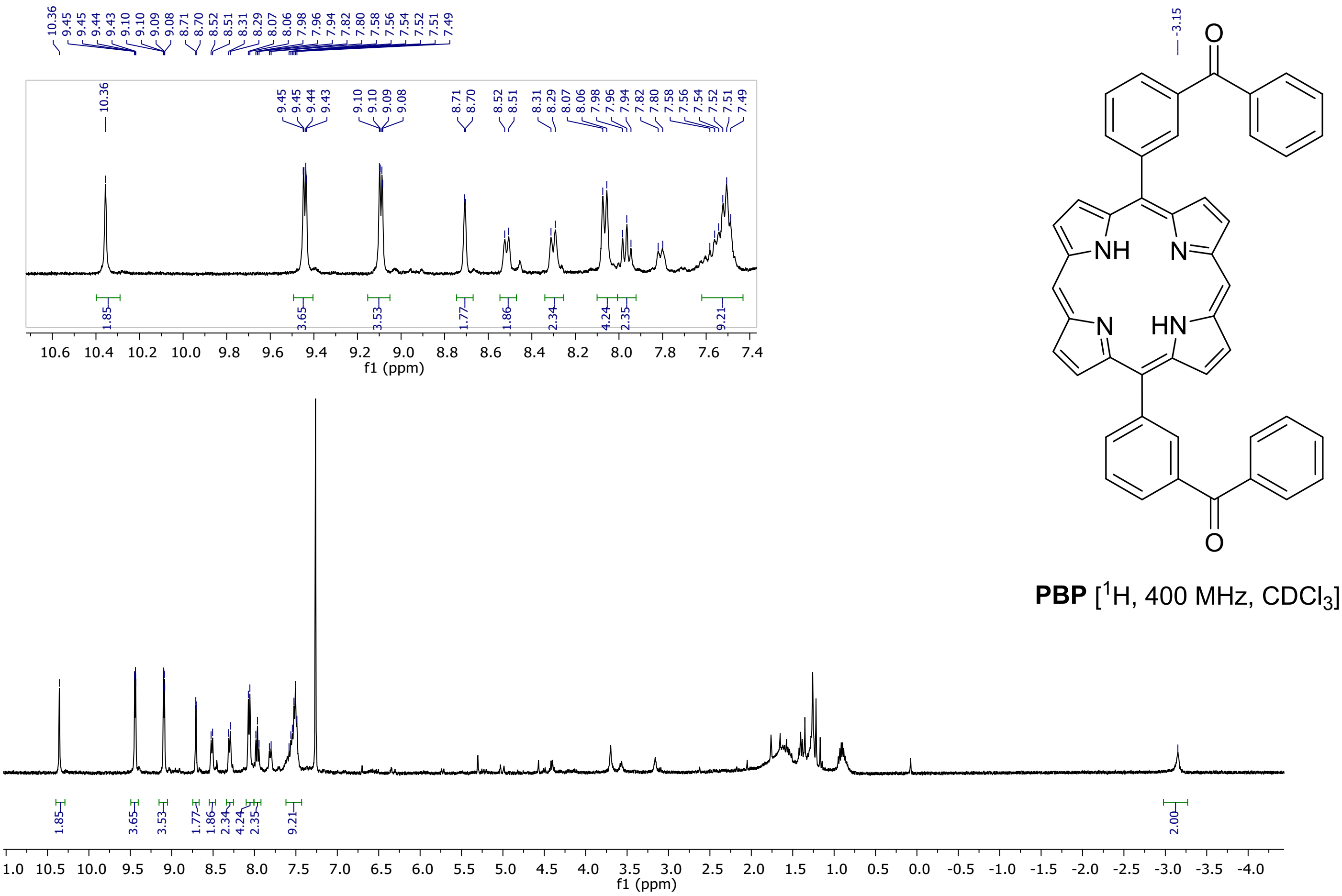


***Figure S1**: ^{1}H NMR spectrum of **PBP** in $CDCl_3$.*

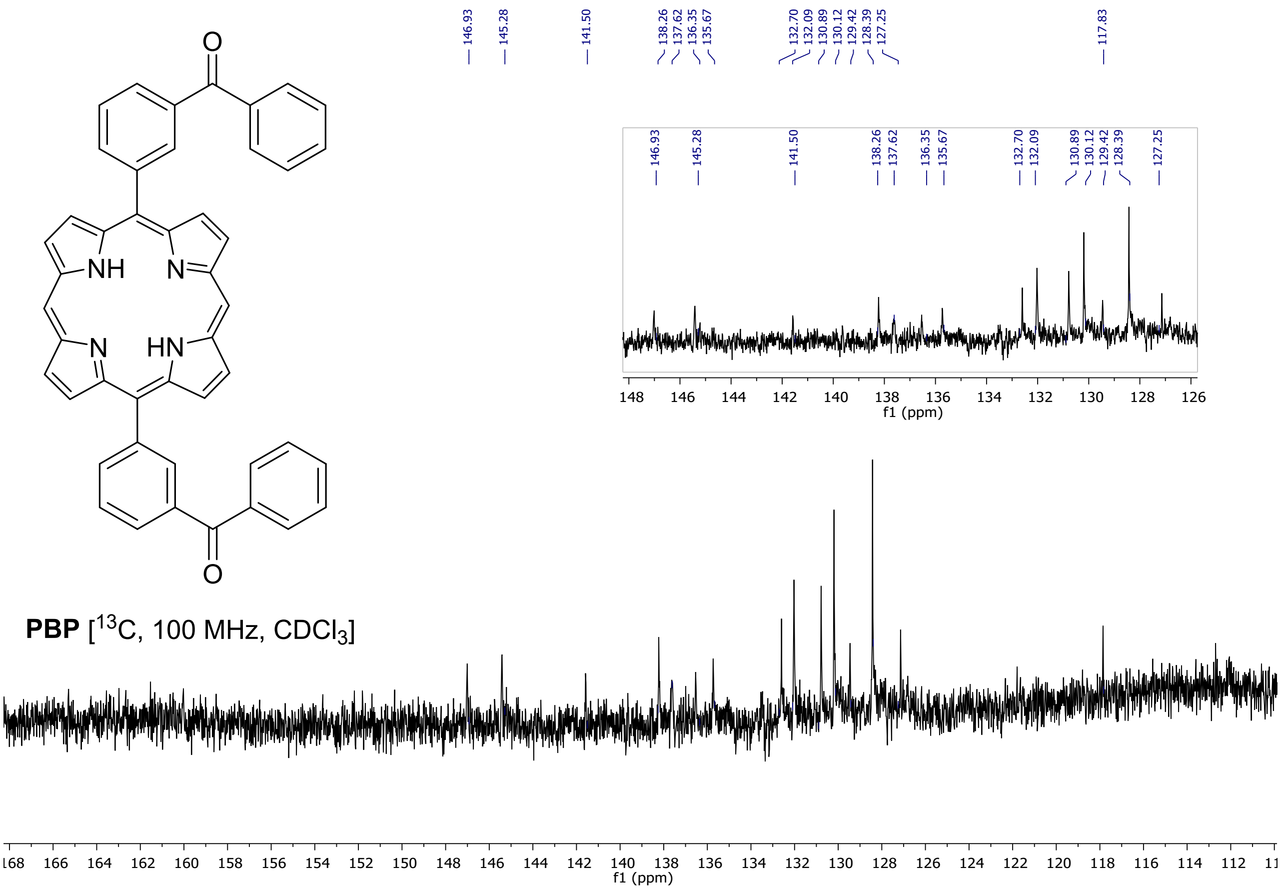


***Figure S2**: ^{13}C NMR spectrum of **PBP** in $CDCl_3$.*

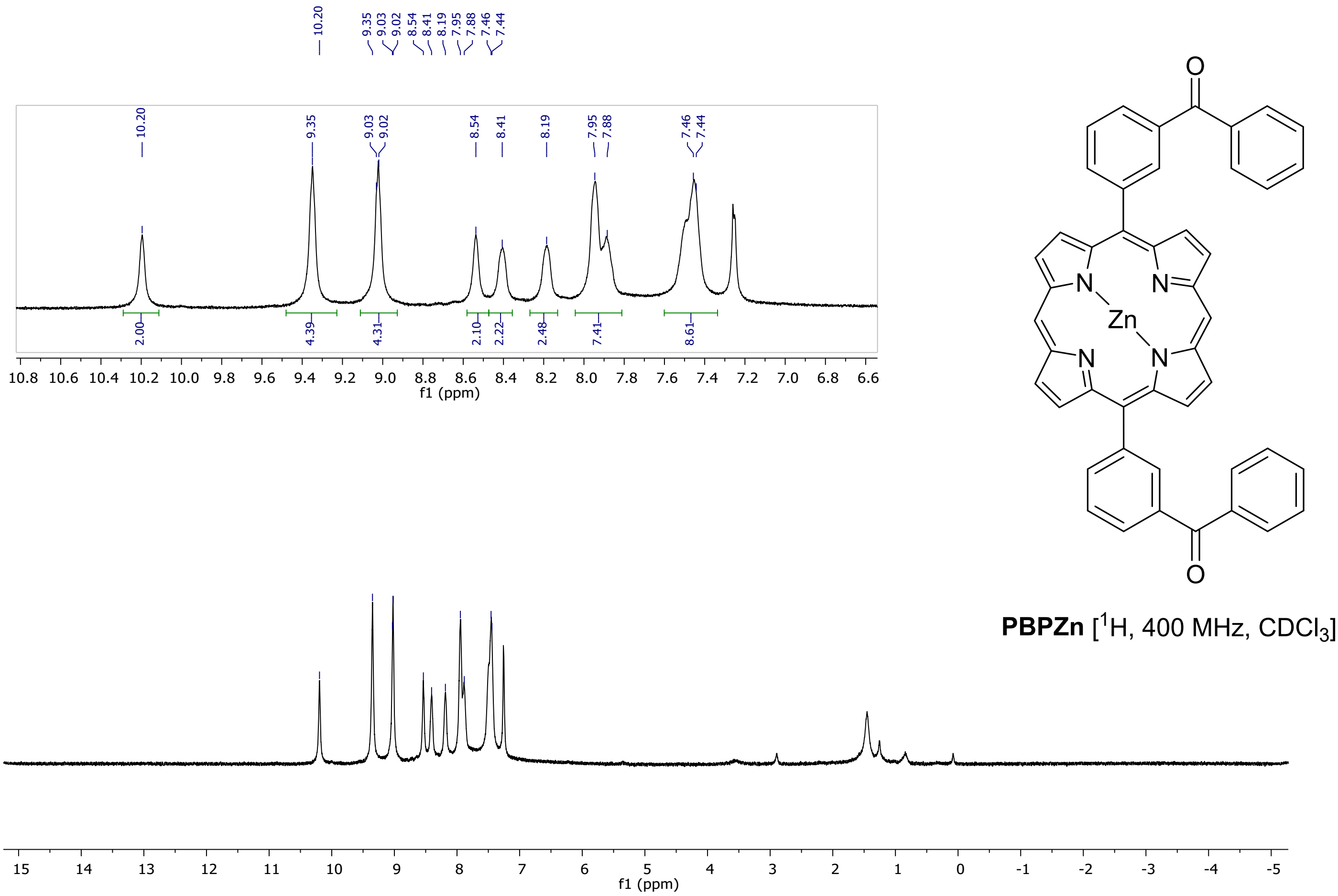


***Figure S3**: ^{1}H NMR spectrum of **PBPZn** in $CDCl_3$.*

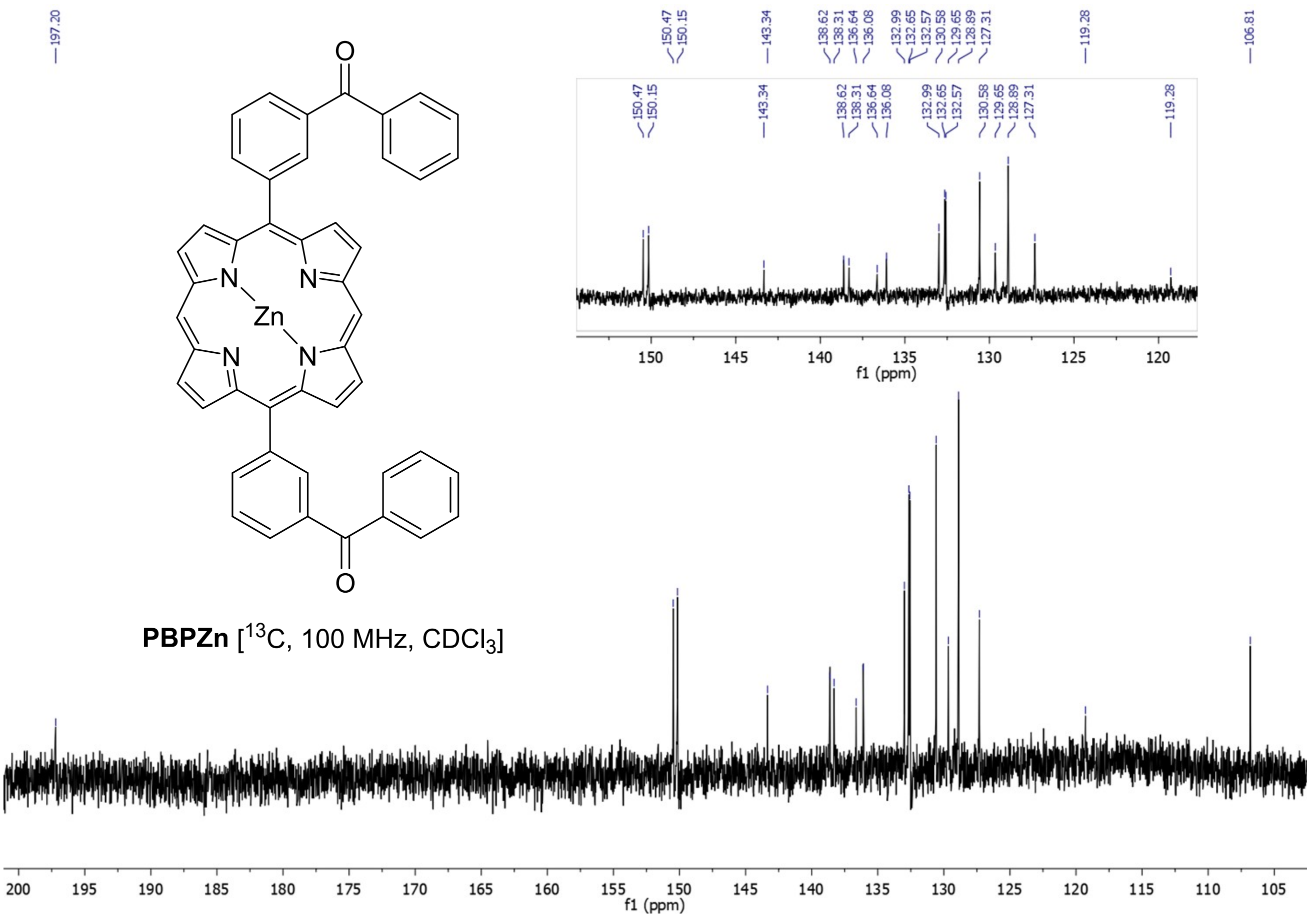


***Figure S4**: ^{13}C NMR spectrum of **PBPZn** in $CDCl_3$.*

Absorption

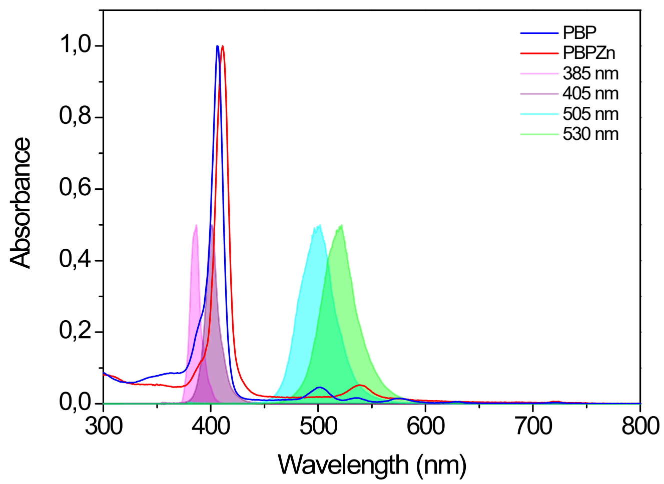


Figure S5: *Absorption spectra of* ***PBP*** *and* ***PBPZn*** *associated with the emission spectra of the LEDs used in this study (LEDs@385, 405, 455 and 530 nm).*

TD-DFT calculations

Figure S6: *Optimal ground-state structures of* ***PBP*** *(left) and* ***PBPZn*** *(right).*

