Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

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

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Contents:

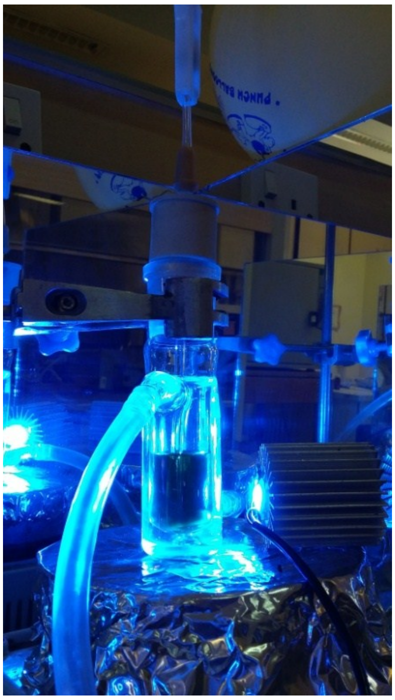
S1: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of H_2TPP

H_2TPP. ^{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_β, s); ^{13}C NMR (400 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_2Cl_2, λ_{max}/nm (log ε): 417 (5.79), 513 (4.58), 548 (4.38), 590 (4.30), 645 (4.29).

S2: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data the 1:2 molecular complex of meso-tetraphenylporphyrin with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, $H_2TPP(DDQ)_2$

$H_2TPP(DDQ)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 145.96 (C_α), 128.95 (C_β), 123.44 (C_{meso}), 139.89 ($C_{1□}$), 138.87 ($C_{2□}$), 128.73 ($C_{3□}$), 130.51 ($C_{4□}$). UV-vis in CH_2Cl_2, λ_{max}/nm (log ε): 441 (4.78), 606 (3.75), 655 (4.23). The DDQ molecules of $H_2TPP(DDQ)_2$, ^{13}C NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 171.81 (C_1), 172.07 (C_4), 143.33 (C_2, C_3), 135.39 (C_5), 87.99 (C_6), 165.43 (C_7), 112.23 (C_8).

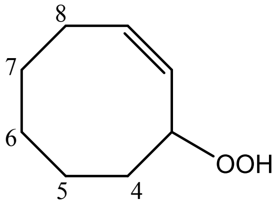
S3: Experimental setup for the photooxidation reactions



S4: ^{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).

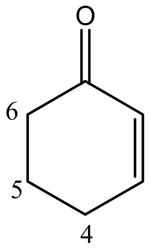
The ^{13}C NMR data of Cyclooct-1-en-3-yl hydroperoxide as the sole product is consistent with the previously reported data[1,2].



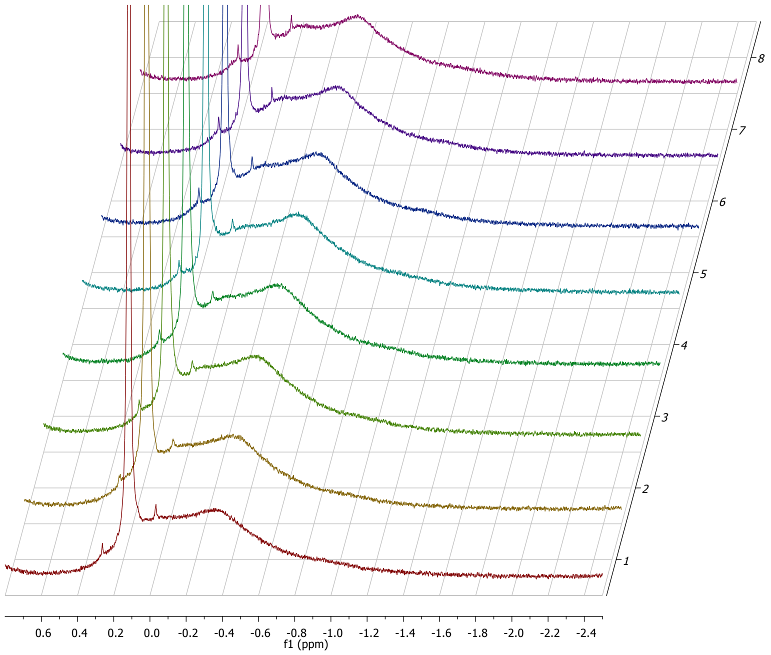
S5: ^{13}C NMR data of 2-cyclohexene-1-one

2-cyclohexene-1-one. ^{13}C NMR (400 MHz, $CDCl_3$, TMS), δ/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).

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



S6. ^{1}H NMR spectrum of $H_2TPP(DDQ)_2$ (spectrum no. 1) in the NH region in $CDCl_3$ acidified by different amounts of acidic $CDCl_3$ (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 procedure[4], 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 block out $\lambda < 400$ nm, an aqueous solution of meso-tetra(4-sulfonatophenyl)porphyrin to filter the wavelength at ca. 405 nm and the brilliant blue R-250 as a useful dye to filter $\lambda \geq 500$ 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 unit[5].

References

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[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.