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## Electronic supplementary information for:

# Photocatalytic oxidation of stilbene by self-assembled stacks of manganese porphyrins

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## Experimental Section:

### Materials

All chemicals were purchased from commercial sources, Sigma-Aldrich, Fluka, Fisher Chemical and J. T. Baker in their higher degree of purity and used as received. Dichloromethane was purified by distillation from calcium hydride and stored under argon. The cyclohexane used was of spectroscopic grade. Deuterated chloroform for NMR analyses was provided with TMS as a 0 ppm reference. Column chromatography was performed using ACROS silica gel (40 – 60  $\mu\text{m}$ ) and BioRad BioBeads SZ-1 were used for size-exclusion chromatography.

### Instrumentation

$^1\text{H}$  NMR spectra were recorded at room temperature on a Varian Inova400 spectrometer. Chemical shifts are reported in ppm vs. TMS.  $\text{CDCl}_3$  was used as solvent and internal standard ( $\delta = 7.27$  ppm). MALDI-ToF MS analyses were performed in reflector mode on a Bruker Biglex III spectrometer using a solution of dithranol (20 mg/ml in chloroform) as the matrix. Ultraviolet-Visible (UV-Vis) absorbance spectra were recorded on a Perkin-Elmer Lambda 2 spectrometer at ambient temperature. Dynamic light scattering (DLS) experiments were performed on a Malvern Zetasizer Nano S equipped with a He-Ne (633 nm, 4 mW) laser and an Avalanche photodiode detector at an angle of  $173^\circ$ . A Xenon lamp (L2274, Hamamatsu) was used as a light source with a switching type power supply (C2577, Hamamatsu).

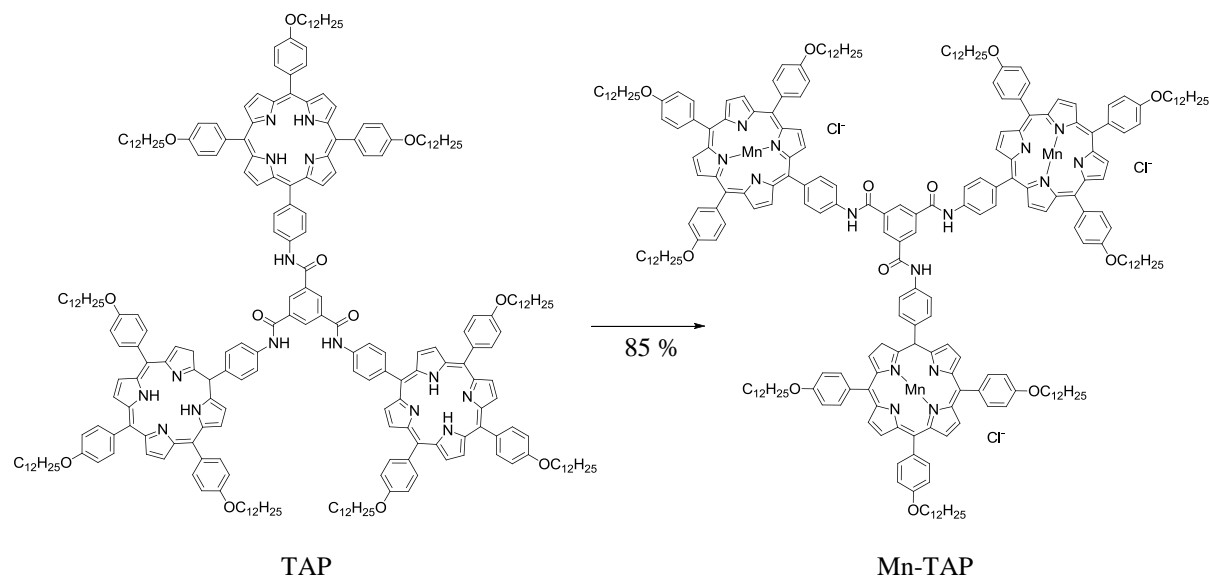
### General procedure for the catalytic epoxidation reactions using Mn-TAP