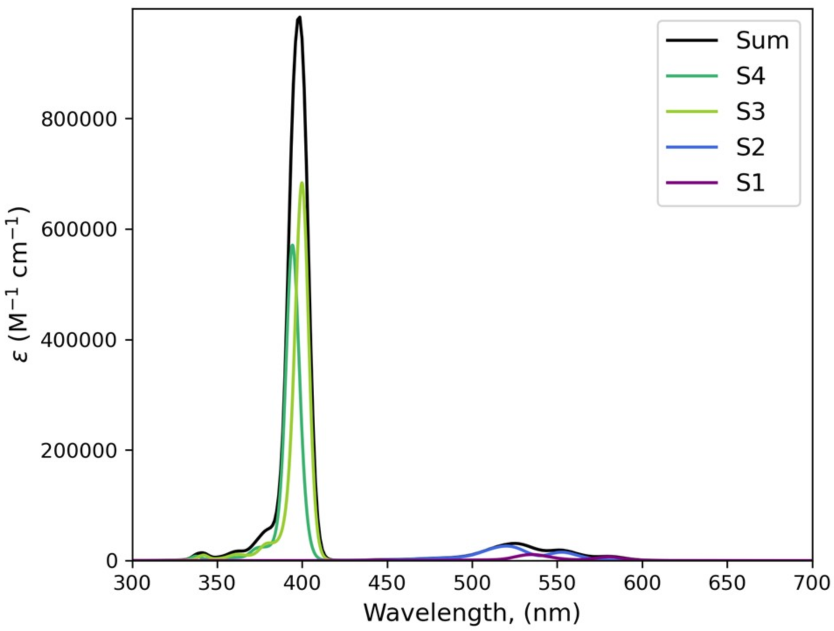


Figure S7: *Vibrationally-resolved spectrum of* ***PBP*** *simulated using the Vertical Hessian model and internal coordinates.*

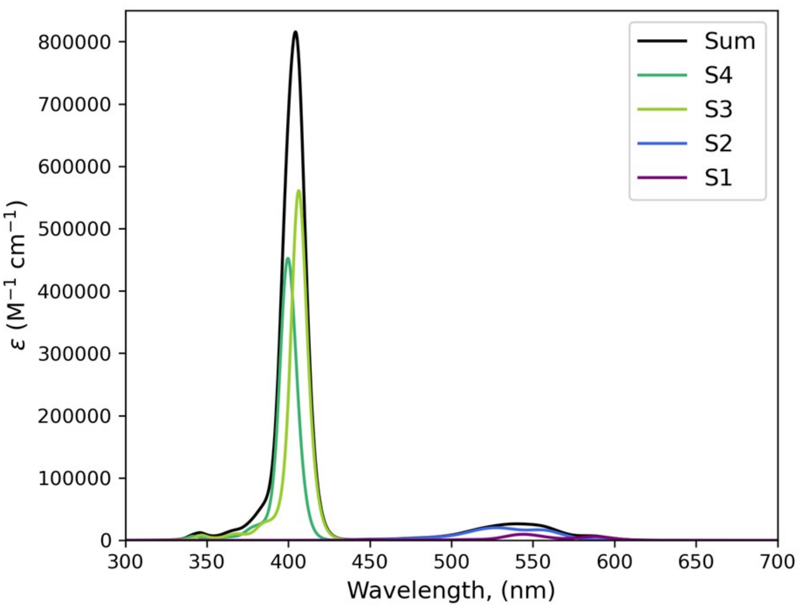


Figure S8: *Vibrationally-resolved spectrum of* ***PBP*** *simulated using the Vertical Hessian model and Cartesian coordinates. The imaginary frequency for the excited states were turned real (one such frequency for S1, S2, and S4)*

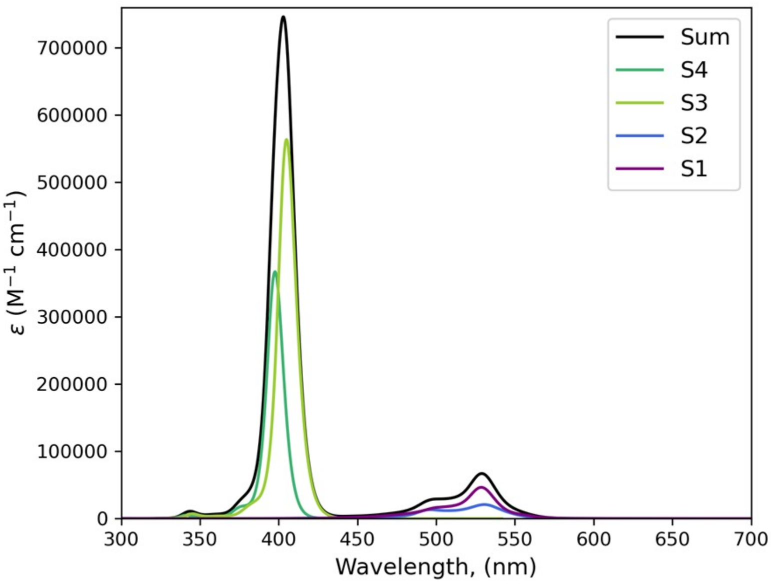


***Figure S9**: Vibrationally-resolved spectrum of **PBPZn** simulated using the Vertical Hessian model and Cartesian coordinates. Note that for both S1 and S4, imaginary frequencies exist in the excited-state (vertical) Hessian, and they have been turned positive.*

