Electronic Supplementary Information
for
Kinetic and mechanistic aspects of solid state, nanostructured porphyrin diacid
photosensitizers in photooxidation of sulfides

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S1: \(^1\)H NMR, \(^{13}\)C NMR and UV-Vis spectral data of the used porphyrins

**H\(_2\)TTPP.** \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS), δ/ppm: -2.77 (2H, br, s, NH), 7.77-7.84 (8H\(_m\) and 4H\(_p,m\)), 8.26-8.27 (8H\(_o\), d), 8.90 (8H\(_p\), s); \(^{13}\)C NMR (~100 MHz, CDCl\(_3\), TMS), δ/ppm: 120.18 (C\(_{meso}\)), 142.20 (C\(_1\)), 134.60 (C\(_2\), C\(_6\)), 126.73 (C\(_3\), C\(_5\)), 127.75 (C\(_4\)), 131.5 (C\(_β\)); UV-vis in CH\(_2\)Cl\(_2\), \(λ_{max}/\text{nm (log}ε)\): 417 (5.79), 513 (4.58), 548 (4.38), 590 (4.30), 647 (4.29).

**H\(_2\)T(2-Me)PP.** \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS), δ/ppm: -2.59 (2H, br, s, NH), 7.54-7.74 (8H\(_m\) and 4H\(_p,m\), meta and para position relative to C atom attached to meso position), 7.99-8.11 (4H\(_o\), m, ortho-position relative to C atom attached to meso position), 8.70 (8H\(_β\), s), 2.01-2.11 (12H Me, m); \(^{13}\)C NMR (~100 MHz, CDCl\(_3\), TMS), δ/ppm: 118.82 (C\(_{meso}\)), 139.54 (C\(_1\)), 139.63 (C\(_2\)), 128.38 (C\(_3\)), 129.22 (C\(_4\)), 124.21 (C\(_5\)), 133.90 (C\(_6\)), 141.48 (C\(_α\)), 129.22 (C\(_β\)), 21.37 (C Me); UV-vis in CH\(_2\)Cl\(_2\), \(λ_{max}/\text{nm (log}ε)\): 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\(_β\), 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\(_α\)), 135.39 (C\(_β\)); UV-vis in CH\(_2\)Cl\(_2\), \(λ_{max}/\text{nm (log}ε)\): 416 (5.64), 512 (4.47), 543 (4.07), 587 (4.15), 643 (3.96).

**H\(_2\)T(4-Cl)PP.** \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS), δ/ppm: -2.83 (2H, br, s, NH), 7.77-7.79 (8H\(_m\), d), 8.15-8.17 (8H\(_o\), d), 8.87(8H\(_β\), s); \(^{13}\)C NMR (~100 MHz, CDCl\(_3\), TMS), δ/ppm: 119.01 (C\(_{meso}\)), 140.37 (C\(_1\)), 135.52 (C\(_2\), C\(_6\)), 127.07 (C\(_3\), C\(_5\)), 134.41(C\(_4\)), 131.64 (C\(_β\)); UV-vis in CH\(_2\)Cl\(_2\), \(λ_{max}/\text{nm (log}ε)\): 418 (5.79), 513 (4.52), 547 (4.25), 590 (4.16), 647 (4.10).

**H\(_2\)T(4-OMe)PP.** \(^1\)H NMR (400 Hz, 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\(_β\), 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\(_β\)), 55.61 (C\(_Me\)); UV-vis in CH\(_2\)Cl\(_2\), \(λ_{max}/\text{nm (log}ε)\): 421 (5.61), 517 (4.32), 555 (4.22), 593 (4.06), 651 (4.11).
**H\textsubscript{2}T(4-Me)PP.** \(^{1}\)H NMR (400 MHz, CDCl\(_3\), TMS), \(\delta/ppm:\) -2.76 (2H, br, s, NH), 7.55-7.58 (8H\_m, d), 8.09-8.12 (8H\_o, d), 8.86(8H\_β, s), 2.65 (12H\_Me, s); \(^{13}\)C NMR (~100 MHz, CDCl\(_3\), TMS), \(\delta/ppm:\) 120.47 (C\textsubscript{meso}), 139.73 (C\_1), 134.92 (C\_2, C\_6), 127.81 (C\_3, C\_5), 137.71 (C\_4), 131.37 (C\_β), 21.57 (C\_Me); UV-vis in CH\(_2\)Cl\(_2\), \(\lambda_{max}/nm\) (log\(\varepsilon\)): 418 (5.89), 516 (4.54), 551 (4.34), 590(4.18), 647 (4.20).

**H\textsubscript{4}TPP(HSO\textsubscript{4})\textsubscript{2}.** \(^{1}\)H NMR (400 MHz, CDCl\(_3\), TMS), \(\delta/ppm:\) 7.984-8.074 (8H\_m and 4H\_p, m), 8.626-8.663 (8H\_o, m), 8.626-8.663 (8H\_β, m), no signal was observed for the NH protons at 20 \(^\circ\)C.; \(^{13}\)C NMR (400MHz, CDCl\(_3\), TMS), \(\delta/ppm:\) 122.63 (C\textsubscript{meso}), 139.93 (C\_1), 139.05 (C\_2, C\_6), 128.12 (C\_3, C\_5), 130.01 (C\_4), 146.05 (C\_α), 128.40(C\_β); UV-vis in CH\(_2\)Cl\(_2\), \(\lambda_{max}/nm\) (log\(\varepsilon\)): 445 (5.70), 611 (3.43), 662 (3.77).