Mn-TAP (0.5 mg, 0.125  $\mu\text{mol}$ , 0.1 mol% with respect to *cis*-stilbene) and DABCO (0.75  $\mu\text{mol}$ , 2 equiv. with respect to Mn-porphyrin) were dissolved in a selected solvent (1 ml) at room temperature. After stirring the mixture for 1 hour, *cis*-stilbene (125  $\mu\text{mol}$ , 22  $\mu\text{l}$ ) and isobutyraldehyde (1.25 mmol, 57  $\mu\text{l}$ , 5 equiv. with respect to *cis*-stilbene) were added. The reaction was set up under the Xenon lamp with oxygen bubbling into the solution. An additional pump was used to keep the solvent volume constant. The catalytic reaction was followed in time by  $^1\text{H}$  NMR, taking samples after 10, 30

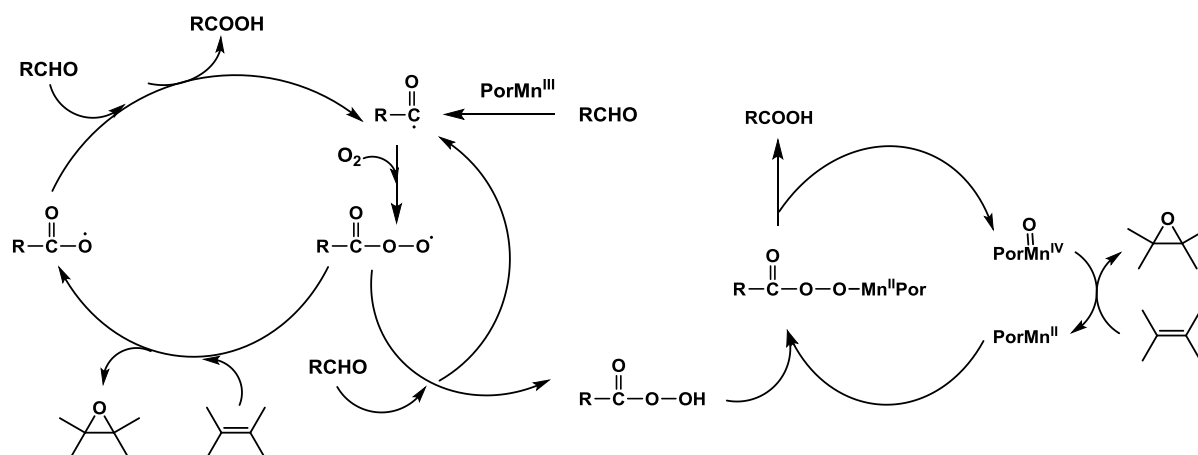
and 60 min. After evaporation of the solvent, mesitylene (0.03 mmol) was added as external standard in every sample, before analysis by  $^1\text{H}$  NMR. Yields were calculated with the integral values of proton signals in the NMR spectra of both the substrate and products relative to those of the mesitylene standard.

### Synthesis of Mn-TAP

Mn-TAP was synthesised according to Scheme 1. TAP was synthesised according to literature procedure.<sup>S1</sup> TAP (70 mg, 0.018 mmol) and  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (44.5 mg, 0.18 mmol) were dissolved in 65 ml of DMF. The mixture was refluxed overnight. After cooling and evaporation of the solvent, the residue was dissolved in 500 ml of  $\text{CH}_2\text{Cl}_2$ . After washing this solution with water, 500 ml of brine was added and the mixture was stirred for 3 h. The organic phase was separated, extracted 3 times with water, and dried with  $\text{MgSO}_4$ . After filtration and evaporation of the solvent, the product was purified by size exclusion column chromatography (eluent: toluene). Yield 85% of Mn-TAP as a green solid. UV-Vis ( $\text{CHCl}_3$ ):  $\lambda = 407, 483, 589, 628$  nm, Maldi-TOF:  $M^+ = 3934$  ( $-\text{Cl}^-$ , 3897 ( $-2 \text{Cl}^-$ ), 3861 ( $-3 \text{Cl}^-$ ). Accurate mass: Calculated for  $(\text{C}_{247}^{13}\text{C}_2\text{H}_{303}\text{N}_{15}\text{O}_{12}^{55}\text{Mn}_3)^{3+}$  (main peak): 1287.3918, measured: 1287.3951.

