

Supporting information

Photodynamic activity attained through the ruptured π -conjugation of pyridyl groups with a porphyrin macrocycle: synthesis and the photophysical and photobiological evaluation of 5-mono-(4-nitrophenyl)-10,15,20-tris-[4-(phenoxy)methyl]pyridine-porphyrin and its Zn(II) complex

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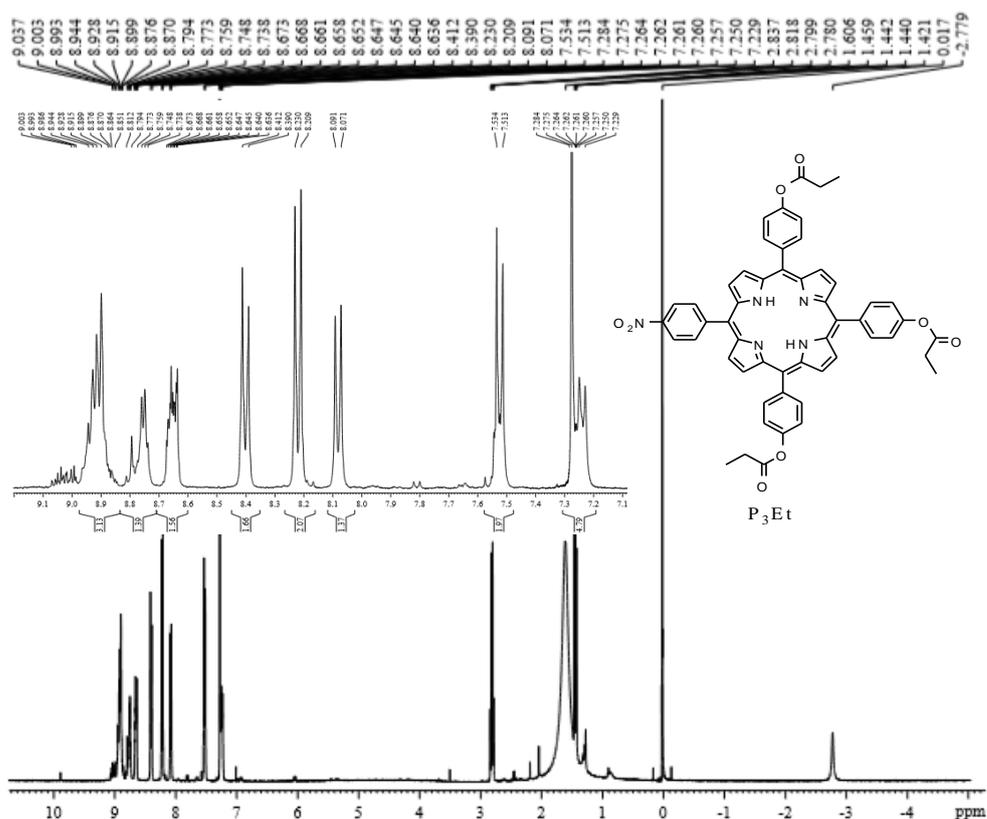
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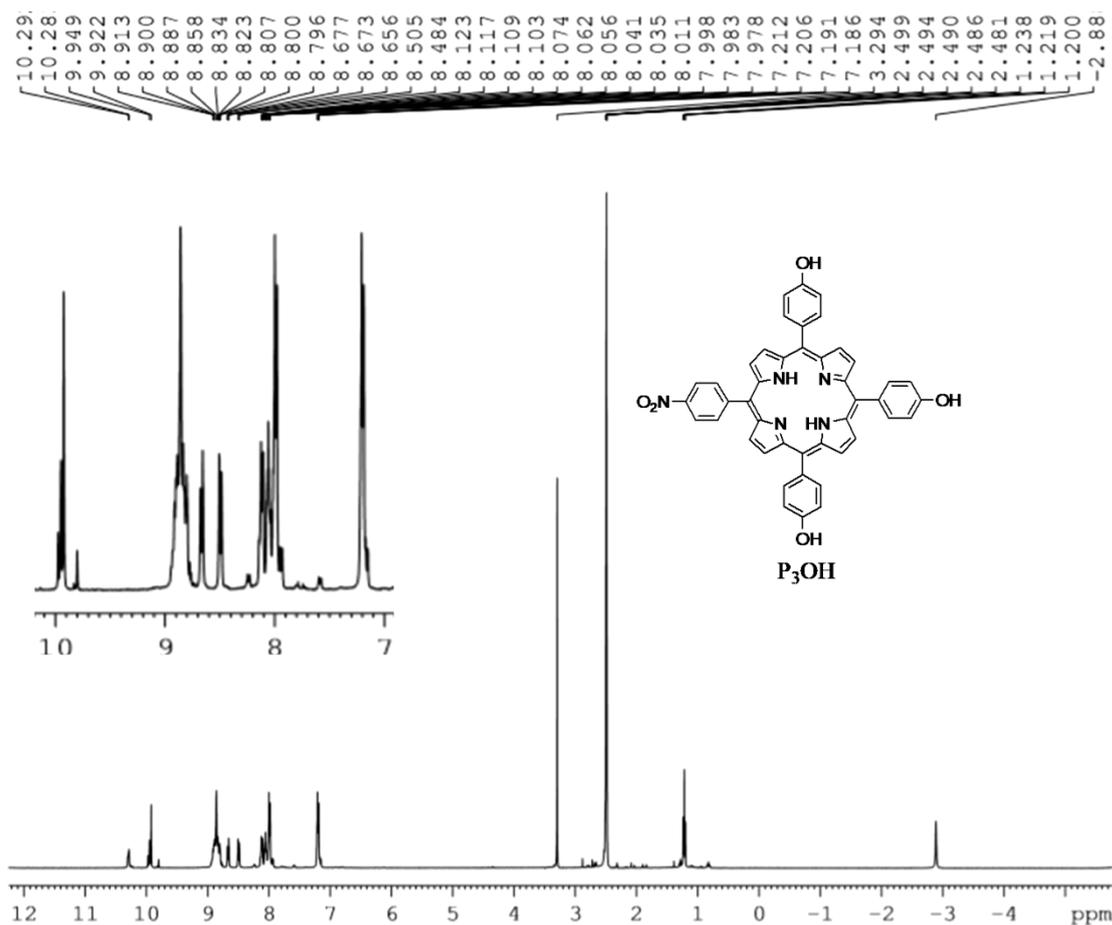
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Table S1: The Gibbs free energies of the compounds and their free energy of solvation (ΔG_{sol}), as determined at the B3LYP/6-31G* level of theory.

