Supporting Information for

A novel porphyrinic photosensitizer based on the molecular complex of mesotetraphenylporphyrin with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone: Higher photocatalytic activity, photooxidative stability and solubility in non-chlorinated solvents

Aida G. Mojarrad and Saeed Zakavi*

Contents:

S1: ¹H NMR, ¹³C NMR and UV-Vis spectral data of meso-tetraphenylporphyrin, H₂TPP

S2: ¹H NMR, ¹³C NMR and UV-Vis spectral data the 1:2 molecular complex of meso-tetraphenylporphyrin with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), H₂TPP(DDQ)₂

S3: Experimental setup for the photooxidation reactions

- S4: ¹³C NMR data of Cyclooct-1-en-3-yl hydroperoxide
- S5: ¹³C NMR data of 2-cyclohexene-1-one

S6. ¹H NMR spectrum of H_2 TPP(DDQ)₂ in the NH region in CDCl₃ acidified by different amounts of acidic CDCl₃.

S7. Chemical actinometry measurements

S1: ¹H NMR, ¹³C NMR and UV-Vis spectral data of H₂TPP

H₂**TPP.** ¹H NMR (400 MHz, CDCl₃, 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_β, s); ¹³C NMR (400 MHz, CDCl₃, TMS), δ/ppm: 120.18 (C_{meso}), 142.20 (C₁), 134.60 (C₂, C₆), 126.73 (C₃, C₅), 127.75 (C₄), 131.5 (C_β); UV-vis in CH₂Cl₂, λ_{max} /nm (log ε): 417 (5.79), 513 (4.58), 548 (4.38), 590 (4.30), 645 (4.29).

S2: ¹H NMR, ¹³C NMR and UV-Vis spectral data the 1:2 molecular complex of mesotetraphenylporphyrin with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, H₂TPP(DDQ)₂

H₂TPP(DDQ)₂. ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: -0.36 (2H, br, s, NH), 8.61 (8H_β, s), 8.68 (8H_o, d), 7.99 (8H_m and 4H_p, m); ¹³C NMR (400 MHz, CDCl₃, TMS), δ/ppm: 145.96 (C_α), 128.95 (C_β), 123.44 (C_{meso}), 139.89 (C₁⁻), 138.87 (C₂⁻), 128.73 (C₃⁻), 130.51 (C₄⁻). UV-vis in CH₂Cl₂, λ_{max} /nm (log ε): 441 (4.78), 606 (3.75), 655 (4.23). The DDQ molecules of H₂TPP(DDQ)₂, ¹³C NMR (400 MHz, CDCl₃, TMS), δ/ppm: 171.81 (C₁), 172.07 (C₄), 143.33 (C₂, C₃), 135.39 (C₅), 87.99 (C₆), 165.43 (C₇), 112.23 (C₈).

S3: Experimental setup for the photooxidation reactions



S4: ¹³C NMR data of Cyclooct-1-en-3-yl hydroperoxide

Cyclooct-1-en-3-yl hydroperoxide. ¹³C NMR (400 MHz, CDCl₃, TMS), δ/ppm: 32.8 (C₄), 26.1 (C₅), 26.3 (C₆), 23.7 (C₇), 28.4 (C₈), 129.6 (C_{unsat}), 131.7 (C_{unsat}), 82.8 (COOH).

The ¹³C NMR data of Cyclooct-1-en-3-yl hydroperoxide as the sole product is consistent with the previously reported data^[1,2].



S5: ¹³C NMR data of 2-cyclohexene-1-one

2-cyclohexene-1-one. ¹³C NMR (400 MHz, CDCl₃, TMS), δ/ppm: 26.3 (C₄), 22.7 (C₅), 37.9 (C₆), 129.9 (C_{unsat}), 150.3 (C_{unsat}), 199.2 (C=O).

The ¹³C NMR data of 2-cyclohexene-1-one is in good agreement with that obtained for authentic sample.



S6. ¹H NMR spectrum of H_2 TPP(DDQ)₂ (spectrum no. 1) in the NH region in CDCl₃ acidified by different amounts of acidic CDCl₃ (2 to 8 spectra).



S7. Chemical actinometry measurements

The solid potassium ferrioxalate was prepared and recrystallized as described by Hatchard, et al.³ The preparation and manipulation of the ferrioxalate solution must be carried out in a darkroom, using a red light. Using the micro-version procedure⁴, a 0.15 M ferrioxalate solution was irradiated with a 10 or a 20 W blue LED lamp in the same geometry as the reaction system and the subsequent change in absorbance at 510 nm was monitored by UV-visible spectroscopy. It should be noted that all the measurements of the photon flux were performed at λ_{emis} = 468 nm. The effective quantum flux for 10 and 20 W red LED lamps with an approximately broad emission band at 633 nm, was measured using a lux meter sensor. In the case of the 150 W

metal halide lamp with emission bands at 365, 405, 436, 546, 579 nm, a series of liquid filter solutions were used to build a monochromatic light source at 436 nm; an aqueous solution containing potassium nitrite and potassium hydrogen phthalate to out λ < 400 nm, an aqueous solution of meso-tetra(4block sulfonatophenyl)porphyrin to filter the wavelength at ca. 405 nm and the brilliant blue R-250 as a useful dye to filter $\lambda \ge 500$ nm. With respect to the emission line at 436 nm transmitted after filtering, the measurement of the luminous flux per unit area (Lx) was carried out to calculate the rate of photon absorption.

The quantum yield of the photooxidation reactions illuminated by LED lamps and the metal halide lamp fitted with a liquid filter solution, was achieved based on the number of the reacted molecules divided by the number of photons absorbed per time unit⁵.

References

[1] R. D. Chambed, G. Sandford, A. Shah, Synth. Commun. **1996**, 26, 1861-1866.

[2] R. W. Denny, A. Nikon, Org. React., 1973, 20, 133-137.

[3] C. G. Hatchard, C. A. Parker, Proc. Roy. Soc. A. 1956, 235, 518.

[4] J. C. Manton, C. Long, J. G. Vos, M. T. Pryce, Dalton Trans. 2014, 43, 3576.

[5] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi in Handbook of Photochemistry, Ch. 12,

Taylor & Francis Group, LLC, 2006, p. 601.