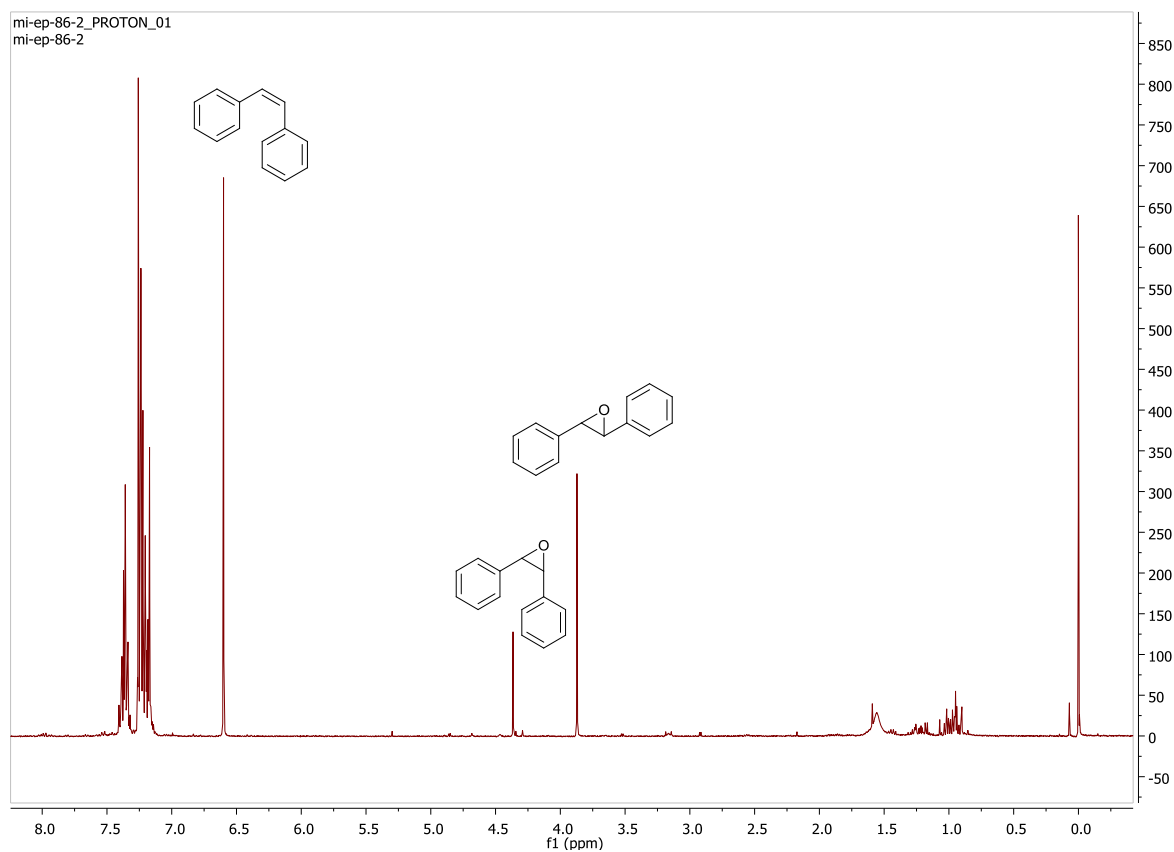


Scheme 1: Insertion of manganese into porphyrin trimer TAP.