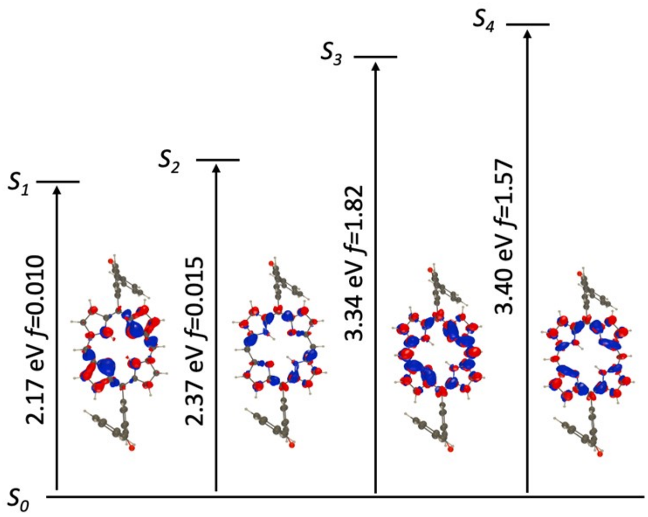


***Figure S10**: Vertical transition energies, associated oscillator strengths and electron density difference plots for **PBP**. In the latter representations, the blue and red lobes correspond to decrease and increase of density upon absorption (threshold 0.005 au).*

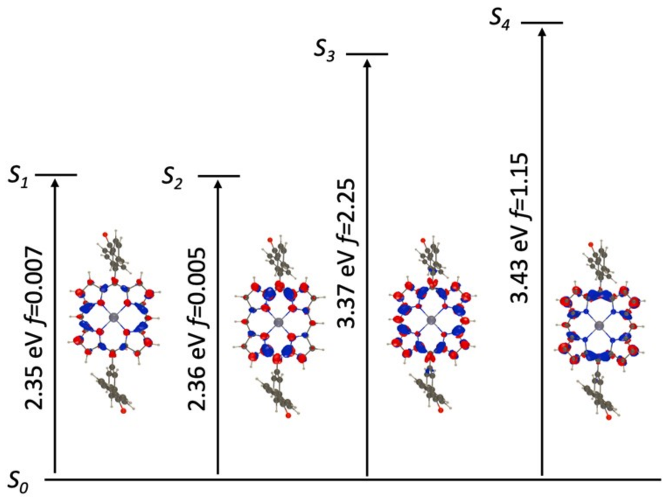


***Figure S11**: Vertical transition energies, associated oscillator strengths and electron density difference plots for **PBPZn**. See previous caption for more details.*

Absorption & emission

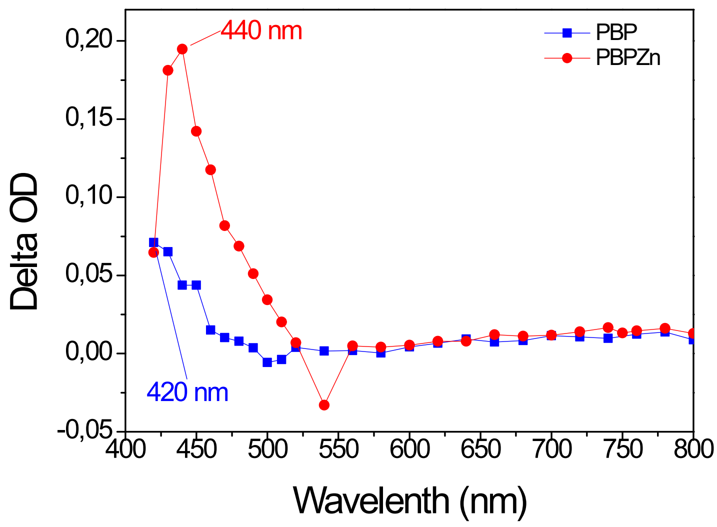
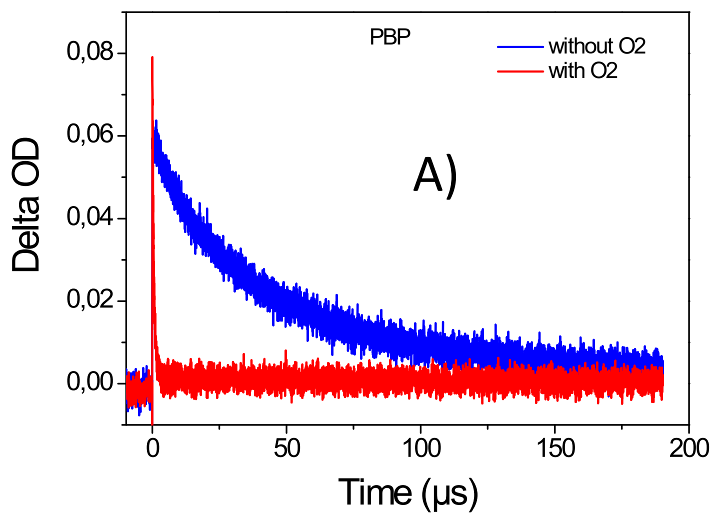


Figure S12: *Transition absorption spectra of **PBP** and **PBPZn** under argon in DCM (λ_{exc} = 385 nm)*



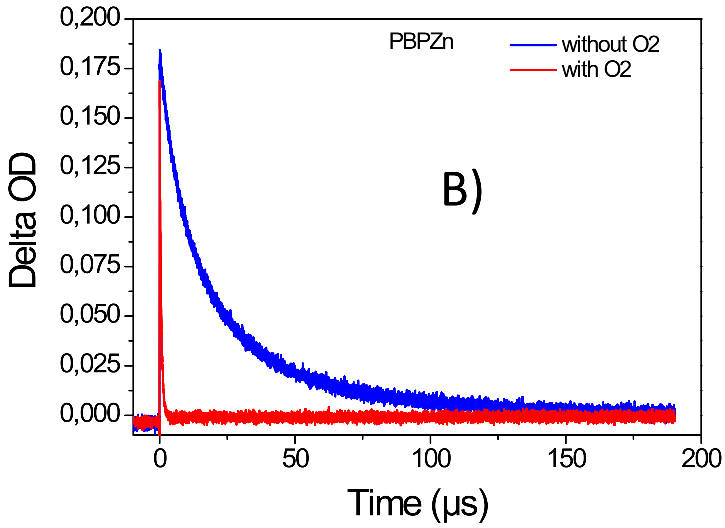


Figure S13: *Decay traces of the triplet excited state of A) **PBP** and B) **PBPZn** after a laser pulse (λ_{ex} = 385 nm) with and without oxygen in DCM.*

Cyclic voltammetry

Table S1: *Redox values and photophysical properties of the photoinitiating compounds*

Molecules	E_{ox} (eV)	E_{red} (eV)	E_S (eV)	E_T (eV)
PBP	1.47	-1.18	2.03	2.95
PBPZn	1.09	-1.48	2.14	2.82
BP	0.16	-1.20		2.38
CQ	0.12	-1.25		2.21
MDEA	0.72		-	-
Iod	-	-0.63	-	-
cysteamine	0.92		-	-
N-acetylcysteine	0.79		-	-

Photostability of the porphyrin derivatives

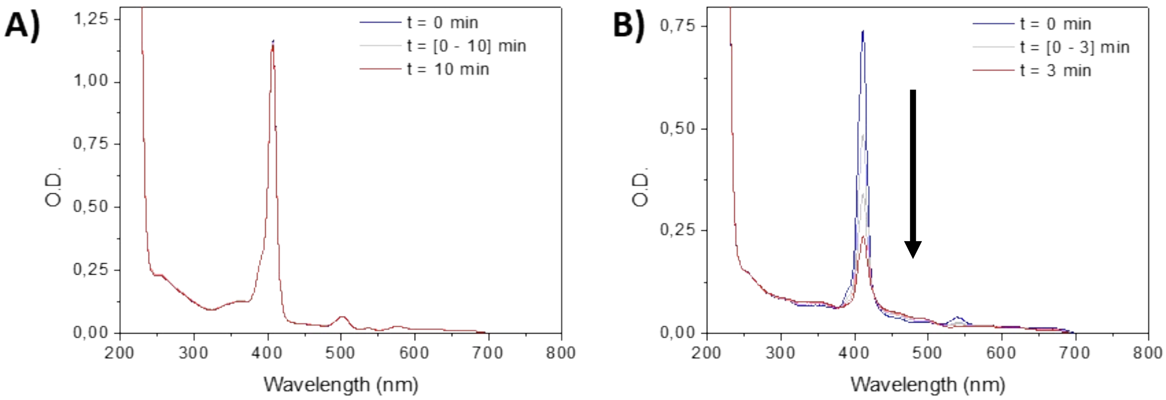


Figure S14*: Photolysis of **A) PBP** and **B) PBPZn** solution under LED@405 nm irradiation. [**PBP**] = 2 x 10^{-6} mol.L^{-1}, [**PBPZn**] = 6 x 10^{-6} mol.L^{-1}, [MDEA] = 2.8 x 10^{-2} mol.L^{-1}. Solvent = DCM.*

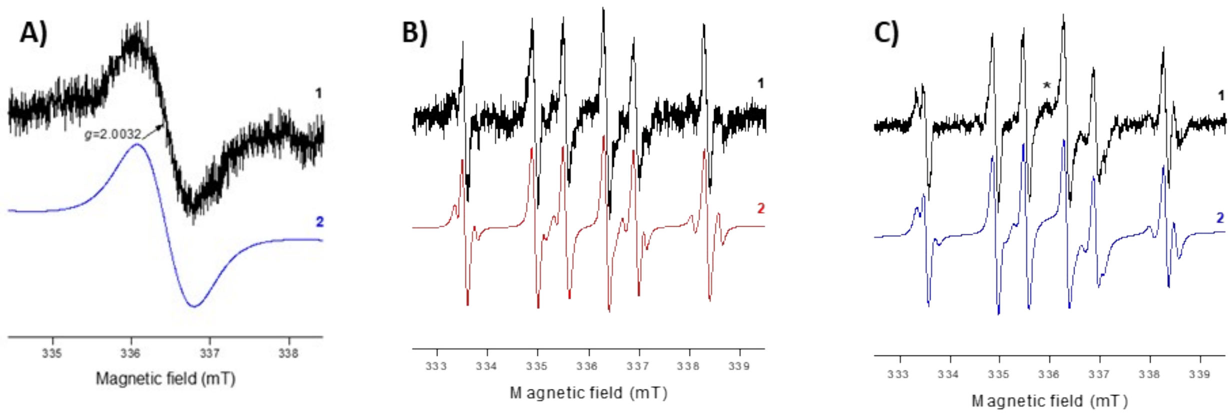


***Figure S15**: The normalized experimental (1) and simulated (2) EPR spectra obtained upon continuous* in situ *LED@400 nm exposure in chloroform under irradiation for (A) **PBPZn**, (B) **PBP** with DMPO and (C) **PBPZn** with DMPO.*

Effect of the addition of MDEA

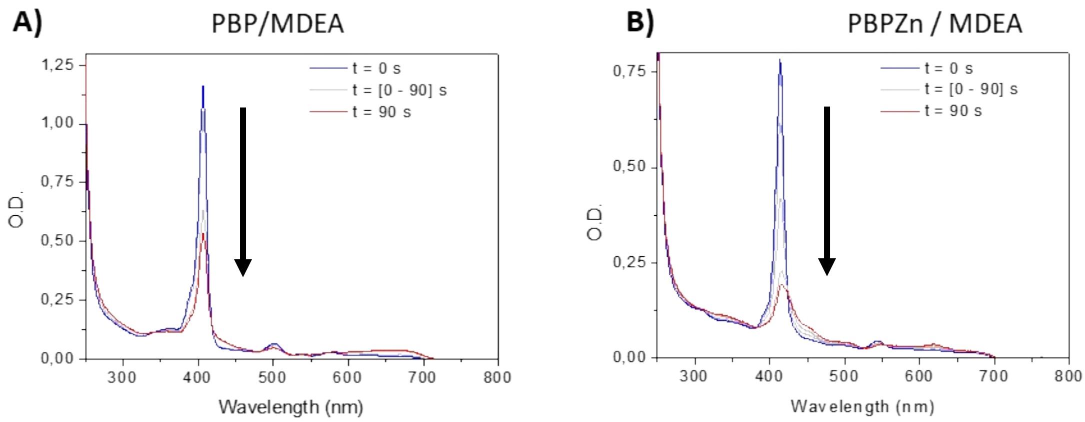


***Figure S16** : Steady state photolysis of A) **PBP**/MDEA and B) **PBPZn**/MDEA systems under air after LED@405 nm exposure. [**PBP**] = 2 x 10^{-6} mol.L^{-1}, [**PBPZn**] = 6 x 10^{-6} mol.L^{-1}, [MDEA] = 2.8 x 10^{-2} mol.L^{-1}. Solvent = DCM.*