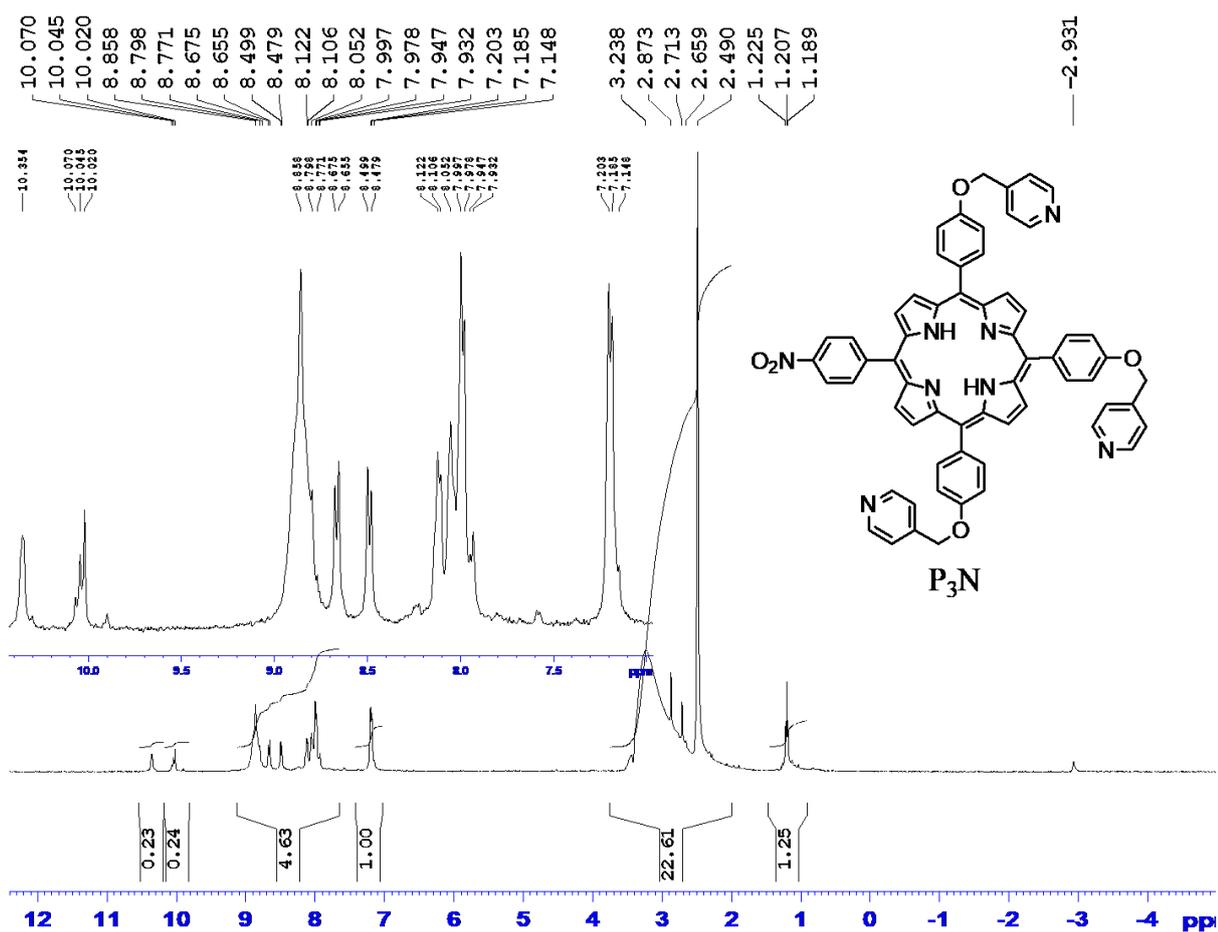
Compounds	Gibbs free energy (a.u.)		ΔG_{sol} (kcal/mol)
	Gas phase	Aqueous media	
(NPh)TPyP (reference)	-2165.847834	-2165.869791	-13.78
(NPh)TPyPZn (reference)	-3943.90699	-3943.937039	-18.86
P ₃ N	-3202.268471	-3202.301349	-20.63
P ₃ NZn	-4980.327341	-4980.368709	-25.96