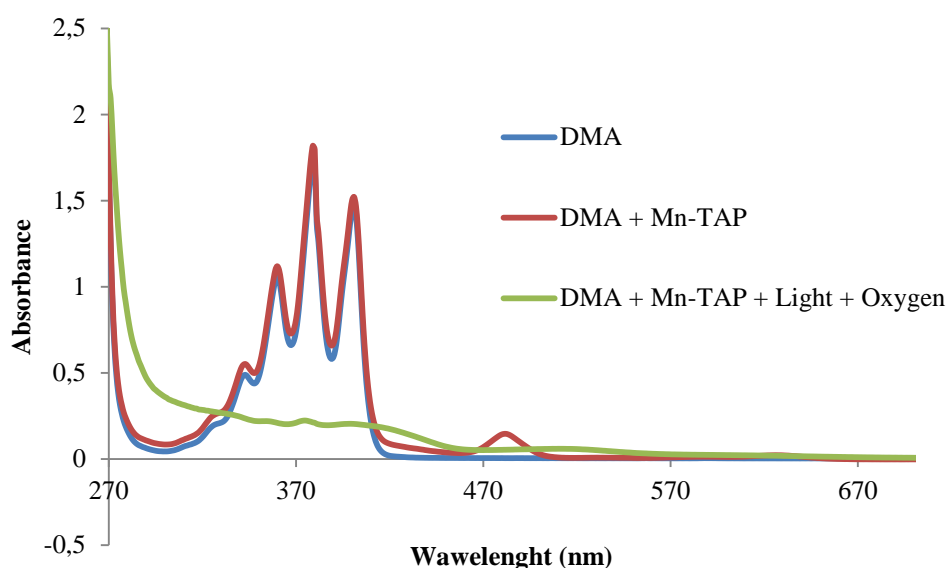


**Figure S1:** Proposed mechanism of olefin epoxidation catalysed by manganese porphyrins in the presence of O<sub>2</sub> and an aldehyde (taken from ref. S2).

According to the mechanism previously described in the literature using O<sub>2</sub> and an aldehyde as co-reductant,<sup>S2</sup> epoxide synthesis occurs after an induction period. The Mn(III) porphyrin and isobutyraldehyde are activated by light and an acyl radical is generated. In the presence of O<sub>2</sub>, this radical reacts to an acylperoxy radical, which is in principle capable of epoxidising the olefin directly. It is however much more favourable for the acylperoxy radical to react with a Mn(II) porphyrin. The resulting Mn(IV)oxo species is able to perform a stereoselective epoxidation of the olefin.



**Figure S2:** <sup>1</sup>H-NMR spectrum of a sample of the crude reaction mixture of a catalytic oxidation of *cis*-stilbene after 30 min under the standard conditions, using Mn-TAP as the catalyst. Signals located between 1.7 and 0.8 ppm belong to the catalyst.

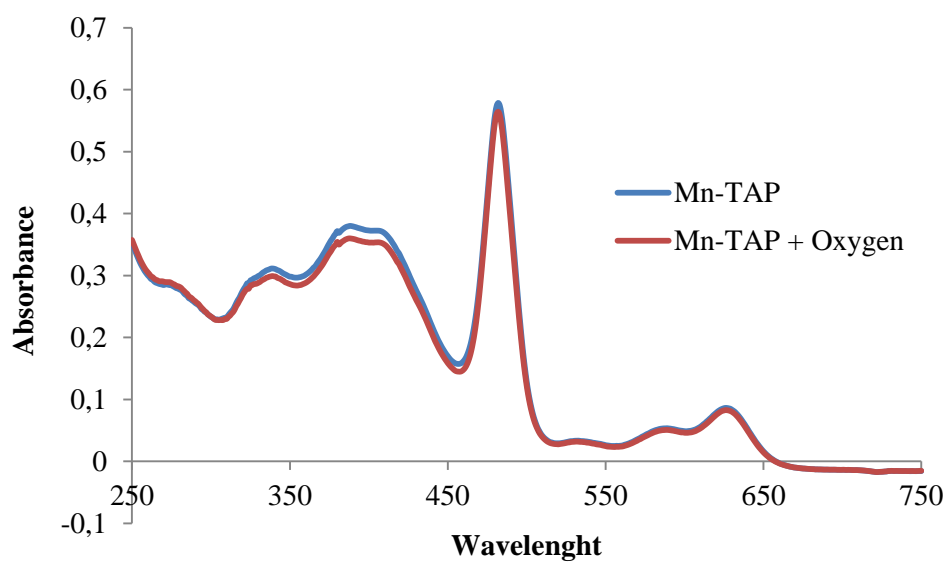


**Figure S3:** UV-Vis spectra of a dichloromethane solution of Mn-TAP and DMA under  $O_2$  atmosphere and intense light. The spectra show the loss of all bands belonging to DMA after 15 min exposure to oxygen atmosphere under intense light, due to the oxidation of DMA by  $^1O_2$  generated in the mixture.