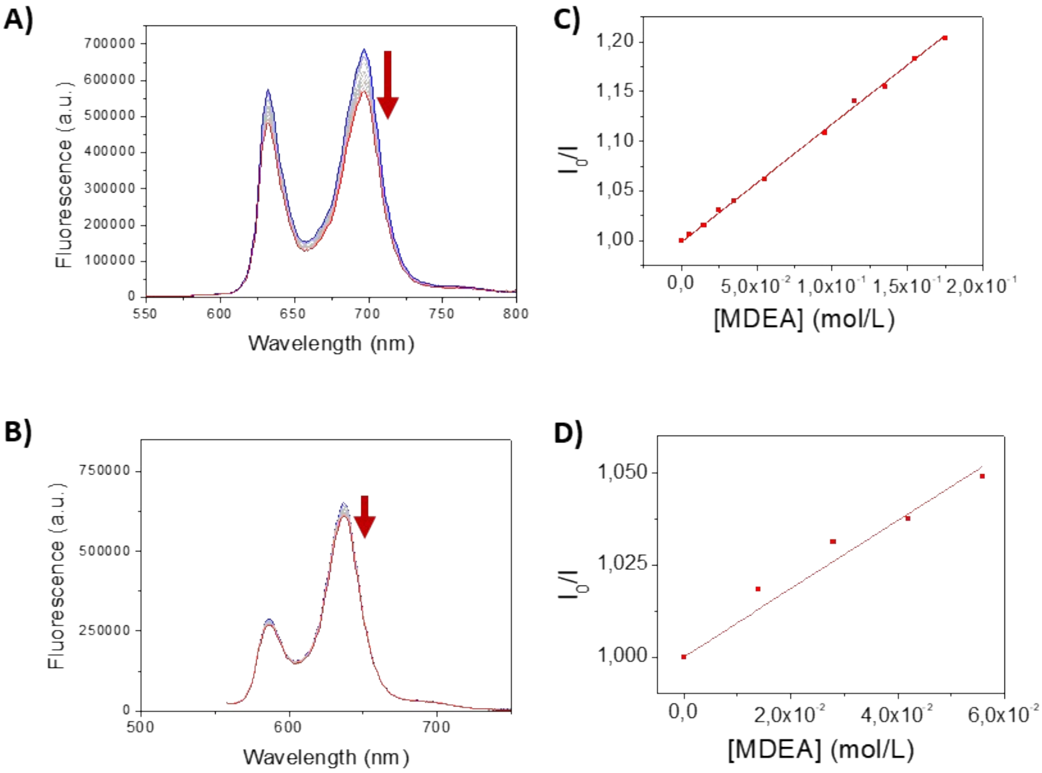


***Figure S17** : Quenching of **A)** **PBP** and **B)** **PBPZn** fluorescence after a gradual addition of MDEA. [**PBP**] =1.2 x 10^{-7} mol.L^{-1}, [**PBPZn**] = 5.2 x 10^{-6} mol.L^{-1} (solvent: THF). Corresponding Stern-Volmer plot for the quenching of the singlet excited state of **C)** **PBP** ($K_{SV}^{PBP/MDEA}$ = 1.2 M^{-1}) and **D)** **PBPZn** ($K_{SV}^{PBPZn/MDEA}$ = 0.7 M^{-1}) with MDEA.*

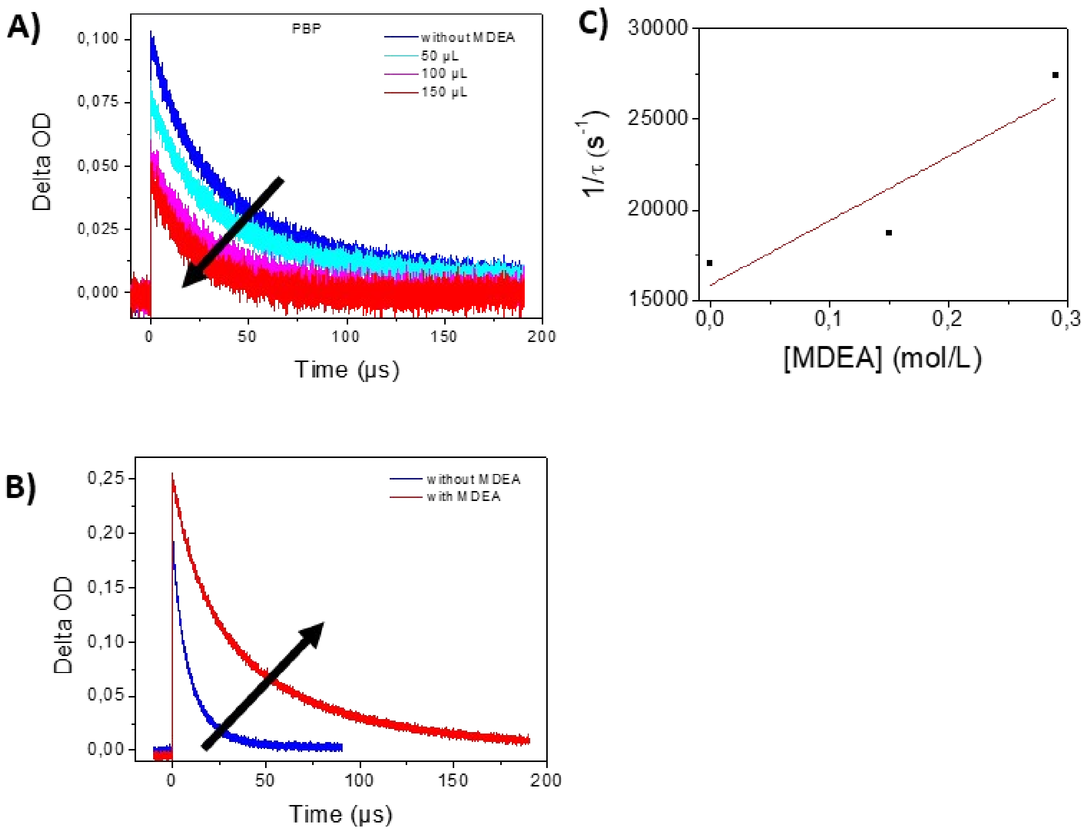


Figure S18 *: Decay traces of **A)** **PBP** and **B)** **PBPZn** triplet excited state after a laser pulse (λ_{ex} = 385 nm) with a gradual addition of MDEA. **C)** Corresponding Stern-Volmer plot for the quenching of the triplet excited state of **PBP** with MDEA. [**PBP**] = 1.1 x 10^{-5} mol.L^{-1} , [**PBPZn**] = 1.7 x 10^{-4} mol.L^{-1} , [MDEA] = 8.7 mol.L^{-1} in DCM.*

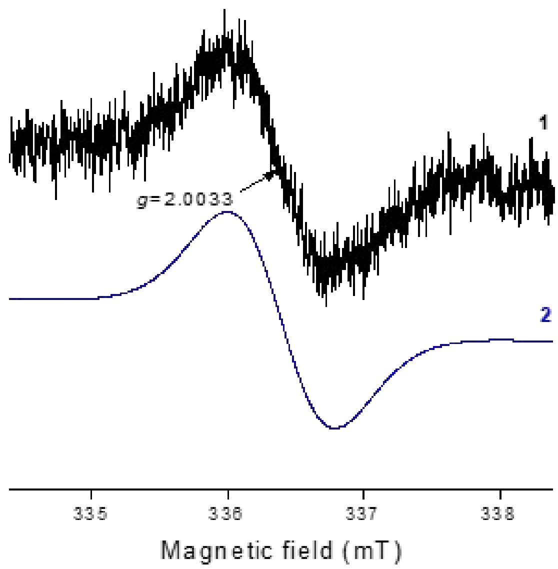


Figure S19: *The normalized experimental (1) and simulated (2) EPR spectra obtained upon continuous in situ LED@400 nm exposure of **PBPZn**/MDEA in chloroform and under argon.*

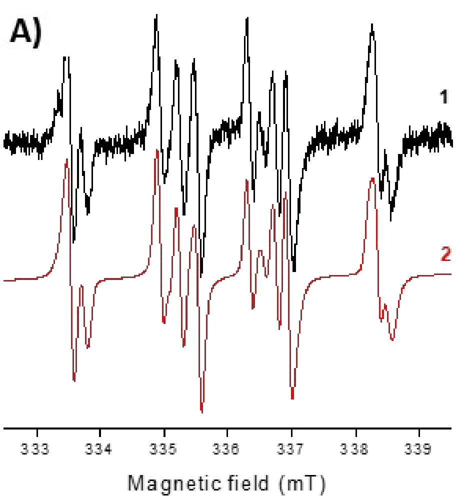


Figure S20 *: The normalized experimental (1) and simulated (2) EPR spectra obtained upon continuous in situ LED@400 nm exposure of porphyrin derivatives in chloroform under argon in the presence DMPO spin trapping agent and MDEA for **A**) **PBP** and **B**) **PBPZn**.*

Effect of the addition of Iod

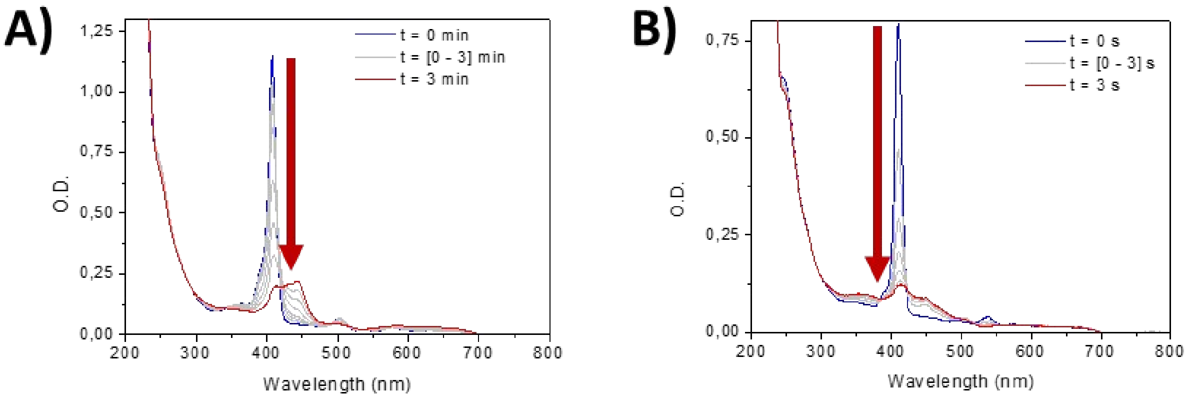


Figure S21*: Steady state photolysis of A) **PBP**/Iod and B) **PBPZn**/Iod systems under air after LED@405 nm exposure. [**PBP**] = 2 x 10^{-6} mol.L^{-1}, [**PBPZn**] = 6 x 10^{-6} mol.L^{-1}, [Iod] = 2.9 x 10^{-5} mol.L^{-1}. Solvent = DCM*