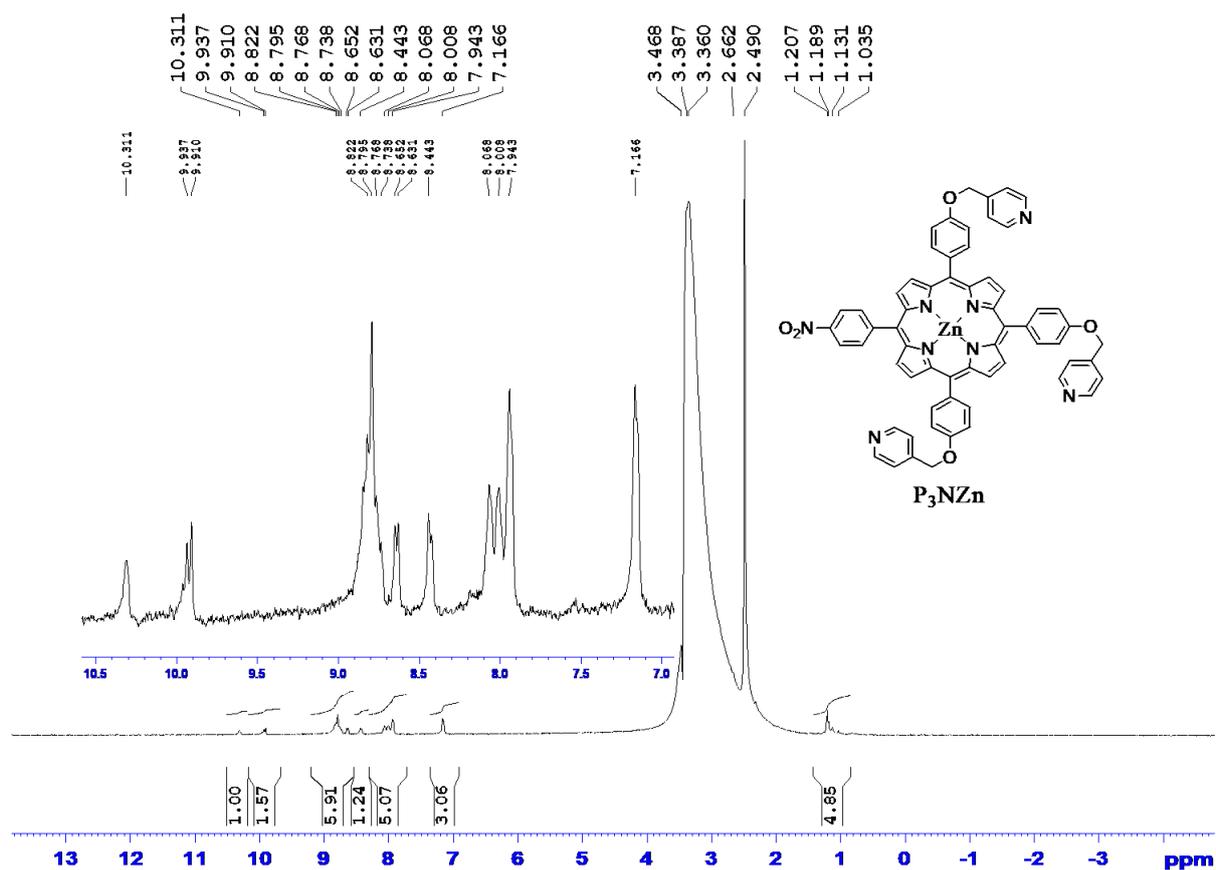
¹H-NMR (400 MHz, CDCl₃ at 300 K), δ : 8.64 (d, 2H; J = 8.12 Hz; 2,6-nitrophenyl), 8.08 (d, 2H; J = 8.01 Hz; 3,5-nitrophenyl), 8.92 (d, 2H; J = 5.12 Hz; β -pyrrole), 8.89 (s, 4H; β -pyrrole), 8.74 (d, 2H; J = 5.10 Hz; β -pyrrole), 8.22 (d, 4H; J = 8.23 Hz; 2,6-phenyl), 7.23 (d, 4H; J = 8.23 Hz; 3,5-phenyl), 8.40 (d, 2H; J = 8.60 Hz; 2,6-phenyl), 7.53 (d, 2H; J = 8.40 Hz; 3,5-phenyl), 1.44 (t, 9H; -CH₃ ester), 2.80 (q, 6H; -CH₂ ester), -2.77 (s, 2H, NH pyrrole). Apart from that, there were distinct signals at δ = 7.27 (s, due to traces of CHCl₃ in CDCl₃) and at 1.60 (s, due to HOD). The peak appeared at δ = 0.017 (s, due to TMS).