The presence of oxygen radicals can be probed with the help of 9,10-dimethylanthracene (DMA).<sup>S3</sup> A reduction in the intensity of bands between 300 and 400 nm in the UV-visible absorption spectra of DMA, should be observed in the presence of  $^1O_2$ . Following this approach, Mn-TAP ( $10^{-5}$  M) and (DMA  $10^{-3}$  M) were dissolved in dichloromethane in an oxygen atmosphere, the mixture was irradiated with a Xenon lamp for 1 min. Substantial changes in the UV-vis absorption spectra of the mixture before and after the exposure to light and oxygen were observed (Fig. S2). After the exposure the spectra showed the loss of all peaks belonging to DMA, suggesting that  $^1O_2$  is involved in the oxidation process.

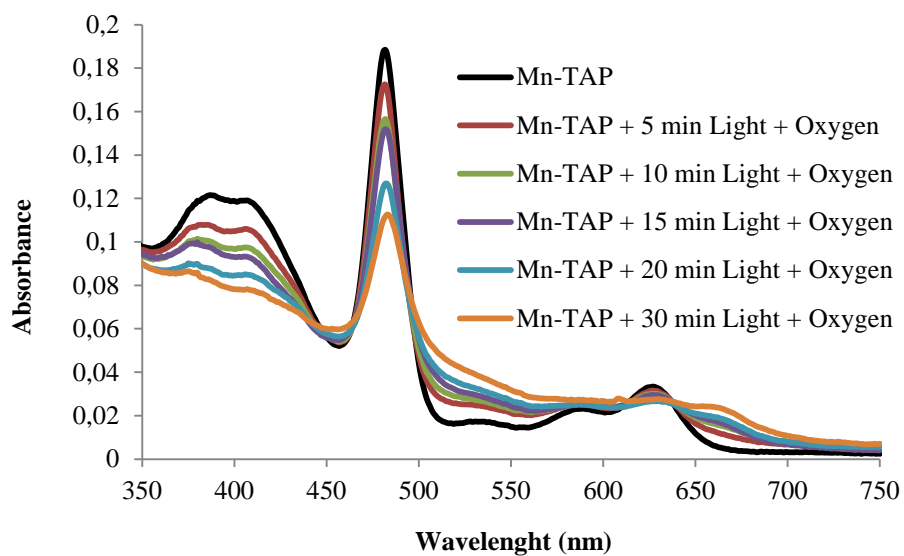
**Table S1:** DLS measurements of assembled Mn-TAP in cyclohexane and CH<sub>2</sub>Cl<sub>2</sub>. Three measurements were performed for each sample. The concentration of Mn-TAP was in all cases 0.125 mM. All samples were centrifuged using a ScanSpeed 1730R equipment (14730 rpm, 5 min.) before every analysis. The polydispersity index was high in all cases indicating a mixture of different lengths of stacks. The number of equiv. of DABCO is with respect to Mn-porphyrin

Equiv. DABCO	Stirring	Cyclohexane	CH <sub>2</sub> Cl <sub>2</sub>
		Z-average (nm)	Z-average (nm)
0	1h	$3.9 \times 10^2$	No particles
1	1h	$3.3 \times 10^2$	No particles
2	1h	$4.0 \times 10^2$	No particles
5	1h	$2.8 \times 10^2$	
10	1h	$3.0 \times 10^2$	
10	18h	$3.0 \times 10^2$	