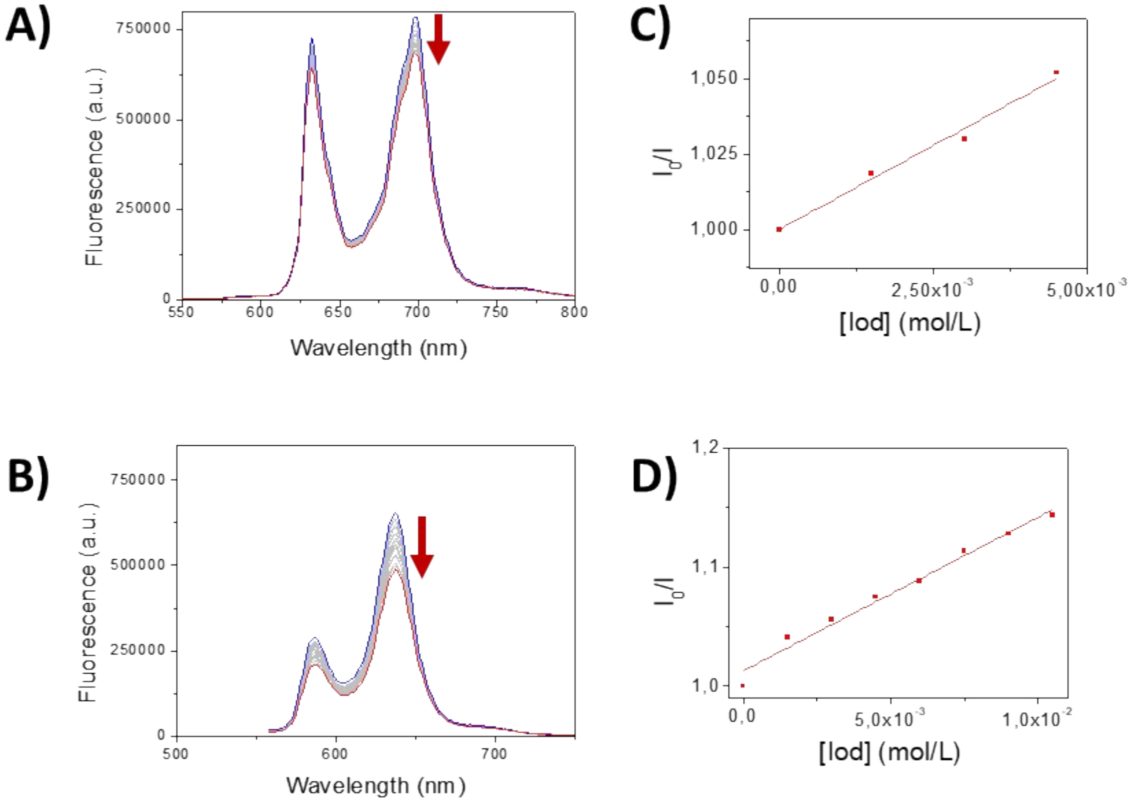


Figure S22: *Quenching of A)* ***PBP*** *and B)* ***PBPZn*** *fluorescence after a gradual addition of Iod. [****PBP****] =1.2 x 10^{-7} mol.L^{-1}, [****PBPZn****] = 5.2 x 10^{-6} mol.L^{-1} (solvent = THF). Corresponding Stern-Volmer plot for the quenching of the singlet excited state of* ***C)*** ***PBP*** *($K_{SV}^{PBP/Iod}$ = 11 M^{-1}) and* ***D)*** ***PBPZn*** *($K_{SV}^{PBPZn/Iod}$ = 13 M^{-1}) with the addition of Iod.*

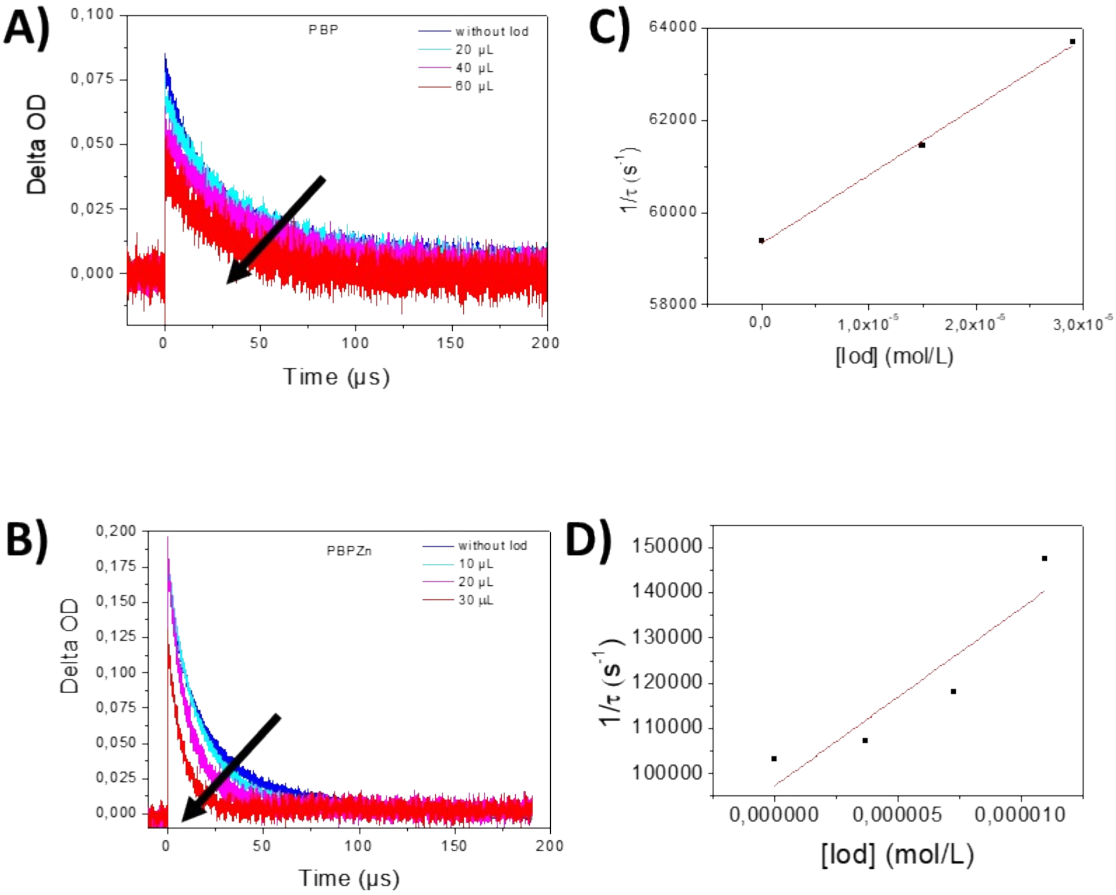


Figure S23: *Decay traces of A)* ***PBP*** *and B)* ***PBPZn*** *triplet state after a laser pulse (λ_{ex} = 385 nm) with a gradual addition of Iod. Corresponding Stern-Volmer plot for the quenching of the triplet excited state of* ***C)*** ***PBP*** *and* ***D)*** ***PBPZn*** with the addition of Iod. *[**PBP**] = 1.1 x 10^{-5} mol.L^{-1} , [**PBPZn**] = 1.7 x 10^{-4} mol.L^{-1} in DCM.*

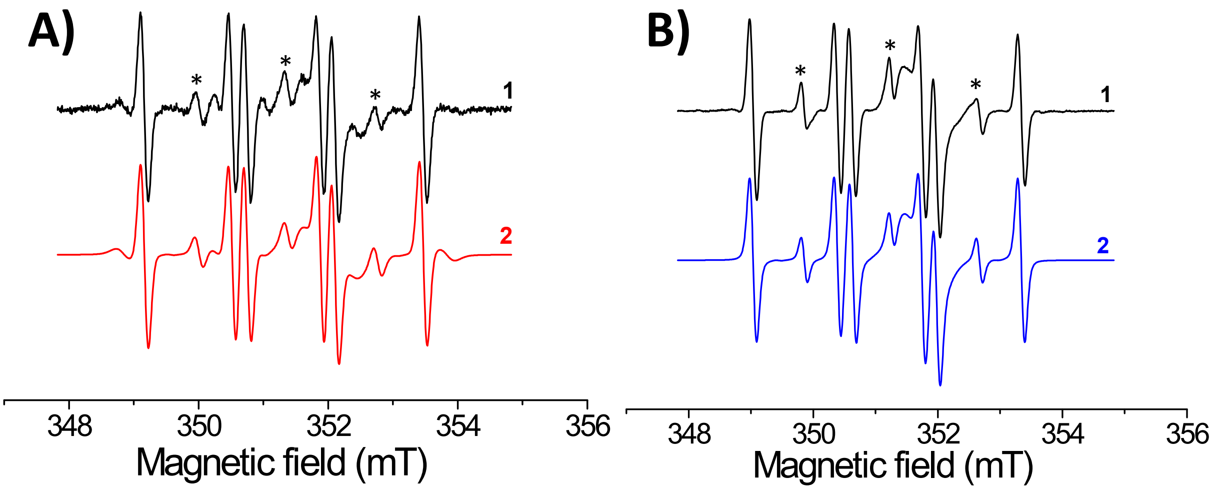


Figure S24: *The normalized experimental (1) and simulated (2) EPR spectra obtained post 120-s LED@405 nm exposure of (A)* ***PBP*** *and (B)* ***PBPZn****. in chloroform under argon in the presence DMPO spin trapping agent and Iod. (* denote the artefactual triplet lines resulting from double addition of MePh radical on DMPO following a mechanism similar to that detailed in Figure S32 with thiyl radicals).*