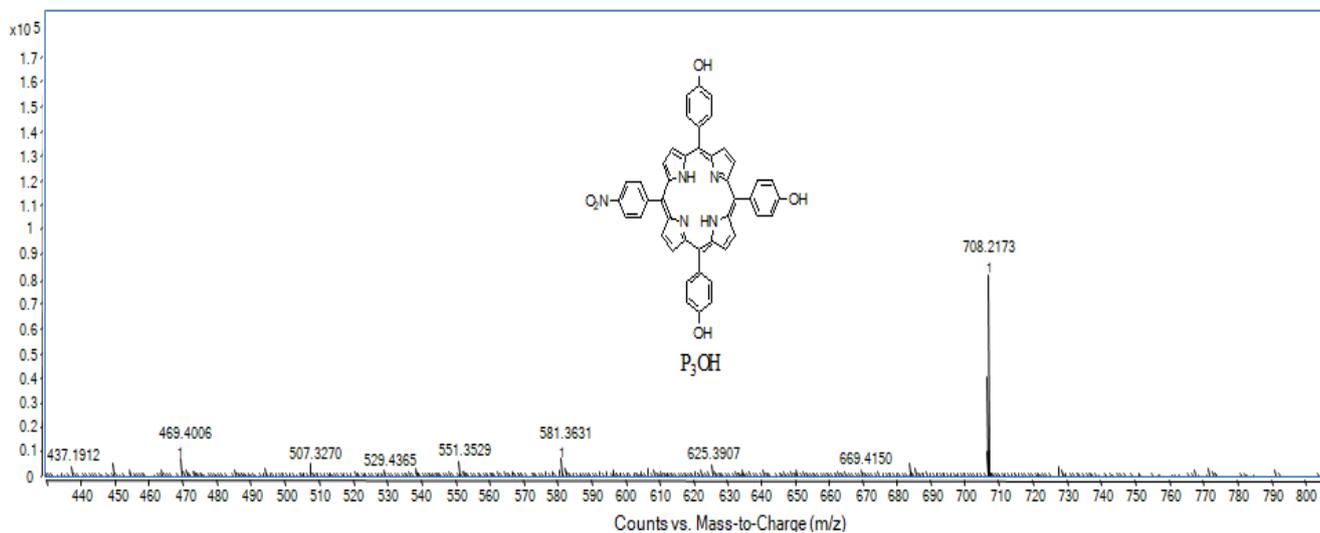
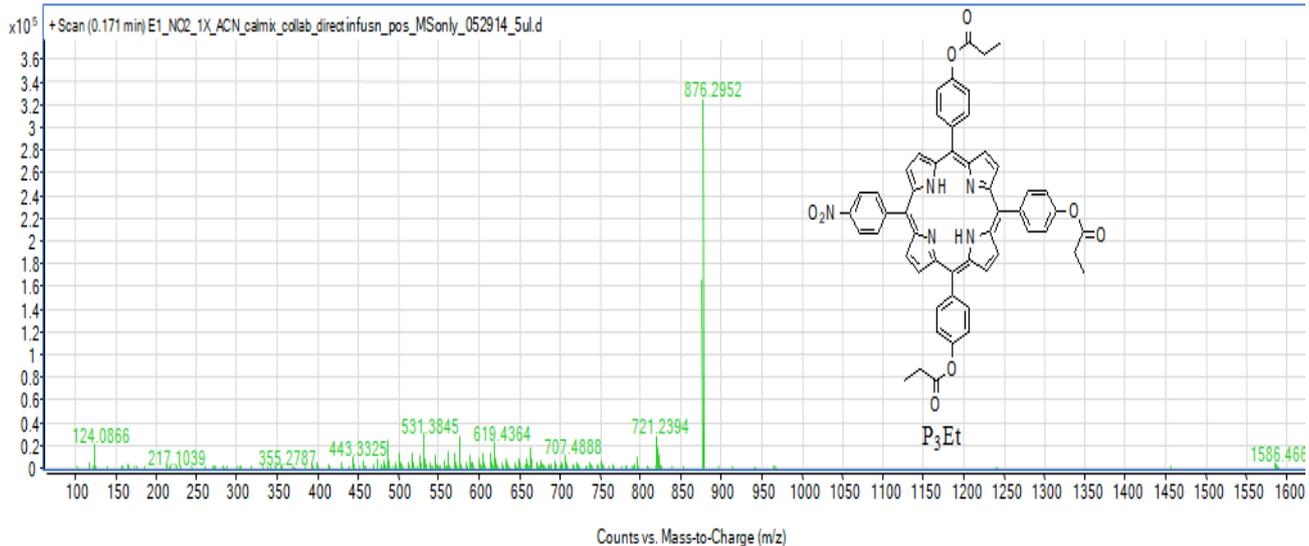
¹H-NMR (400 MHz, DMSO-d₆ at 300 K), δ = 10.30 (s, 3H; -OH), 9.92 (d, 2H; 2,6-nitrophenyl), 8.91 (d, 2H; β-pyrrole), 8.85 (s, 4H; β-pyrrole), 8.82 (d, 2H; β-pyrrole), 8.75 (d, 2H; 2,6-phenyl), 8.50 (d, 2H; 2,6-phenyl), 8.10 (d, 2H; 3,5-nitrophenyl), 7.99 (d, 4H; 2,6-phenyl), 7.21 (d, 2H; 3,5-phenyl), $\bar{\nu}$ -2.88 (s, 2H; NH pyrrole). Other distinct signals at δ = 2.49 (s, due to traces of DMSO in DMSO-d₆) and at 3.29 (br, due to HOD) were also observed.