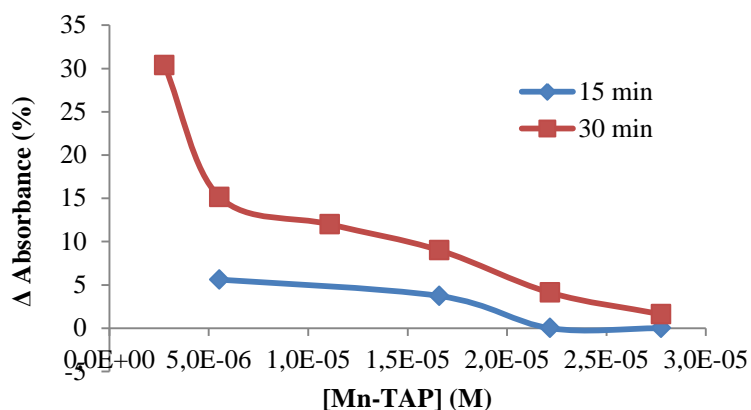
**Figure S4:** UV-vis spectra revealing the effect of O<sub>2</sub> on Mn-TAP in the dark at room temperature. Oxygen was bubbled into a Mn-TAP solution in CH<sub>2</sub>Cl<sub>2</sub> for 2 hours in the dark.



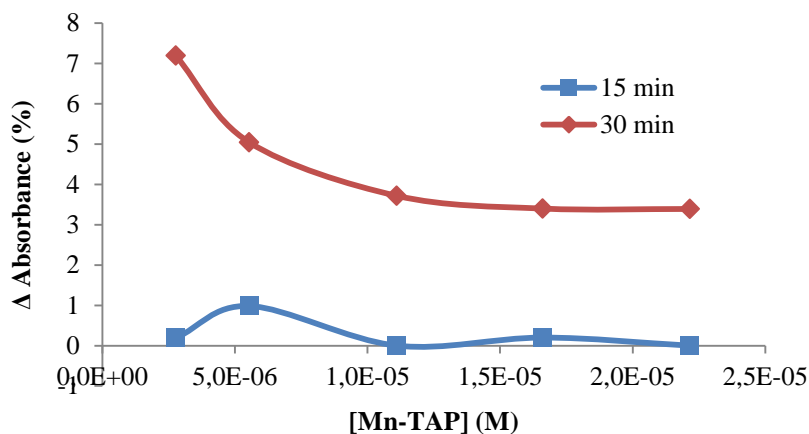


**Figure S5:** UV-Vis spectra of Mn-TAP in CH<sub>2</sub>Cl<sub>2</sub> after incubation with intense light and O<sub>2</sub> at different time intervals at room temperature, showing the gradual decomposition of the catalyst.

