Supporting information for

Novel metal free porphyrinic photosensitizers supported on solvent-induced Amberlyst-15 nanoparticles with a porous structure

Akram Heydari-turkmani, Saeed Zakavi* and Nasser Nikfarjam*

A Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran. E-mail: zakavi@iasbs.ac.ir.

S1: ¹H NMR, ¹³C NMR and UV-Vis spectral data of the used porphyrins

Figure S1: Experimental setup for the photooxidation reactions

S2: ¹³C NMR data of cyclooct-1-en-3-yl-hydroperoxide

S3: ¹³C NMR data of 2-cyclohexene-1-one

Figure S2: FT-IR spectra of H₂TPP, Amberlyst and H₂TPP@nanoAmberlyst

S1: ¹H NMR, ¹³C NMR and UV-Vis spectral data of the used porphyrins

H₂TPP. ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: -2.77 (2H, br, s, NH), 7.77-7.84 (8Hₘ and 4Hₚ, m), 8.26-8.27 (8Hₗ, d), 8.90 (8Hₗ, s); ¹³C NMR (~100 MHz, CDCl₃, TMS), δ/ppm: 120.18 (Cₘeso), 142.20 (C₁), 134.60 (C₂, C₆), 126.73 (C₃, C₅), 127.75 (C₄), 131.5 (C₁), 129.22 (C₂, C₆), 133.90 (C₃), 141.48 (C₁), 21.37 (C₆); UV-vis in CH₂Cl₂, λₘₐₓ/nm (logε): 417 (5.79), 513 (4.58), 548 (4.38), 590 (4.30), 647 (4.29).

H₂T(2-Me)PP. ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: -2.59 (2H, br, s, NH), 7.54-7.74 (8Hₘ and 4Hₚ, m, meta and para-position relative to C atom attached to meso position), 7.99-8.11 (4Hₘ, m, ortho-position relative to C atom attached to meso position), 8.70 (8Hₗ, s), 2.01-2.11 (12Hₘeso, m); ¹³C NMR (~100 MHz, CDCl₃, TMS), δ/ppm: 118.82 (Cₘeso), 139.54 (C₁), 139.63 (C₂), 128.38 (C₃), 129.22 (C₄), 124.21 (C₅), 133.90 (C₆), 141.48 (C₁), 21.37 (C₆); UV-vis in CH₂Cl₂, λₘₐₓ/nm (logε): 416 (6.04), 512 (4.74), 545 (4.34), 589 (4.34), 645 (4.25).
**H$_2$T(2-Cl)PP.** $^1$H NMR (400 MHz, CDCl$_3$, TMS), δ/ppm: -2.62 (2H, br, s, NH), 7.66-7.87 (8H$_m$ and 4H$_p$, m, meta and para-position relative to C atom attached to meso position), 8.10-8.26 (4H$_o$, m, ortho-position relative to C atom attached to meso position), 8.72 (8H$_b$, s); $^{13}$C NMR (~100 MHz, CDCl$_3$, TMS), δ/ppm: 116.76 (C$_{meso}$), 137.10 (C$_1$), 136.94 (C$_2$), 129.01 (C$_3$), 129.93 (C$_4$), 125.32 (C$_5$), 135.52 (C$_6$), 140.50 (C$_a$), 135.39 (C$_b$); UV-vis in CH$_2$Cl$_2$, $\lambda_{max}$/nm (logε): 416 (5.64), 512 (4.47), 543 (4.07), 587 (4.15), 643 (3.96).

**H$_2$T(4-OMe)PP.** $^1$H NMR (400 MHz, CDCl$_3$, TMS), δ/ppm: -2.72 (2H, br, s, NH), 7.29-7.32 (8H$_m$, d), 8.15-8.17 (8H$_o$, d), 8.89 (8H$_b$, s), 4.13 (12H$_{Me}$, s); $^{13}$C NMR (~100MHz, CDCl$_3$, TMS), δ/ppm: 119.75 (C$_{meso}$), 134.67 (C$_1$), 135.62 (C$_2$, C$_6$), 112.20 (C$_3$, C$_5$), 159.39 (C$_4$), 131.34 (C$_b$), 55.61 (C$_{Me}$); UV-vis in CH$_2$Cl$_2$, $\lambda_{max}$/nm (logε): 421 (5.61), 517 (4.32), 555 (4.22), 593 (4.06), 651 (4.11).

**Figure S1:** Experimental setup for the photooxidation reactions

**S2:** $^{13}$C NMR data of cyclooct-1-en-3-yl-hydroperoxide

**Cyclooct-1-en-3-yl-hydroperoxide.** $^{13}$C NMR (400 MHz, CDCl$_3$, TMS), δ/ppm: 32.8 (C$_4$), 26.1 (C$_5$), 26.3 (C$_6$), 23.7 (C$_7$), 28.4 (C$_8$), 129.6 (C$_{unsat}$), 131.7 (C$_{unsat}$), 82.8 (COOH).
The $^{13}$C NMR data of cyclooct-1-en-3-yl-hydroperoxide as the sole product is consistent with the previously reported data [1,2].

![Diagram of cyclooct-1-en-3-yl-hydroperoxide]

**S3:** $^{13}$C NMR data of 2-cyclohexene-1-one

**2-cyclohexene-1-one.$^{13}$C NMR (400 MHz, CDCl$_3$, TMS), $\delta$/ppm: 26.3 (C$_4$), 22.7 (C$_5$), 37.9 (C$_6$), 129.9 (C$_{unsat}$), 150.3 (C$_{unsat}$), 199.2 (C=O).**

![Diagram of 2-cyclohexene-1-one]
Figure S2: FT-IR spectra of H$_2$TPP, Amberlyst and H$_2$TPP@nanoAmberlyst

References