¹H-NMR (400 MHz, DMSO-d₆ at 300 K), δ: 10.35 (d, 6H; 2,6-pyridine), 10.04 (d, 2H; *J* = 10.00 Hz; 2,6-nitrophenyl), 8.85 (s, 4H; β-pyrrole), 8.66 (d, 2H; *J* = 8.00 Hz; β-pyrrole), 8.48 (d, 2H; *J* = 8.00 Hz; β-pyrrole), 8.12 (d, 6H; 3,5-pyridine), 7.94 (d, 2H; 3,5-nitrophenyl), 7.99 (d, 6H; *J* = 7.60 Hz; 2,6-phenyl), 7.18 (d, 6H; *J* = 7.60 Hz; 3,5-phenyl). δ = -2.93 (s, 2H; NH pyrrole), 2.71 (s, 6H; -OCH₂). Signals at δ = 2.49 (s, due to traces of DMSO in DMSO-d₆), 3.33 (br, due to HOD), and ethanol at (1.20 t, -CH₃, 3.52 overlapped, -CH₂) were also observed.



1H -NMR (400 MHz, $DMSO-d_6$ at 300 K), δ : 10.31 (d, 6H; 2,6-pyridine), 9.92 (d, 2H; $J = 10.80$ Hz; 2,6-nitrophenyl), 8.76 (s, 4H; β -pyrrole), 8.64 (d, 2H; $J = 8.40$ Hz; β -pyrrole), 8.44 (d, 2H; $J = 8.40$ Hz; β -pyrrole), 8.06 (d, 6H; 3,5-pyridine), 8.00 (d, 2H; 3,5-nitrophenyl), 7.94 (d, 6H; $J = 7.60$ Hz; 2,6-phenyl), 7.16 (d, 6H; $J = 7.60$ Hz; 3,5-phenyl), 2.66 (s, 6H; $-OCH_2$). Residual signals at $\delta = 2.49$ (s, due to traces of DMSO in $DMSO-d_6$) and at 3.46 (br, due to HOD), ethanol (1.18 t, $-CH_3$, 3.66 m, $-CH_2$).



