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# SUPPLEMENTARY INFORMATION

Evidence for photosensitised hydrogen production from water in the absence of precious metals, redox-mediators and co-catalysts

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# Metallation of H<sub>2</sub>(TPPS)<sup>4-</sup> to form the ZnP starting complex:



The water soluble free-base porphyrin ligand 5,10,15,20-Tetrakis-(4-sulfonatophenyl)-21*H*,23*H*-porphin (Sigma-Aldrich) was dissolved in 100 mL of methanol and a 10-fold excess of zinc acetate (99.99%, Sigma-Aldrich) was added. The mixture was refluxed at 40 °C overnight and total conversion to the metallated product was confirmed by monitoring the characteristic UV-vis signals. Solvent was evaporated. No further work-up was done according to the literature procedure,<sup>[1],</sup> in which it was stated that remaining zinc acetate would not negatively influence photoreactions of the anionic Zn(TPPS)<sup>4-</sup> complex (or ZnP) present in solution.

<sup>1</sup>**H-NMR (300 MHz, D<sub>2</sub>O):** 8.97 (s, 8H, β-pyrrole protons), 8.25 (AB quartet, 16H,  $\Delta v_{AB}$  = 51.3 Hz,  $J_{AB}$  = 8.5 Hz, phenyl protons) 4.78 (solvent peak), 2.15 (s, methyl protons of remaining acetate)

[1] Y. Amao, T. Watanabe, Appl. Catal. B: Environ. 2009, 86, 109-113.

#### Spectral variations upon photolysis:

The following experiments were performed as specified in the experimental part and Table 1 of the main paper (3 mL of aqueous solution, inert gas saturation, sealed 1 cm quartz cuvettes, HBO-lamp with longpass filters) unless otherwise stated. Donors (TEOA, TEA, Na<sub>2</sub>SO<sub>3</sub>) and buffer ingredients were obtained from Sigma-Aldrich and used as received.

#### Zn(TPPS)<sup>4-</sup> in water: Generation of photolysis products with a phlorin-type spectrum:

• ZnP (1  $\mu$ mol) in pure H<sub>2</sub>O



Figure S1: Full UV-vis spectra for the black solid curve displayed in Figure 2.

#### Zn(TPPS)<sup>4-</sup> in 10% aqueous TEOA solution, pH 7:

ZnP (2.5 µmol) in 10% TEOA aqueous solution. pH adjusted to 7



**Figure S2:** Full UV-vis spectra for the red dotted/dashed curve in Figure 2 as well as for long-term photolysis data from Table 1, Entry 1.

# Zn(TPPS)<sup>₄-</sup> in 10% TEOA solution, pH 11.5.

• ZnP (2.7 µmol) in 10% TEOA aqueous solution. pH unadjusted (measured as 11.5)



Figure S3: Full UV-vis spectra for Table 1, Entry 2.

# *Zn*(*TPPS*)<sup>4-</sup> *in sulfite solution, high dye concentration:*

 ZnP (5.7 µmol) in 0.6 mmol Na<sub>2</sub>SO<sub>3</sub> aqueous solution. pH unadjusted (measured value 8.0)



Figure S4: Full UV/vis spectra for Table 1, Entry 3.

\* Note that in Fig. S4 the spectral regions marked with an asterisk (corresponding to very low light transmission caused by the sample) artifacts with smaller absorption values than physically meaningful are plotted!

### Zn(TPPS)<sup>4-</sup> in sulfite solution, low dye concentration

ZnP (0.2 μmol) in 2.4 mmol Na<sub>2</sub>SO<sub>3</sub> aqueous solution. pH unadjusted, measured as pH= 8. This reaction (Table 1, Entry 4) was performed in a round-bottom flask and no UV/vis spectra were measured for it.

# Zn(TPPS)<sup>₄</sup> in 2% TEA solution, pH 10:

 ZnP (0.7 µmol) in 2% TEA aqueous solution. Buffered with phosphate buffer, sample adjusted to pH =10



Figure S5: Full UV/vis spectra for Table 1, Entry 5.

### Zn(TPPS)<sup>4-</sup> in 2% TEA solution, pH 10:

 ZnP (0.6 μmol) in 2% TEA aqueous solution. Buffered with phosphate buffer, adjusted to pH =10



Figure S6: Full UV/vis spectra for Figure 5.

# Photogeneration of hydroporphyrins followed by <sup>1</sup>H-NMR spectroscopy:



**Figure S7:** 300 MHz <sup>1</sup>H- NMR spectrum of the anionic Zn(TPPS)<sup>4-</sup> complex (or **ZnP**) in D<sub>2</sub>O at 298K.



**Figure S9:** Absorption spectral changes observed upon visible-light photoreduction of **ZnP** by triethanolamine in D<sub>2</sub>O at 298 K. Irradiation carried out within a NMR-tube in the presence of air. Reaction conditions: Initial zinc porphyrin concentration  $1.3 \times 10^{-4}$  M, solvent 0.5 mL D<sub>2</sub>O/TEOA (10%), 100W Xe-lamp equipped with a water IR-filter and a longpass cutoff-filter > 400 nm. See also Fig. S3!

The spectral changes shown in Fig. S9 are consistent with the photochemical conversion of **ZnP** into the pyrrole-ring reduced hydroporhyrin zinc chlorin **ZnC**. These photoinduced variations of the zinc porphyrin complex are accompanied by diagnostic changes of the <sup>1</sup>H-NMR singals of the porphyrin ligand  $\beta$ -pyrrole and phenyl group protons (Fig. S10) in reasonable agreement with the effects reported for free-base tetraarylporphyrins photolyzed in organic solvents [2].

[2] Y. Harel, J. Manassen, J. Am. Chem. Soc. 1978, 100, 6228-6234.



**Figure S10:** Changes of the  $\beta$ -pyrrole proton signals in the <sup>1</sup>H-NMR spectrum of **ZnP** upon photochemical reduction in the presence of TEOA (t= 0, 10, and 40 min irradiation times). Sample and reaction conditions are identical with the data shown in Fig. S9 above! **Inset:** Rising new proton NMR signals that can be assigned to the hydrogenated  $\beta$ -positions of reduced pyrrole rings [2].