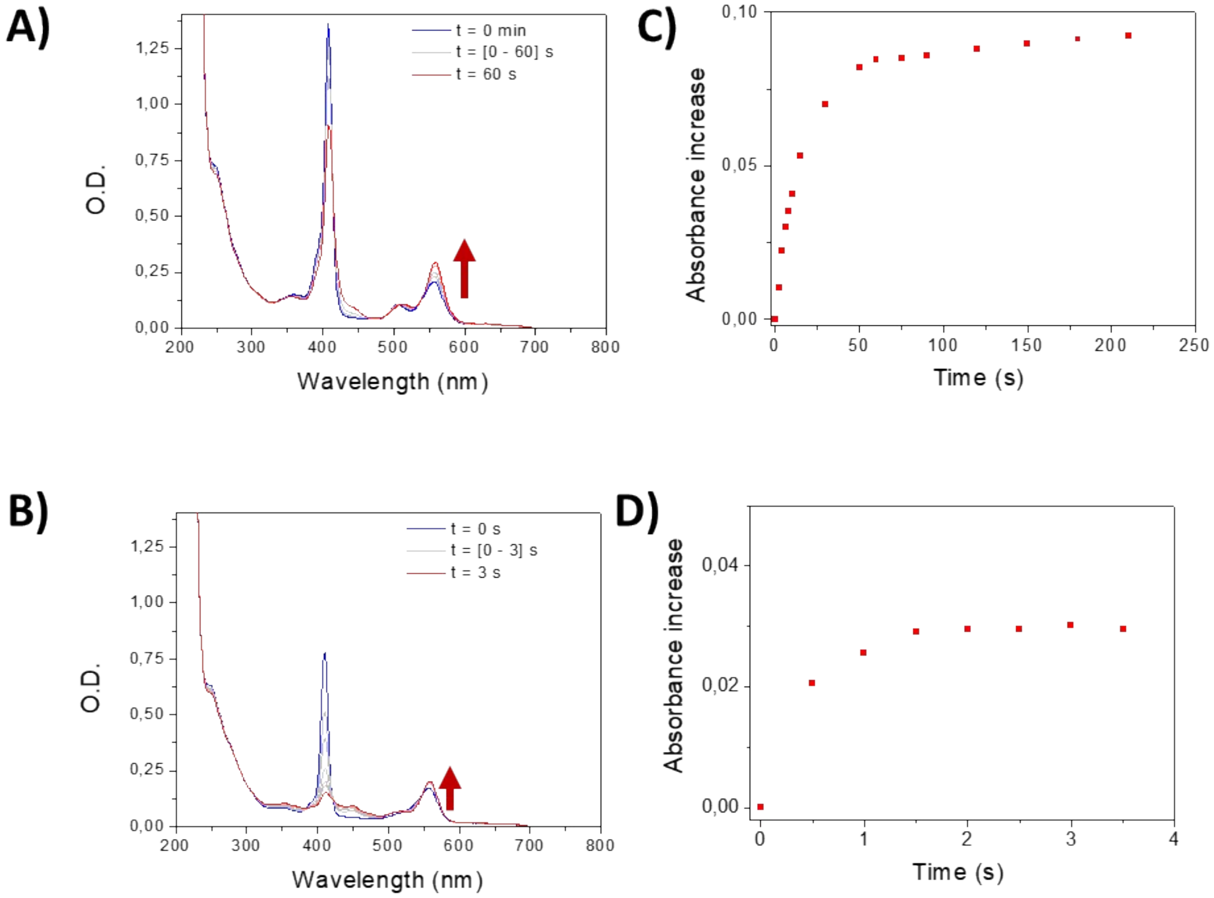


***Figure S25**: Steady-state photolysis of **A)** **PBP**/Iod/rhodamine B and **B)** **PBPZn**/Iod/rhodamine B after irradiation by LED@405 nm under air conditions. Absorbance increase at 570 nm along time for **C)** **PBP** and **D)** **PBPZn**. **[PBP]** = 2 x 10^{-6} mol.L^{-1}, **[PBPZn]** = 6 x 10^{-6} mol.L^{-1}, [Iod] = 2.9 x 10^{-5} mol.L^{-1}, [RhB] = 2.4 x 10^{-5} mol.L^{-1}.*

Effect of the addition of cysteamine

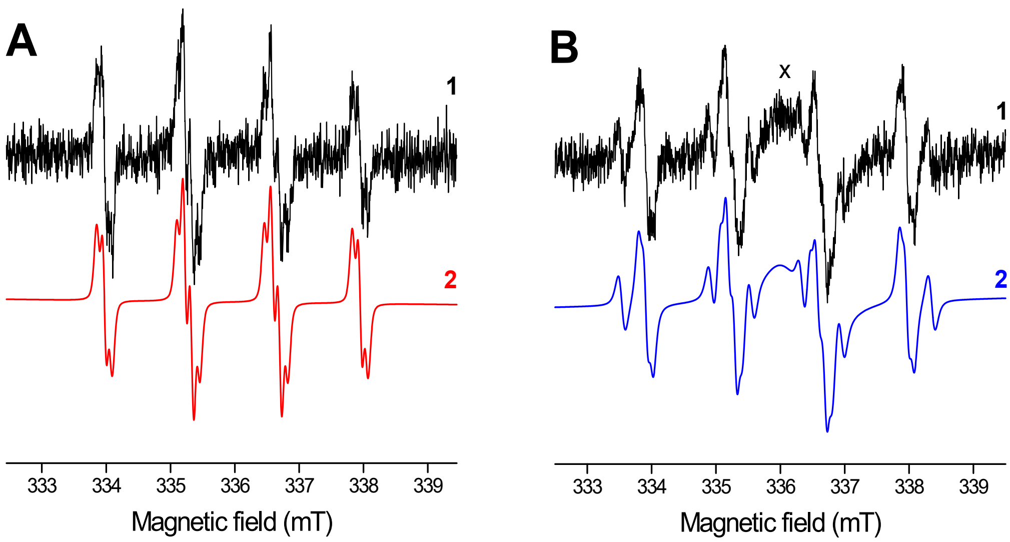


***Figure S26**: The normalized experimental (1) and simulated (2) EPR spectra obtained upon continuous in situ LED@400 nm exposure of (A) **PBP** and (B) **PBPZn** in chloroform and under argon in the presence DMPO spin trapping agent and cysteamine: × denotes the broad signal assigned to PBPZn$^{\bullet-}$.*

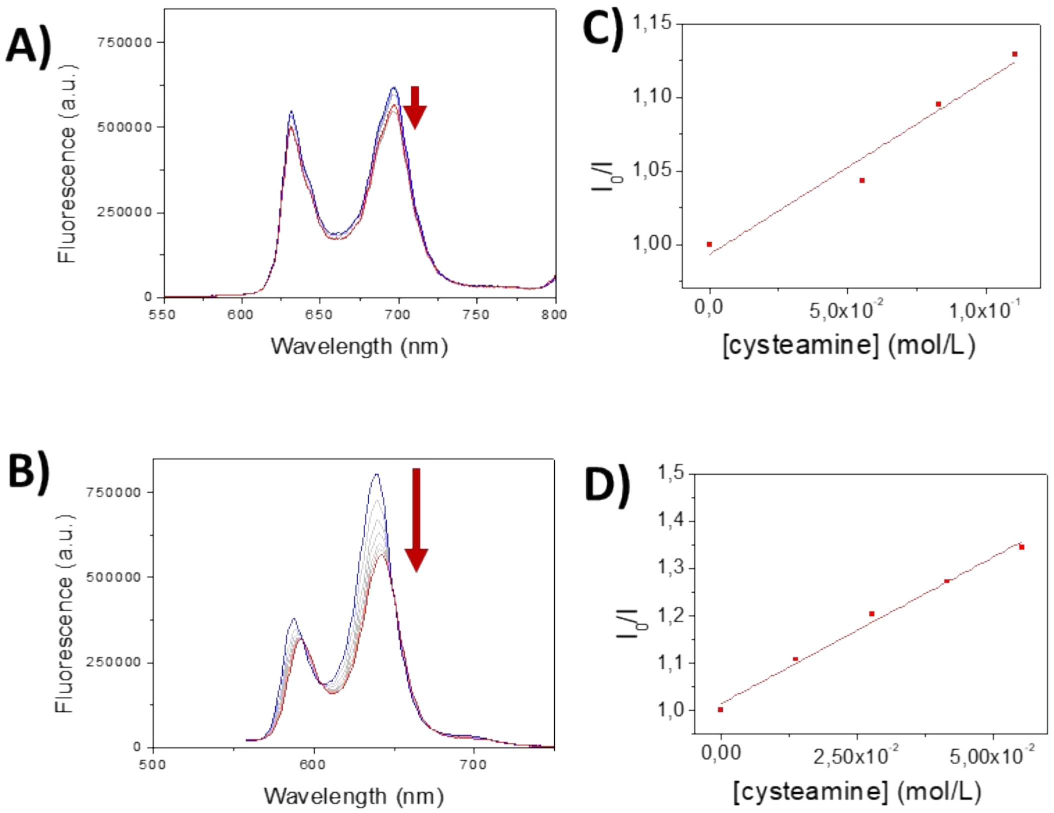


*Figure **S27**: Quenching of A) **PBP** and B) **PBPZn** fluorescence after a gradual addition of cysteamine. [**PBP**] =1.2 x 10^{-7} mol.L^{-1}, [**PBPZn**] = 5.2 x 10^{-6} mol.L^{-1} (solvent = THF). Corresponding Stern-Volmer plot for the quenching of the singlet excited state of **C) PBP** ($K_{SV}^{PBP/cysteamine}$ = 1.2 M^{-1}) and **D) PBPZn** ($K_{SV}^{PBPZn/cysteamine}$ = 6.2 M^{-1}).*

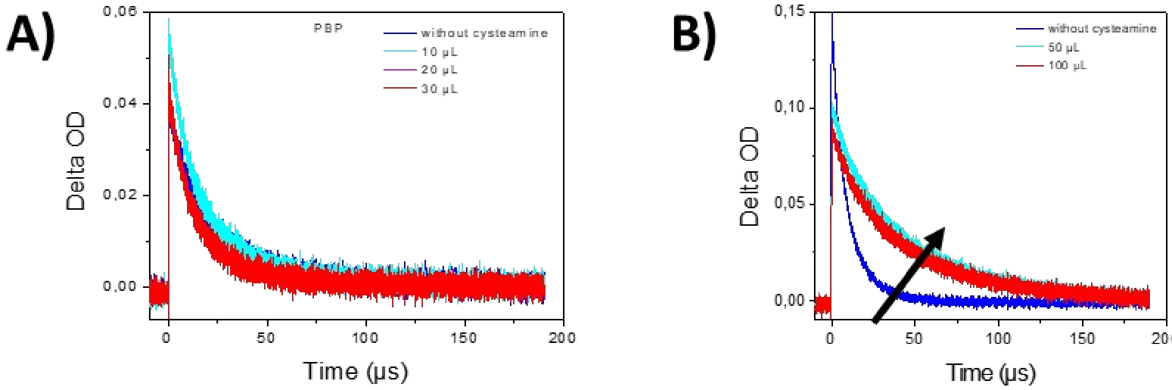


Figure S28: *Decay traces of A)* ***PBP*** *and B)* ***PBPZn*** *triplet state after a laser pulse (λ_{ex} = 385 nm) with a gradual increase of the cysteamine concentration. [**PBP**] = 1.1 x 10^{-5} mol.L^{-1} , [**PBPZn**] = 1.7 x 10^{-4} mol.L^{-1} in DCM.*

