Supporting information

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

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Figure 52: " ¹ C NMR spectrum of PBP in CDCl ₃
Figure 33: ¹ H NMR spectrum of PBP2n in CDCl ₈
Figure 53: ¹² C MMR spectrum of PBP2 in CDC],
Figure SS: 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)
Sector (200, Fos), Fos, Park 10, 200, Fost, PBP (left) and PBPZn (right)
Figure 52: Vibrationally-resolved spectrum of PBP simulated using the Vertical Hessian model and internal coordinates. S7 Figure 58: 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 51, 52, and 54). S7 Figure 59: 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 51: Vibrationally-resolved spectrum of PBP simulated using the Vertical Ressnammoder and international control in the simulated using the Vertical Ressnammoder and international control in the simulated using the Vertical Ressnammoder and Cartesian coordinates. The imaginary frequency for the excited states were turned real (one such frequency for 51, 52, and 54). Figure 59: Vibrationally-resolved spectrum of PBPZn simulated using the Vertical Hessian model and Cartesian coordinates. Note that for both 51 and 54, imaginary frequencies exist in the excited-state (vertical) Hessian, and they have been turned positive
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). S7: 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. S8: 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). S9: Figure S11: Vertical transition energies, associated oscillator strengths and electron density difference plots for PBP. S9: S12: Transition absorption spectra of PBP and PBPZn under argon in DCM (λ_{esc} = 385 nm). S10 Figure S12: Transition absorption spectra of PBP and PBPZn under argon in DCM (λ_{esc} = 385 nm). S10 S12: S12: The signe S12: Caracis of the triplet excited state of A) PBP and B) PBPZn after a laser pulse (k_{esc} = 385 nm). S10 S12: S13: Decay traces of the triplet excited state of A) PBP and B) PBPZn (B) PBPZn after a laser pulse (k_{esc} = 385 nm). S10 Figure S15: The normalized experimental (1) and simulated (2) EPR spectra obtained upon continuous in situ ED@400 nm exposure in chloroform under irradiation for (A) PBPZn, (MDEA) e .2.8 x 10 ² mol.1 ⁻¹ , Solvent = DCM. S12 Figure S16: Steady state photolysis of A) PBP/MDEA and B) PBPZn/MDEA as PBPZn/MDEA systems under air after LED@405 nm S12 Figure S17: Quenching of A) PBP and B) PBPZn fluorescence after a gradual addition of MDEA. (PBP] = 1.2 x 10 ⁻⁷ mol.1 ⁻¹ , (MDEA] = 8.7 mol.1 ⁻¹ in DCM. S12 Figure S19: The normalized experimental (1) and simulated (2) EPR spectra obtained upon continuous in situ LED@400 nm exposure of PBP2n/MDEA in chloroform under argon. S14 Figure S19: The
scoordinates. The imaginary frequency for the excited states were turned real (one such frequency for S1, S2, and S4). S7 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
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coordinates. Note that for both S1 and S4, imaginary frequencies exist in the excited-state (vertical) Hessian, and they nave been turned positive
Figure S10: Vertical transition energies, associated oscillator strengths and electron density difference plots for PBP. n the latter representations, the blue and red lobes correspond to decrease and increase of density upon absorption threshold 0.005 au)
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Figure 31: Vertical transition energies, associated oscillator strengths and electron density difference plots for PBPZn. See previous caption for more details
See previous caption for more details
Figure S12: Transition absorption spectra of PBP and PBPZn under argon in DCM ($\lambda_{exc} = 385 \text{ nm}$)
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
Sigure S14: Photolysis of A) PBP and B) PBPZn solution under LED@405 nm irradiation. [PBP] = 2×10^{-6} mol.L ⁻¹ , [PBPZn] = 6×10^{-6} mol.L ⁻¹ , [MDEA] = 2.8×10^{-2} mol.L ⁻¹ . Solvent = DCM
Figure S14: Photolysis of A) PBP and B) PBPZn solution under LED@405 nm irradiation. [PBP] = 2×10^{-6} mol.L ⁻¹ , [PBPZn] = 6×10^{-6} mol.L ⁻¹ , [MDEA] = 2.8×10^{-2} mol.L ⁻¹ . Solvent = DCM
= 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. S12 Figure S16 : Steady state photolysis of A) PBP/MDEA and B) PBPZn/MDEA systems under air after LED@405 nm exposure. [PBP] = 2×10^{-6} mol.L ⁻¹ , [PBPZn] = 6×10^{-6} mol.L ⁻¹ , [MDEA] = 2.8×10^{-2} mol.L ⁻¹ . Solvent = DCM. S13 Figure S17 : Quenching of A) PBP and B) PBPZn fluorescence after a gradual addition of MDEA. [PBP] = 1.2×10^{-7} mol.L ⁻¹ , (PBPZn] = 5.2×10^{-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. S13 Figure S18 : Decay traces of A) PBP and B) PBPZn triplet excited state after a laser pulse ($\lambda_{ex} = 385$ 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] = 1.1×10^{-5} mol.L ⁻¹ , [PBPZn] = 1.7×10^{-4} mol.L ⁻¹ , [MDEA] = 8.7 mol.L ⁻¹ in DCM. S14 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. S14 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. S15 Figure S21: Steady state photolysis of A) PBP/lod and B) PBPZn/lod systems under air after LED@405 nm exposure. (PBP] = 2×10^{-6} mol.L ⁻¹ , [PBPZn] = 6×10^{-6} mol.L ⁻¹ , [Iod] = 2.9×10^{-5} mol.L ⁻¹ . Solvent = DCM. S15 Figure S22: Quenching of A) PBP and B) PBPZn fluorescence after a gradual addition of lod. [PBP] = 1.2×10^{-7} mol.L ⁻¹ , (PBPZn] = 5.2×10^{-6} mol.L ⁻¹ (solvent = THF). Corresp
