

Supplementary Information

Characterization of a Non-Aggregating Silicon(IV) Phthalocyanine in Aqueous Solution: Toward Red-Light-Driven Photocatalysis based on Earth-Abundant Materials

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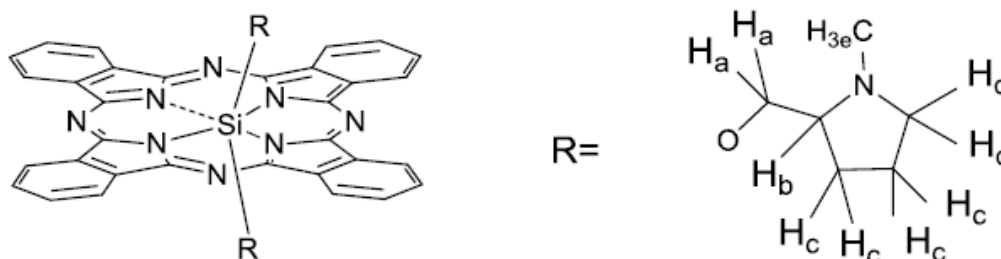
Materials and Methods:

All chemicals and solvents were of reagent grade quality and were obtained from commercial suppliers. 1-Methylpyrrolidin-2-yl-methanol and dichloro-phthalocyaninato-silicon(IV) were purchased from Aldrich. For NMR analysis, a Bruker Biospin 200 MHz spectrometer was used. UV-Vis-spectra were recorded with a Varian Cary 50 diode array spectrophotometer. All luminescence measurements were carried out at room temperature using a Horiba JobinYvon Fluorolog-3 spectrofluorometer equipped with two doublegrating monochromators, a R928P photomultiplier, and an FL-1040 phosphorimeter. All emission spectra were corrected for wavelength-dependent instrument and detector response and verified by collecting the corresponding excitation spectra. Emission quantum yields were measured relative to zinc phthalocyanine in DMSO as a standard ($\Phi_F = 0.20$) [1] and corrected for solvent refractive index differences. Luminescence lifetime data were obtained by time-correlated single photon counting (TCSPC) experiments on a PicoQuant lifetime fluorescence spectrophotometer (FluoTime 100) equipped with a TimeHarp 200 PCI-board and a pulsed diode laser driver at 10 MHz repetition rate. A violet picosecond pulsed diode laser (PicoQuant PDL 800-B) with an excitation wavelength of 400 nm was used as the light-source. Laser flash photolysis experiments were conducted on an LKS-80 kinetic spectrometer (Applied Photophysics) equipped with a calibrated high sensitivity thermopile head power sensor (Ophir Photonics). Samples were irradiated with 355 nm light from a Nd:YAG laser (Quantel Brilliant). Data were acquired and analyzed with the Applied Photophysics software. All continuous-wave irradiation experiments with red light were carried out using an ALUSTAR 3W high-power LED-Module with a maximum at 623 nm. Photolysis with monochromatic light was carried out with an Ushio Xe/Hg UXM-200H (200W) lamp equipped with an AMKO Multimode4-AT grating monochromator.

Synthesis of the **SiPc** complex was carried out according to published procedures as described below [2]:

Bis[(N-methyl-pyrrolidin-2-yl)methoxy]-phthalocyaninato-silicon(IV):

A mixture of unsubstituted dichloro-phthalocyaninato-silicon (50 mg, 0.0817 mmol), NaH (0.735 mmol, 17.6 mg) and (1-methylpyrrolidin-2-yl)methanol (28.21 mg, 0.245 mmol) in dry toluene (25 mL) was refluxed for 6 hours under N₂. After the reaction mixture was centrifuged, the filtrate was evaporated and the residue was washed with n-hexane (3x30 mL) and dried *in vacuo*. The crude product was subjected to aluminum oxide column chromatography and was purified by using dichloromethane/methanol (10/1) as eluent.

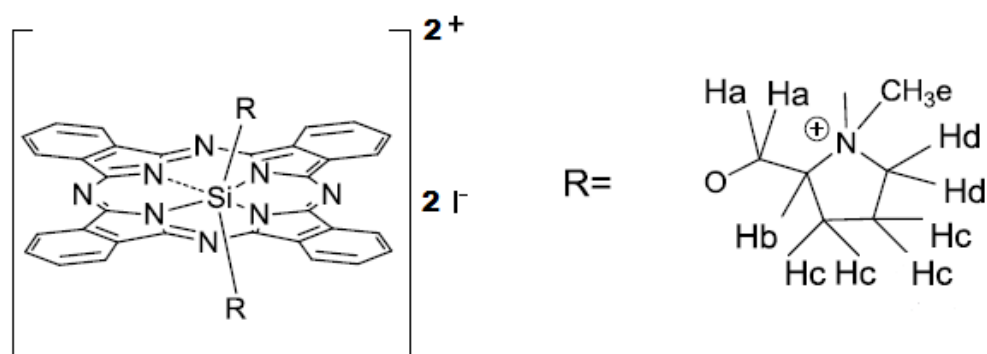


Yield: 38 mg (61.2 %). IR $\nu_{\max}/(\text{cm}^{-1})$: 2773; 1611; 1519; 1471; 1426; 1333; 1287; 1163; 1119; 1076; 985; 908; 757. ¹H NMR (CDCl₃): -2.29-(-1.85) (d,4H,H_a); (-0.54)- (-0.77) (m,2H,H_b); 1.26-1.27 (m,8H,H_c); 1.62-2.07 (t,4H,H_d); 2.08-3.20 (s,4H,H_e); 8.05-8.07 (m,8H,H_β); 9.33-9.35 (m,8H,H_α).