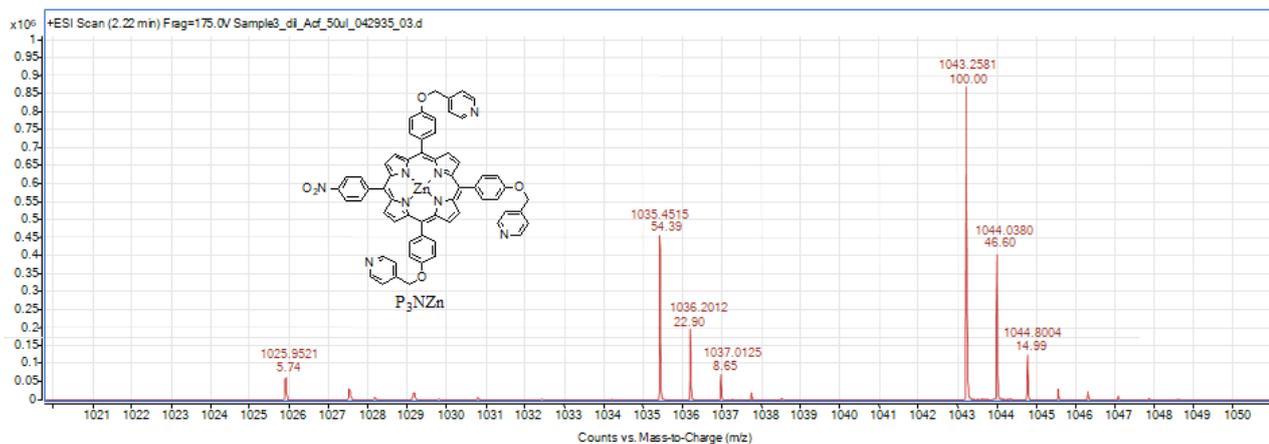
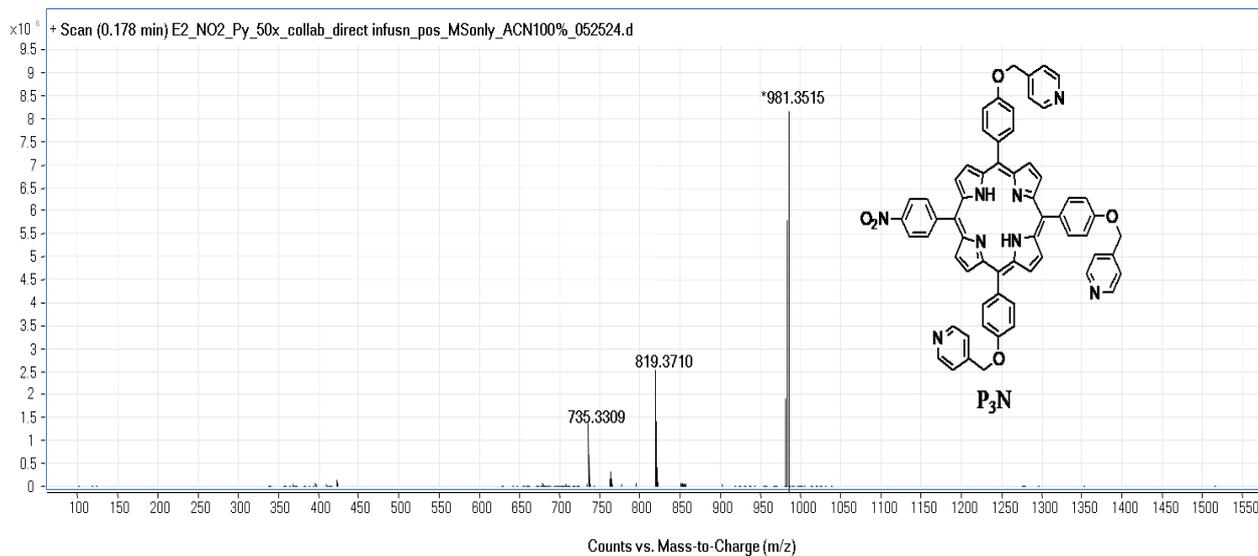


Fig. S1: Overlaid absorption spectra of the target photosensitizers P_3N and P_3NZn recorded in water (at $10\ \mu\text{M}$ concentration) at 90 days interval.

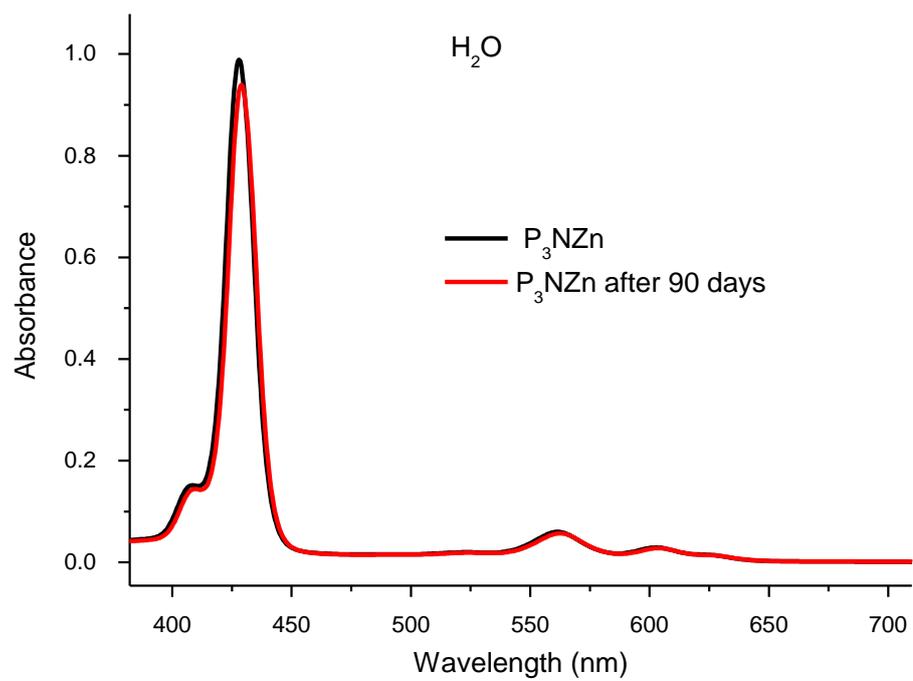
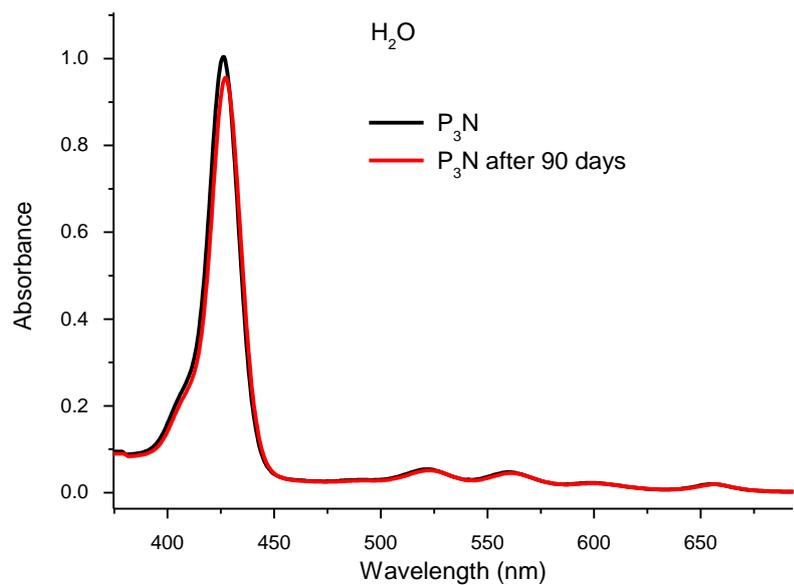