**S2.** Experimental setup for the photooxidation reactions

![Experimental setup](image)

**S3: Procedures for the oxidation of different sulfides and characterization of the oxidation products**

**Methyl phenyl sulfoxide:** Methyl phenyl sulfide (409.20 mg, 3.3 mmol) was performed according to the general procedure using H\textsubscript{2}TPP@nanoAmb (0.66 \(\times\) 10\(^{-3}\) mmol). Crude material
was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Methyl phenyl sulfoxide; yield: 92%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta=$ 7.56–7.38 (m, 5H), 2.61 (s, 3H).

**Ethyl phenyl sulfoxide:** Ethyl phenyl sulfide (465.18 mg, 3.3 mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Ethyl phenyl sulfoxide; yield: 97%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta=$ 7.60–7.45 (m, 4H), 2.91-2.82 (m, 1H), 2.77-2.68 (m, 1H), 1.15 (t, 3H).
4-Chlorophenyl methyl sulfoxide: 4-Chlorophenyl methyl sulfide (675.16 mg, 3.3 mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Chlorophenyl methyl sulfoxide; yield: 99%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.57-7.55 (m, 2H), 7.47-7.45 (m, 2H), 2.69 (s, 3H).
4-Methoxyphenyl methyl sulfoxide: 4-Methoxyphenyl methyl sulfide (564.83 mg, 3.3mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Methoxy phenyl sulfoxide; yield: 95%. $^1$H NMR (400 MHz, CDCl$_3$): δ= 7.42 (d, 2H), 6.85 (d, 2H), 3.65 (s,3H), 2.51 (s,3H).
4-Cyanophenyl methyl sulfoxide: 4-Cyano phenyl methyl sulfide (492.36 mg, 3.3 mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Cyanophenyl methyl sulfoxide; yield: 93%. $^1$H NMR (400 MHz, CDCl$_3$): δ= 7.82-7.80 (m, 2H), 7.75-7.73 (m, 2H), 2.74 (s, 3H).
1-methyl 4- methyl phenyl sulfoxide: 1-methyl 4- methyl phenyl sulfide (468.47 mg, 3.3 mmol) was performed according to the general procedure using H₂TPP@nanoAmb (0.66 × 10⁻³ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 1-methyl 4- methyl phenyl sulfoxide; yield: 99%. ¹H NMR (400 MHz, CDCl₃): δ= 7.46-7.44 (d, 2H), 7.24-7.22 (d, 2H), 2.63 (s, 3H), 2.33 (s, 3H).
4-Flourophenyl methyl sulfoxide: 4-Flourophenyl methyl sulfide (797.74 mg, 3.3 mmol) was performed according to the general procedure using H₂TPP@nanoAmb (0.66 x 10⁻³ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Flourophenyl methyl sulfoxide; yield: 99%. H NMR (400 MHz, CDCl₃): δ = 7.68-7.64 (m, 2H), 7.28-7.21 (m, 2H), 2.72 (s, 3H).
2-Chlorophenyl methyl sulfoxide: 2-Chlorophenyl methyl sulfide (675.16 mg, 3.3 mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 2-Chlorophenyl methyl sulfoxide; yield: 99%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.87-7.88 (d, 1H), 7.47-7.34 (m, 2H), 7.31-7.29 (m, 1H), 2.74 (s, 3H).
Diallyl sulfoxide: Dibutyl sulfide (335.40 mg, 3.3 mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Diallyl sulfoxide; yield: 97%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$= 5.94-5.83 (m, 2H), 5.46-5.35 (m, 4H), 3.55-3.37 (d, 4H).
**Dibutyl sulfoxide:** Dibutyl sulfide (405.54 mg, 3.3 mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Dibutyl sulfoxide; yield: 70%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.72-2.59 (m, 4H), 1.78-1.70 (m, 4H), 1.55-1.40 (m, 4H), 0.94 (t, 6H).
**Benzyl phenyl sulfoxide:** Benzyl phenyl sulfide (660.99 mg, 3.3 mmol) was performed according to the general procedure using H$_2$TPP@nanoAmb (0.66 × 10$^{-3}$ mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Benzyl phenyl sulfoxide; yield: 75%. $^1$H NMR (400 MHz, CDCl$_3$): δ= 7.43-7.7.22 (m, 8H), 6.97 (d, 2H), 4.07-4.04 (d, 1H), 3.99-3.96 (d, 1H).
S5. The change in the UV–vis spectrum of DPBF upon irradiation with a 10W red LED lamp in the presence of the immobilized porphyrins.
S6. Photooxidation of different sulfides by H$_2$TPP@nanoAmb.$^a$

<table>
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<tr>
<th>Substrate</th>
<th>Product</th>
<th>Conversion$^b$ <a href="%25">Selectivity</a></th>
<th>TON [TOF(h$^{-1}$)]</th>
</tr>
</thead>
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<td><img src="image2.png" alt="Product" /></td>
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<td>4950 [1650]</td>
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</tbody>
</table>

$^a$ The catalyst and substrate were used in 1:5000 molar ratio. A 20 W white LED lamp was used as the light source. $^b$ For a reaction time of 3 h in 1:1 acetonitrile (5 mL)/ water (5 mL) solvent mixture.