Effect of the addition of *N*-acetylcysteine

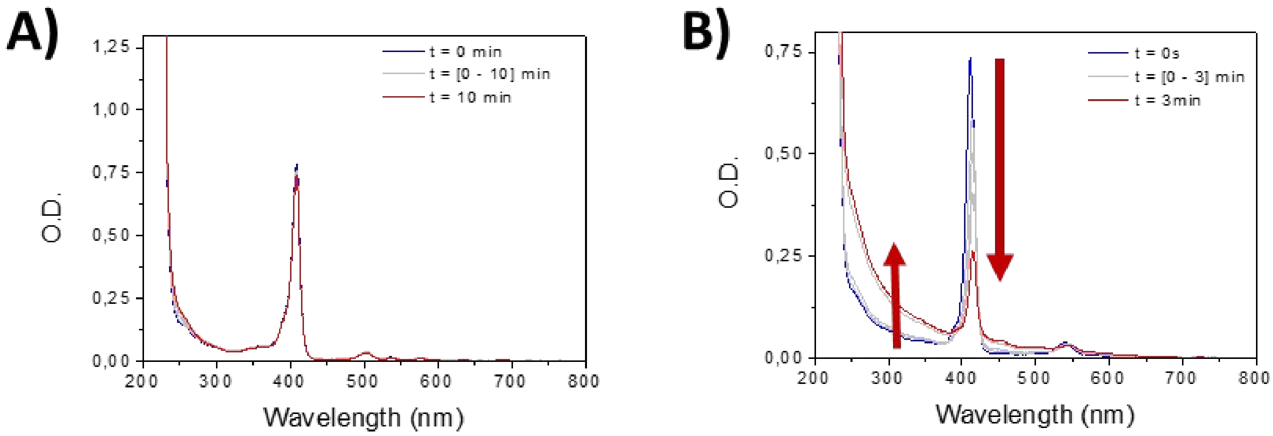


Figure S29: *Steady state photolysis of A)* ***PBP****/N-acetylcysteine and B)* ***PBPZn****/N-acetylcysteine systems under air after LED@405 nm exposure. [**PBP**] = 2 x 10^{-6} mol.L^{-1}, [**PBPZn**] = 6 x 10^{-6} mol.L^{-1}, [N-acetylcysteine] = 1.1 x 10^{-4} mol.L^{-1}. Solvent = DCM.*

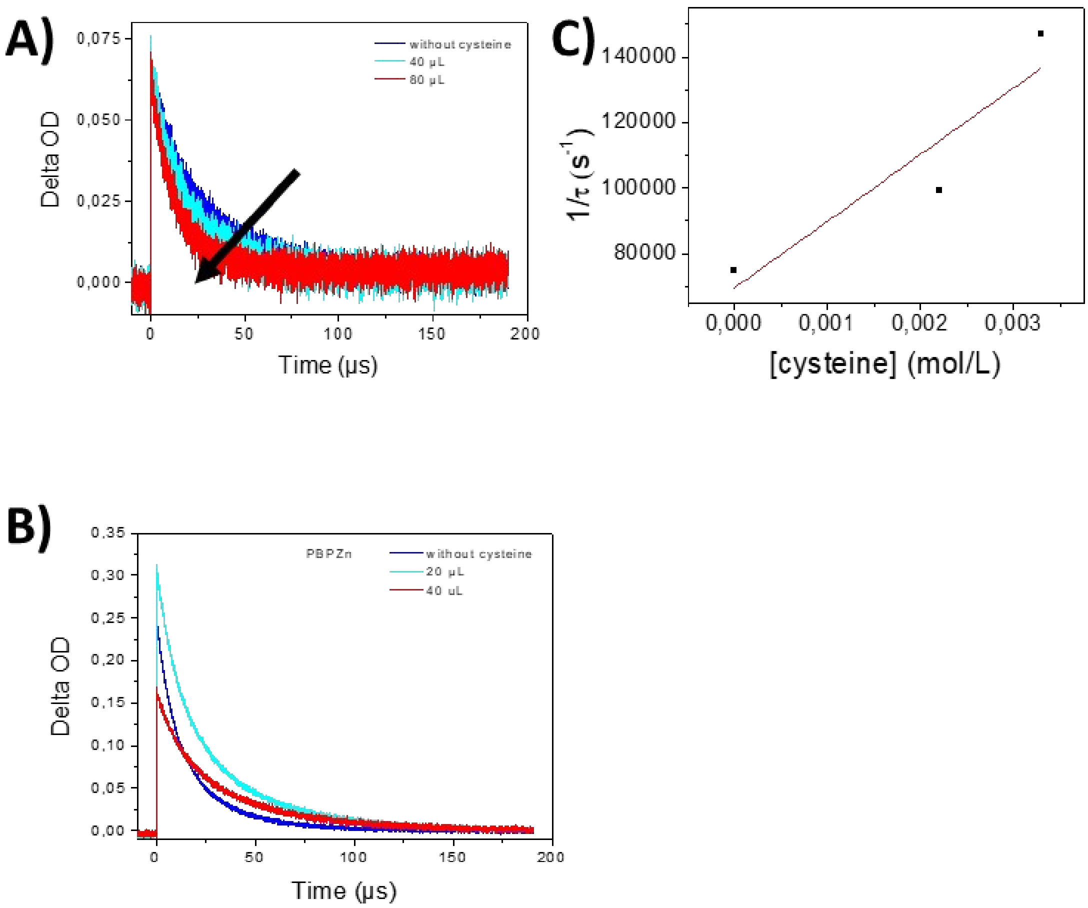


***Figure S30**: Decay traces of A) **PBP** and B) **PBPZn** triplet state after laser pulses (λ_{ex} = 385 nm) with a gradual addition of N-acetylcysteine. Corresponding Stern-Volmer plot for the quenching of the triplet excited state of **C) PBP** with N-acetylcysteine. [**PBP**] = 1.1 x 10^{-5} mol.L^{-1} , [**PBPZn**] = 1.7 x 10^{-4} mol.L^{-1} in DCM.*

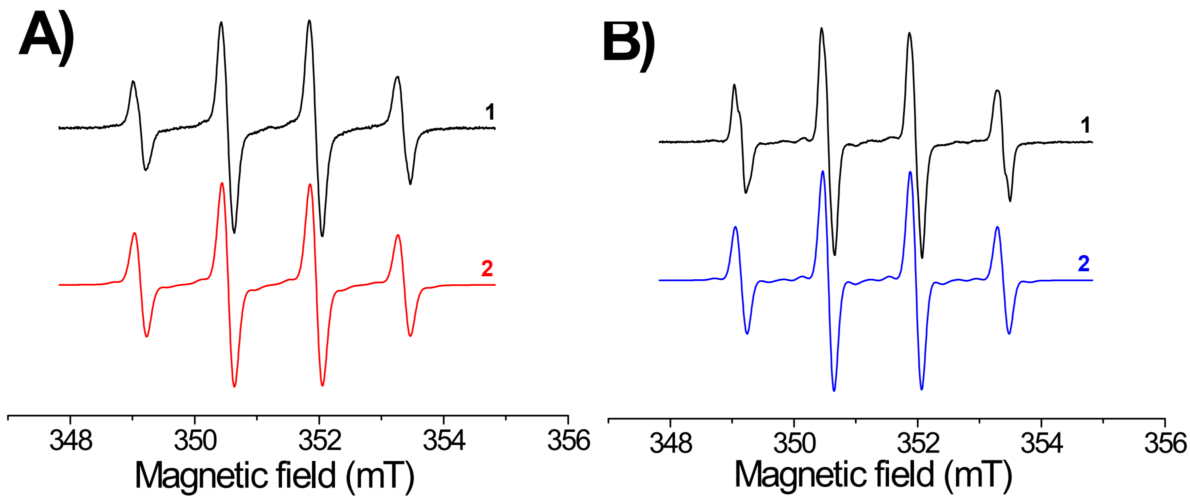


***Figure S31**: The normalized experimental (1) and simulated (2) EPR spectra obtained upon continuous in situ LED@405 nm exposure of (A) **PBP** and (B) **PBPZn** in chloroform and under argon in the presence of DMPO spin trapping agent and N-acetylcysteine.*

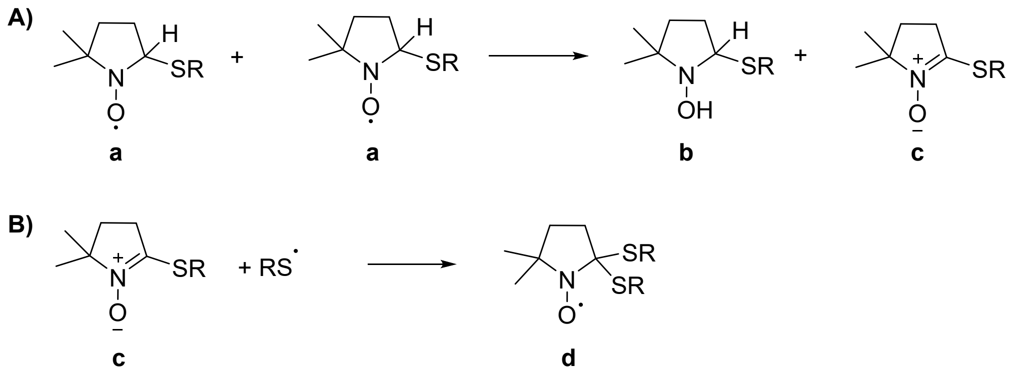


***Figure S32**: **A**) Dismutation reaction between two DMPO-SR adduct **a** leading to the formation of hydroxylamine **b** and nitrone **c** by redox reaction. **B**) Reaction between nitrone **c** and thiyl radical leading to nitroxide **d**.*

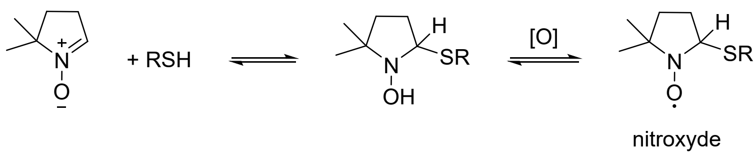


***Figure S33**: Forrester-Hepburn mechanism*

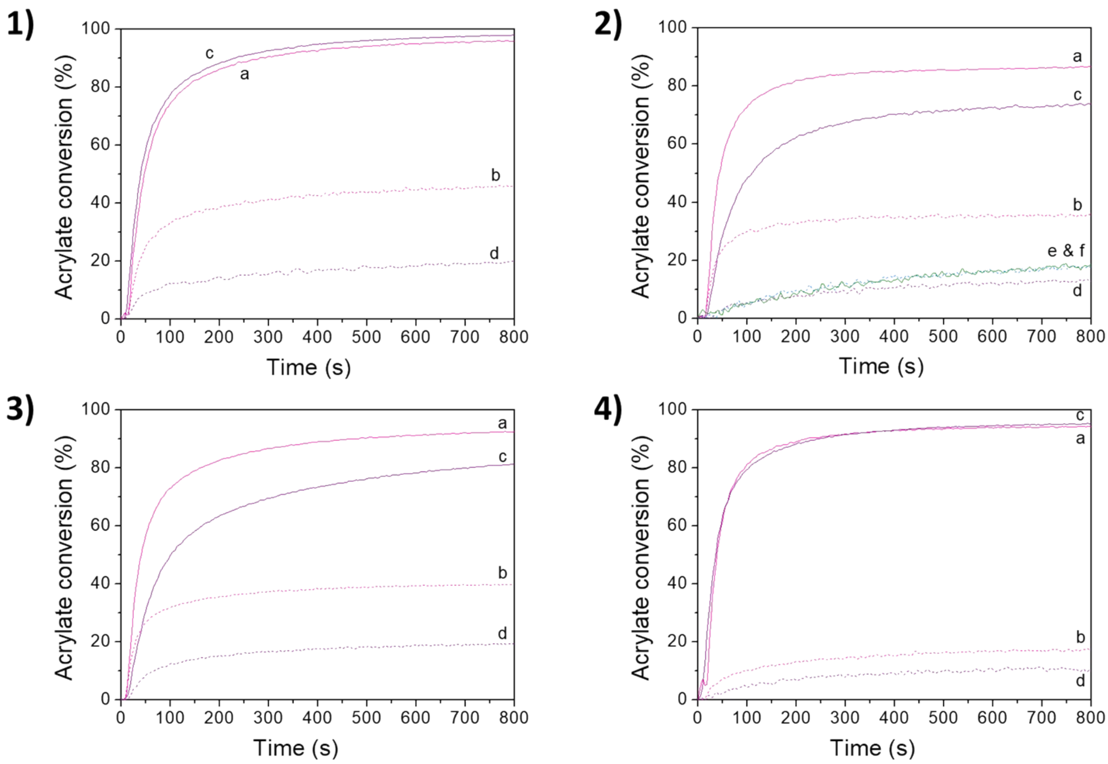


***Figure S34**: Polymerization profiles (acrylate function conversion vs. irradiation time) for SOA in laminate (solid line) and under air (dash line) in the presence of 1) BP/MDEA (0.5%/2% w/w), 2) BP/Iod (0.5%/2% w/w), 3) BP/cysteamine (0.5%/1% w/w), 4) BP/N-acetylcysteine (0.5%/2% w/w) upon irradiation of (a) LED@385 nm in laminate, (b) LED@385 nm under air, (c) LED@405 nm in laminate, (d) LED@405 nm under air, (e) LED@505 nm under air and (f) LED@530 nm in laminate.*