LED@400 nm exposure in chloroform under irradiation for (A) PBPZn , (B) PBP with DMPO and (C) PBPZn with DMPO. S12 Figure S16 : Steady state photolysis of A) PBP/MDEA and B) PBPZn/MDEA systems under air after LED@405 nm exposure. [PBP] = 2×10^{-6} mol.L ⁻¹ , [PBPZn] = 6×10^{-6} mol.L ⁻¹ , [MDEA] = 2.8×10^{-2} mol.L ⁻¹ . Solvent = DCM
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
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Figure S17 : Quenching of A) PBP and B) PBPZn fluorescence after a gradual addition of MDEA. [PBP] = $1.2 \times 10^{-7} \text{ mol.L}^{-1}$, [PBPZn] = $5.2 \times 10^{-6} \text{ mol.L}^{-1}$ (solvent: THF). Corresponding Stern-Volmer plot for the quenching of the singlet excited state of C) PBP ($K_{SV}^{PBP/MDEA} = 1.2 \text{ M}^{-1}$) and D) PBPZn ($K_{SV}^{PBPZn/MDEA} = 0.7 \text{ M}^{-1}$) with MDEA
$[PBPZn] = 5.2 \times 10^{-6} \text{ mol.L}^{-1} \text{ (solvent: THF). Corresponding Stern-Volmer plot for the quenching of the singlet excited state of C) PBP (K_{SV}^{PBP/MDEA} = 1.2 M^{-1}) and D) PBPZn (K_{SV}^{PBPZn/MDEA} = 0.7 M^{-1}) with MDEA$
State of C) PBP ($K_{SV}^{PBP/MDEA} = 1.2 \text{ M}^{-1}$) and D) PBPZn ($K_{SV}^{PBPZn/MDEA} = 0.7 \text{ M}^{-1}$) 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
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
[PBP] = $1.1 \times 10^{-5} \text{ mol.L}^{-1}$, [PBPZn] = $1.7 \times 10^{-4} \text{ mol.L}^{-1}$, [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
The 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
for A) PBP and B) PBPZn
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 , [lod] = 2.9 x 10 ⁻⁵ mol.L ⁻¹ . Solvent = DCMS15 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
$[PBP] = 2 \times 10^{-6} \text{ mol.L}^{-1}, [PBPZn] = 6 \times 10^{-6} \text{ mol.L}^{-1}, [lod] = 2.9 \times 10^{-5} \text{ mol.L}^{-1}.$ Solvent = DCMS15 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
Figure S22: Quenching of A) PBP and B) PBPZn fluorescence after a gradual addition of lod. [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
$[PBPZn] = 5.2 \times 10^{-6} \text{ mol.L}^{-1}$ (solvent = THF). Corresponding Stern-Volmer plot for the quenching of the singlet excited
state of C) PBP ($K_{SV}^{PBP/Iod} = 11 \text{ M}^{-1}$) and D) PBPZn ($K_{SV}^{PBPZn/Iod} = 13 \text{ M}^{-1}$) 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 lod. 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 DCMS17
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)S17
Figure S25: Steady-state photolysis of A) PBP/lod/rhodamine B and B) PBPZn/lod/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
$10^{-6} \text{ mol.L}^{-1}$, [PBPZn] = 6 x $10^{-6} \text{ mol.L}^{-1}$, [Iod] = 2.9 x $10^{-5} \text{ mol.L}^{-1}$, [RhB] = 2.4 x $10^{-5} \text{ mol.L}^{-1}$ S18
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 ^{•-}
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 ($K_{SV}^{PBP/cysteamine} = 1.2 \text{ M}^{-1}$) and D) PBPZn ($K_{SV}^{PBPZn/cysteamine} = 6.2 \text{ M}^{-1}$)
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] = $1.1 \times 10^{-5} \text{ mol}.\text{L}^{-1}$. [PBPZn] = $1.7 \times 10^{-4} \text{ mol}.\text{L}^{-1}$ in DCM
Figure S29: Steady state photolysis of A) PBP/N-acetylcysteine and B) PBPZn/N-acetylcysteine systems under air after
$IED@405 \text{ nm} exposure. [PBP] = 2 \times 10^{-6} \text{ mol.} I^{-1}. [PBPZn] = 6 \times 10^{-6} \text{ mol.} I^{-1}. [N-acetylcysteine] = 1.1 \times 10^{-4} \text{ mol.} I^{-1}. Solvent$
= DCM
Figure S30 : Decay traces of A) PBP and B) PBP7n 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] = 1.1×10^{-5} mol L ⁻¹ [PBP7 n] = 1.7×10^{-4} mol L ⁻¹ in DCM S21
Figure S21 : The normalized experimental (1) and simulated (2) EDR spectra obtained upon continuous in situ LED@405.
nm exposure of (A) PBP and (B) PBP7n in chloroform and under argon in the presence of DMPO spin transing agent
and N-acetylcysteine
Figure S22: A) Dismutation reaction between two DMPO-SR adduct a leading to the formation of hydroxylamine b and
nitrone c by redex reaction B) Peaction between two Divisions adduct a reading to the formation of hydroxylamine b and
Figure \$22: Forrester Hendurn mechanism
Figure \$33. For ester-riepburn mechanism
rigure 354. Polymenization promes (acrystate function conversion vs. in addition time) for SOA in familiate (solid line) and under siz (dash line) in the presence of 1) $PP/MDEA (0.5\%/2\% w/w) = 2) PP/(add (0.5\% w/w) = 2) PP/(add (0.5$
and under all (dash line) in the presence of 1) $BP/NDEA (0.5%/2% w/w), 2) BP/100 (0.5%/2% w/w), 3) BP/Cysteanline (0.5%/2% w/w), 4) BP/N acatyleysteine (0.5%/2% w/w) upon irradiation of (a) LED@28E nm in laminate (b)$
(0.5%/1% w/w), 4) BP/N-acetylcystellie $(0.5%/2% w/w)$ upon infaulation of (a) LED@565 mm under sir (b) LED@405 nm under sir (c) LED@605 nm under sir and (f)
LED@385 nm under air, (c) LED@405 nm in laminate, (d) LED@405 nm under air, (e) LED@505 nm under air and (l)
LED@530 nm in laminate
Figure 535: Polymerization profiles (acrylate function conversion vs. irradiation time) for SOA in faminate (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-
acetyicysteine $(0.5\%/2\% \text{ W/W})$ 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