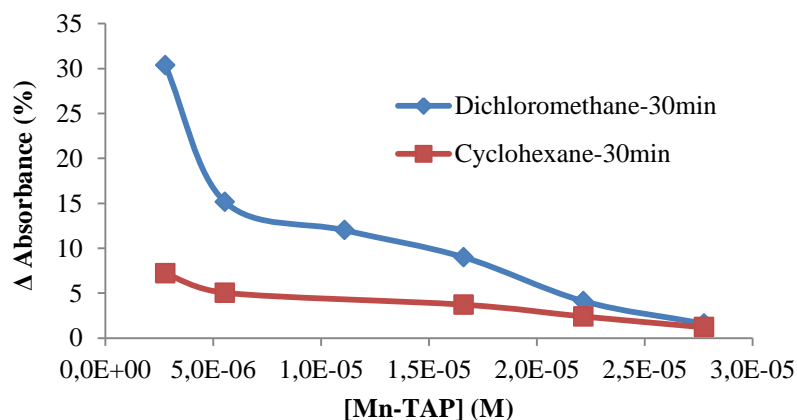
### Dichloromethane



### Cyclohexane

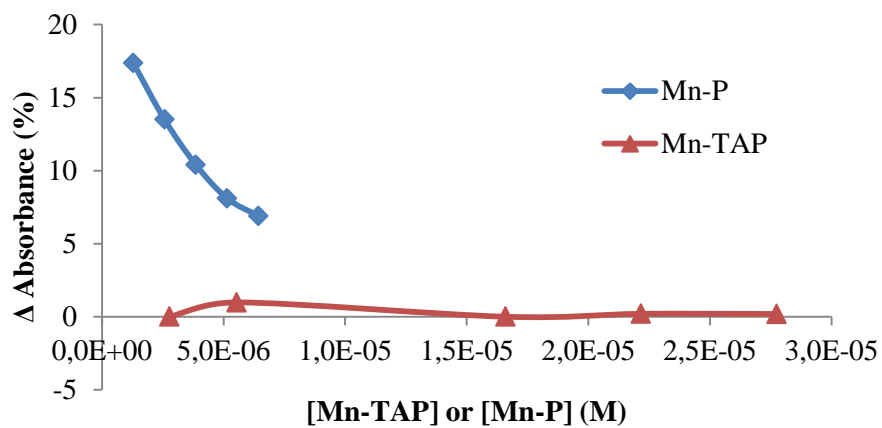


### Comparison Dichloromethane-Cyclohexane



**Figure S6:** Degradation of Mn-TAP dissolved in CH<sub>2</sub>Cl<sub>2</sub> or cyclohexane under intense light and O<sub>2</sub> at room temperature. The Mn-TAP decomposition was calculated analysing the decrease in the Soret Band in UV-Vis spectrum after 15 min or 30 min.

$$\Delta \text{ Absorbance (\%)} = \frac{([\text{Absorbance (Soret band)}]_{0\text{min}} - [\text{Absorbance (Soret band)}]_{30\text{min}}) * 100}{[\text{Absorbance (Soret band)}]_{0\text{min}}}$$

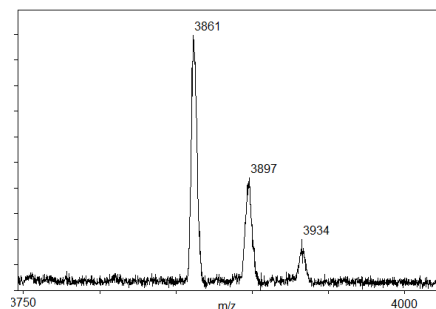


**Figure S7:** Comparative study of the decomposition of Mn-TAP and Mn-P dissolved in cyclohexane under intense light and O<sub>2</sub> at room temperature.

A)

Relative conductivity	
$\Lambda_{\text{MnTAP}}/\Lambda_{\text{TAP}}$	1.17
$\Lambda_{\text{MnP}}/\Lambda_{\text{P}}$	1.61
$\Lambda_{\text{MnTAP}}/\Lambda_{\text{DMF}}$	20.08
$\Lambda_{\text{MnP}}/\Lambda_{\text{DMF}}$	4.02

B)



**Figure S8** A) Conductivity measurements of Mn-TAP and Mn-P, relative to the conductivity of their free base porphyrin analogues TAP and P, in DMF solution. The concentration of the catalysts was in all cases  $3 \times 10^{-5}$  M and the conductivities were measured at 25°C. B) MALDI-TOF spectrum of Mn-TAP and the assignment of each peak.

The conductivity measurements showed that manganese porphyrins (Mn-TAP and Mn-P) have a similar conductivity as their free base porphyrin analogues. Thus, the presence of the MnCl centre does not have a remarkable effect on the conductivity values. Both catalysts show a slightly higher conductivity than the pure solvent (DMF). Based on these results, we propose that in solution the chloride atoms are strongly coordinated to the manganese centres. Coordination of the chloride atoms is further supported by the MALDI-TOF spectrum of Mn-TAP, which shows three different peaks belonging to  $M^+ = 3934$  (-Cl), 3897 (-2Cl) and 3861 (-3Cl).

### Supporting reference

<sup>S1</sup>R. van Hameren, P. Schön, A. M. van Buul, J. Hoogboom, S. V Lazarenko, J. W. Gerritsen, H. Engelkamp, P. C. M. Christianen, H. A. Heus, J. C. Maan, T. Rasing, S. Speller, A. E. Rowan, J. A. A. W. Elemans, and R. J. M. Nolte, *Science*, 2006, **314**, 1433–1436.

<sup>S2</sup>X. Zhou and H. Ji, *Chem. Eng. J.*, 2010, **156**, 411–417.

<sup>S3</sup>N. J. In. Turro, *Modern Molecular Photochemistry; Benjamin / Cummings: Menlo Park, CA*, 1978, 579–611.