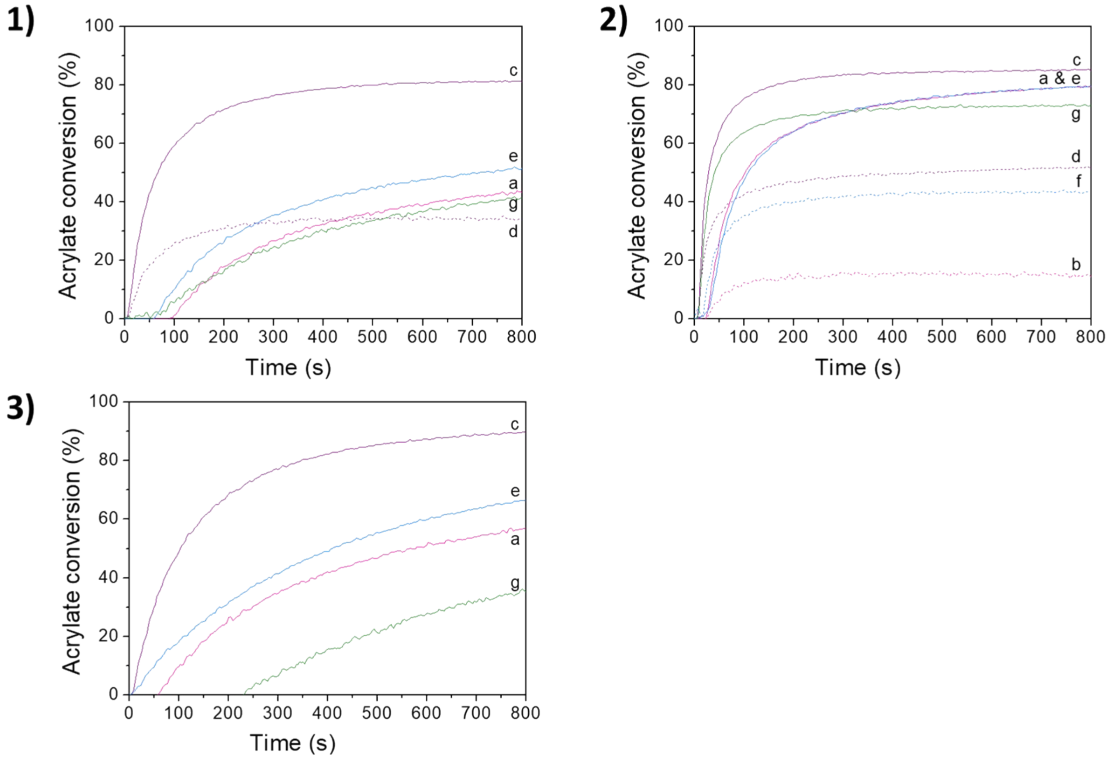


Figure S35*: Polymerization profiles (acrylate function conversion vs. irradiation time) for SOA in laminate (solid line) and under air (dash line) in the presence of 1) CQ/MDEA (0.5%/2% w/w), 2) CQ/Iod (0.5%/2% w/w), 3) BP/N-acetylcysteine (0.5%/2% w/w) upon irradiation with (a) LED@385 nm in laminate, (b) LED@385 nm under air, (c) LED@405 nm in laminate, (d) LED@405 nm under air, (e) LED@505 nm in laminate, (d) LED@505 nm under air, (f) LED@530 nm in laminate and (g) LED@530 nm under air.*

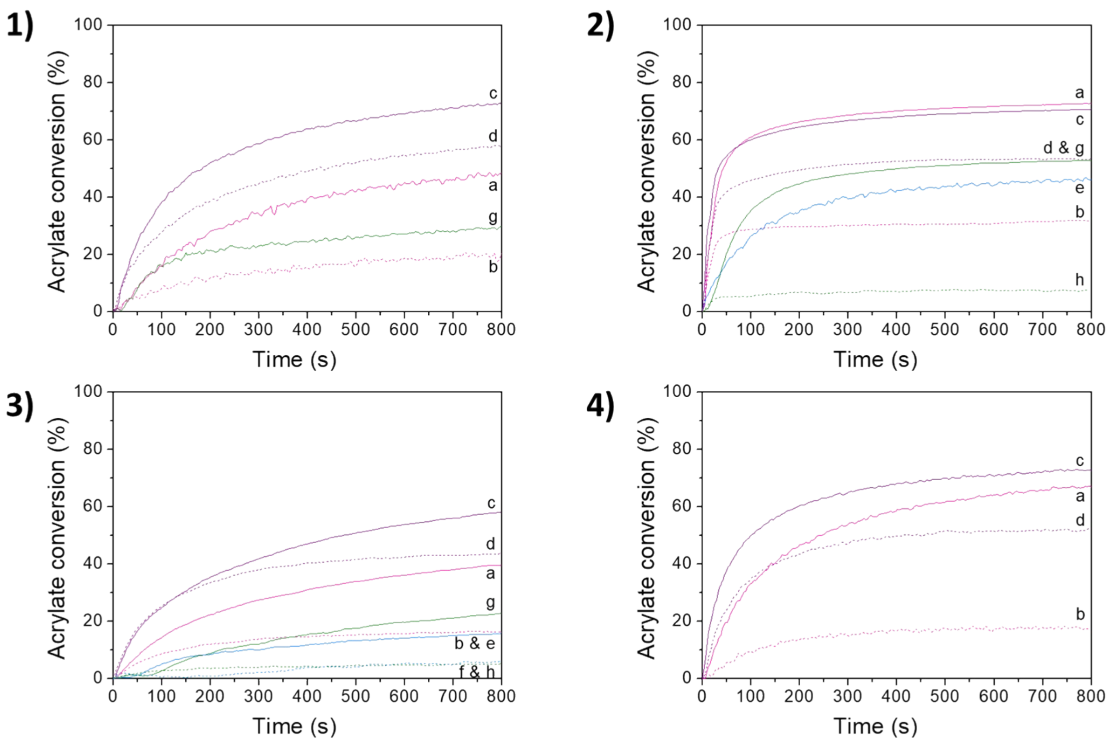


***Figure S36**: Polymerization profiles (acrylate conversion vs. irradiation time) for SOA in laminate (solid line) and under air (dash line) in the presence of **1)** **PBP**/MDEA (0.5%/2% w/w), **2)** **PBP**/Iod (0.5%/2% w/w), **3)** **PBP**/cysteamine (0.5%/1% w/w) and **4)** **PBP**/N-acetylcysteine (0.5%/2% w/w) upon irradiation with (a) LED@385 nm in laminate, (b) LED@385 nm under air, (c) LED@405 nm in laminate, (d) LED@405 nm under air, (e) LED@505 nm in laminate, (d) LED@505 nm under air, (f) LED@530 nm in laminate and (g) LED@530 nm under air.*

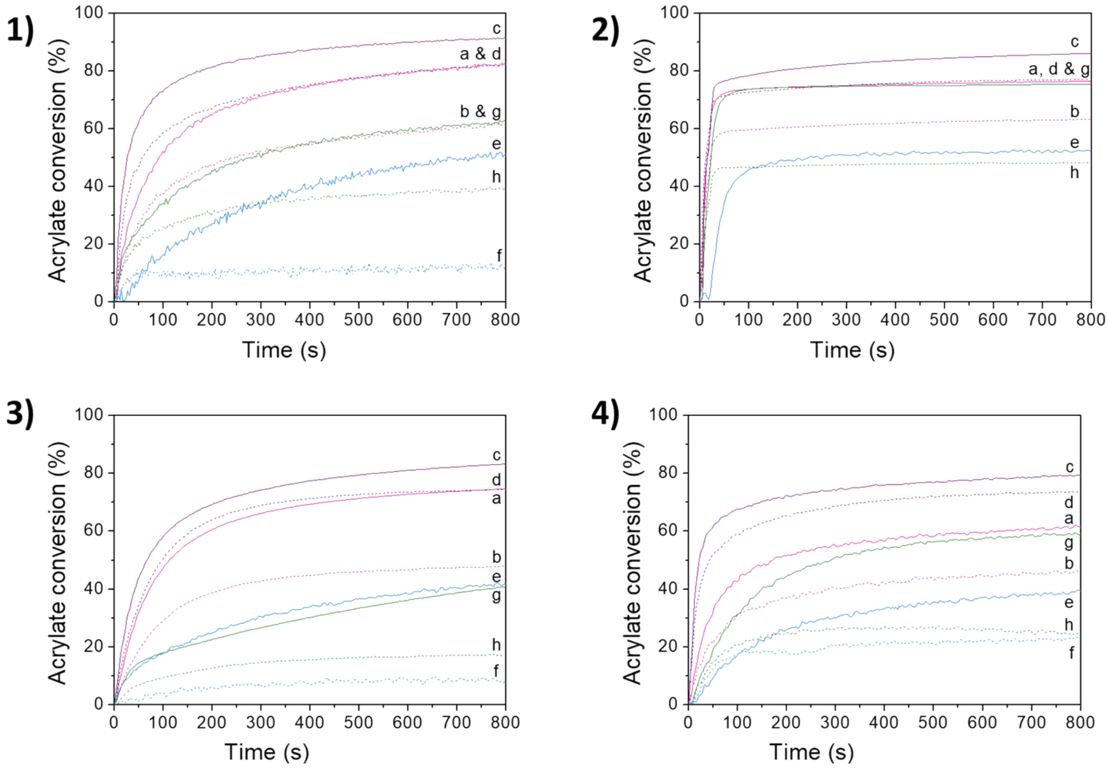


***Figure S37**: Polymerization profiles (acrylate function conversion vs. irradiation time) for SOA in laminate (solid line) and under air (dash line) in the presence of **1)** **PBPZn**/MDEA (0.5%/2% w/w), **2)** **PBPZn**/Iod (0.5%/2% w/w), **3)** **PBPZn**/cysteamine (0.5%/1% w/w) and **4)** **PBPZn**/N-acetylcysteine (0.5%/2% w/w) upon irradiation with (a) LED@385 nm in laminate, (b) LED@385 nm under air, (c) LED@405 nm in laminate, (d) LED@405 nm under air, (e) LED@505 nm in laminate, (d) LED@505 nm under air, (f) LED@530 nm in laminate and (g) LED@530 nm under air.*

***Figure S38**: Optical image of the **PBPZn**-based pellet*