Fig. S2: Overlaid absorption spectra of the target photosensitizers P_3N and P_3NZn recorded in DMSO (at 10 μM concentration) at 90 days interval.

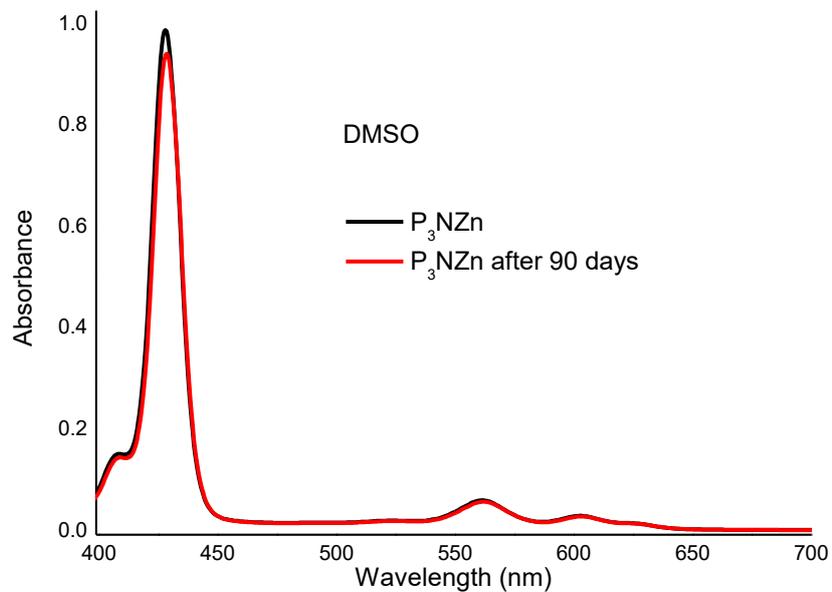
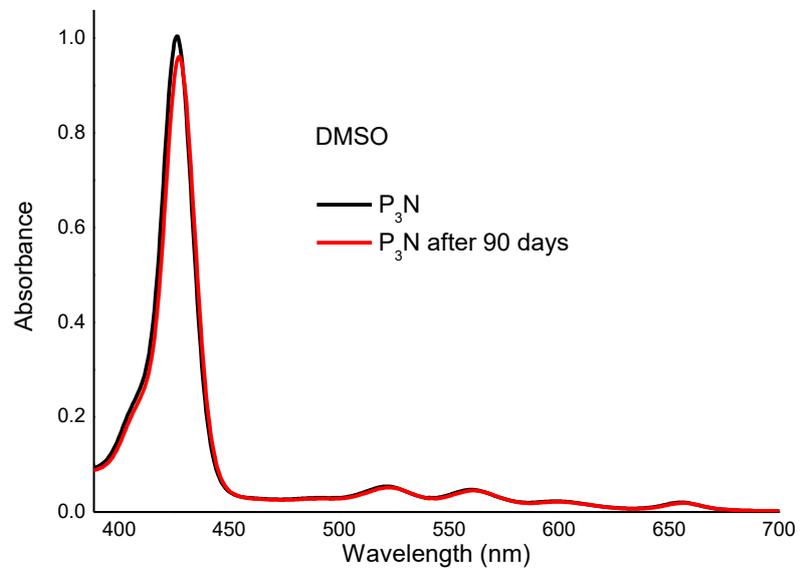


Fig. S3: Optimized geometries of the reference porphyrins free base **(NPh)TPyP**, and its corresponding zinc(II)-complex **(NPh)TPyPZn**, along with the target photosensitizers with distal pyridyl groups, **P₃N** and **P₃NZn** at the B3LYP/6-31G* level of theory in aqueous media.