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 11</sup> Figure S2: ¹³C NMR spectrum of PBP in CDCl₃.



Figure S4: ¹³C NMR spectrum of PBPZn in CDCl₃.



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.



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

Molecules	E _{ox} (eV)	E _{red} (eV)	E _s (eV)	E⊤ (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		-	-

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

Photostability of the porphyrin derivatives



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



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



Figure S17: Quenching of **A**) **PBP** and **B**) **PBPZn** fluorescence after a gradual addition of MDEA. [PBP] = 1.2×10^{-7} mol.L⁻¹, [**PBPZn**] = 5.2×10^{-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 ($\lambda_{ex} = 385$ 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**/lod and B) **PBPZn**/lod systems under air after LED@405 nm exposure. [**PBP**] = $2 \times 10^{-6} \text{ mol.L}^{-1}$, [**PBPZn**] = $6 \times 10^{-6} \text{ mol.L}^{-1}$, [lod] = $2.9 \times 10^{-5} \text{ mol.L}^{-1}$. Solvent = DCM



Figure S22: Quenching of A) **PBP** and B) **PBPZn** fluorescence after a gradual addition of Iod. [**PBP**] = $1.2 \times 10^{-7} \text{ mol.L}^{-1}$, [**PBPZn**] = $5.2 \times 10^{-6} \text{ mol.L}^{-1}$ (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 ($\lambda_{ex} = 385 \text{ nm}$) with a gradual addition of lod. Corresponding Stern-Volmer plot for the quenching of the triplet excited state of **C**) **PBP** and **D**) **PBPZn** with the addition of lod. [**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 lod. (* 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**/lod/rhodamine B and **B**) **PBPZn**/lod/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**] = $2 \times 10^{-6} \text{ mol.L}^{-1}$, [**PBPZn**] = $6 \times 10^{-6} \text{ mol.L}^{-1}$, [Iod] = $2.9 \times 10^{-5} \text{ mol.L}^{-1}$, [RhB] = $2.4 \times 10^{-5} \text{ mol.L}^{-1}$.



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: \times denotes the broad signal assigned to PBPZn^{*-}.



Figure S27: Quenching of A) PBP and B) PBPZn fluorescence after a gradual addition of cysteamine. [PBP] = 1.2×10^{-7} mol.L⁻¹, [PBPZn] = 5.2×10^{-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**] = $2 \times 10^{-6} \text{ mol.L}^{-1}$, [**PBPZn**] = $6 \times 10^{-6} \text{ mol.L}^{-1}$, [N-acetylcysteine] = $1.1 \times 10^{-4} \text{ mol.L}^{-1}$. Solvent = DCM.



Figure S30: Decay traces of A) **PBP** and B) **PBPZn** triplet state after laser pulses ($\lambda_{ex} = 385 \text{ nm}$) 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**.



а

С

1)

3)

ΰ 100



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.

100 200 300 400 500 600 700 800

Time (s)

ò

800

600

Time (s)



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/lod (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.



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/lod (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