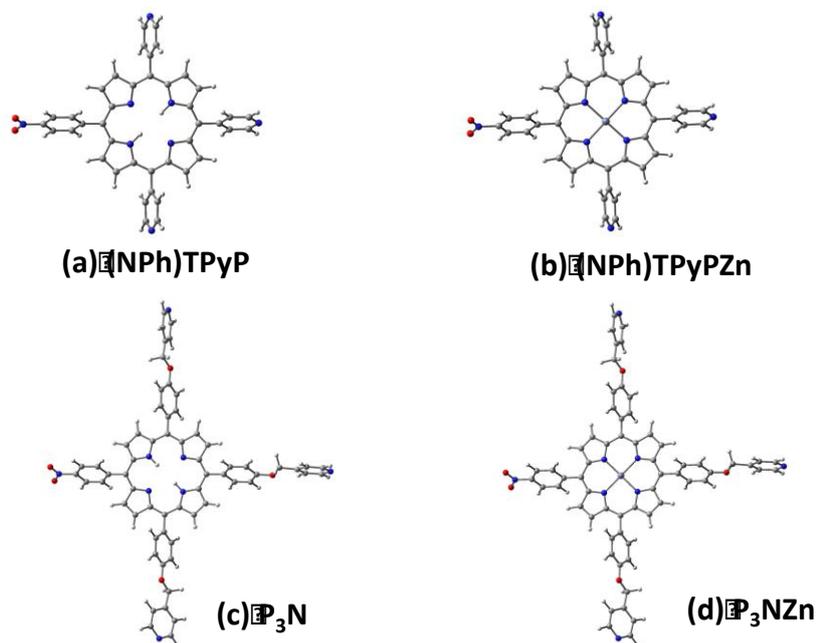


Fig. S4: Plot of kinetics of photooxidation of DMA by the target PSs **P₃N** and **P₃NZn** in DMSO.

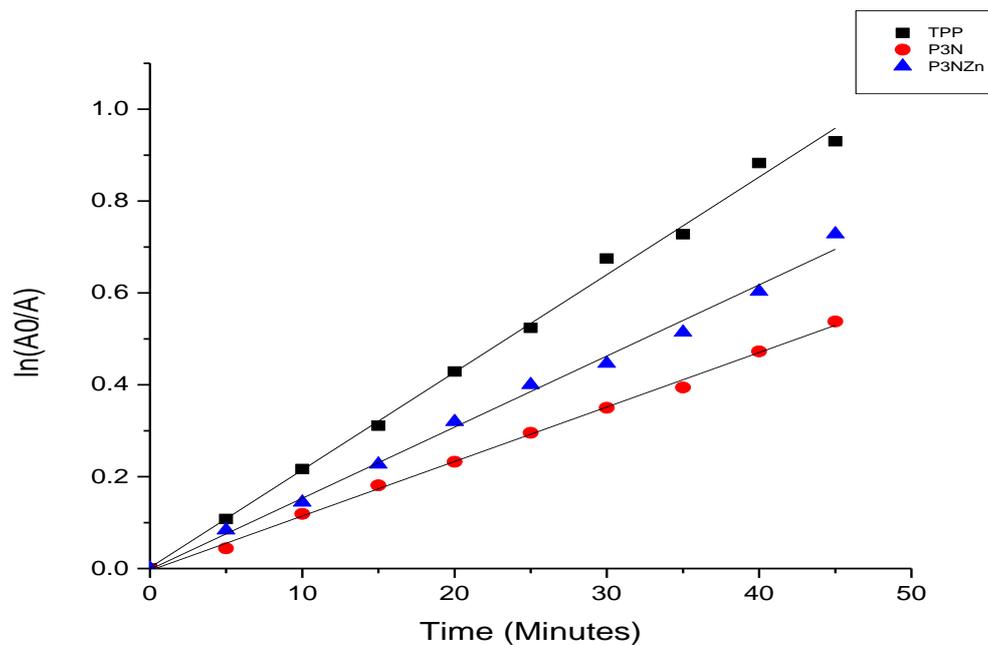


Table S2: Rate constant (k) for photooxidation of DMA in DMSO by target PSs and respective singlet oxygen quantum yield (Φ_{Δ}).

Compound	Rate constant (k) min^{-1}	Singlet oxygen quantum yield (Φ_{Δ})
P₃NZn	0.01546	0.73
P₃N	0.01186	0.66