Found for C₄₄H₄₀N₁₀O₂Si (%): C, 69.10; H, 5.54; N, 17.39. Calculated (%): C,68.73; H, 5.24; N, 17.01.

Bis[(N,N-dimethyl-pyrrolidinium-2-yl)-methoxy]-phthalocyaninato-silicon(IV), (SiPc):

Quaternization of the neutral compound bis[(N-methyl-pyrrolidin-2-yl)methoxy]-phthalocyaninato-silicon(IV) was carried out as previously described [2]. Briefly, the neutral silicon phthalocyanine complex (100 mg, 0.13 mmol) was dissolved in CH₂Cl₂ (30 cm³) and stirred with an excess of CH₃I (185 mg, 1.56 mmol) at room temperature for 4h. The mixture was then filtered and the precipitate was washed with CH₂Cl₂ (5x 30 mL) and dried *in vacuo*.



Yield:

72 mg (52.9%). IR ν_{max} /(cm⁻¹): 2883; 1976; 1610; 1521; 1472; 1429; 1335; 1292; 1166; 1114; 1080; 957; 910; 791; 757. ¹H NMR (DMSO-d₆): -2.30-(-2.22) (d,4H,H_a); -1.81-(-1.77) (m,2H,H_b); 1.65-1.87 (m,8H,H_c); 2.25-2.33 (m,4H,H_d); 3.06 (s, 12H, H_e); 8.28-8.34 (m, 8H,H_β); 9.45-9.51 (m,8H,H_α). Mass (MALDI-TOF): m/z calculated for C₄₆H₄₆N₁₀O₂Si²⁺ [M-2I+1]⁺: 800.01; found 800.08. Found for C₄₆H₄₆N₁₀I₂Si (%):C, 52.50; H, 4.38; N: 13.28. Calculated (%): C, 52.48; H, 4.40; N, 13.30.

The quaternized compound **SiPc** was characterized by an excellent water-solubility following Lambert-Beer's law in the concentration range studied:

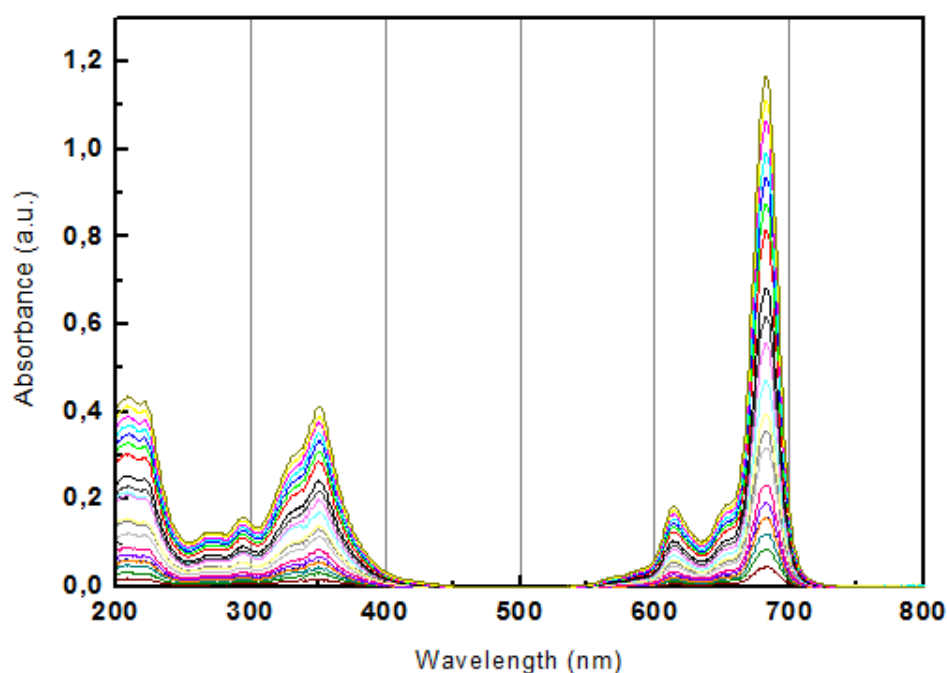


Fig. S1: UV-Vis absorption spectra of **SiPc** samples in water at 298K recorded at increasing concentrations to demonstrate the absence of aggregation phenomena.

Setup for Photoreaction Quantum Yield Determinations:

A home-built optical bench mounted system producing an electrical signal proportional to the photon flux absorbed by the investigated samples was used for exact conversion quantum yield determinations. The technical details of this setup are following the quantum counter setup reported and tested recently by Riedle et. al. [4], which allows for a convenient absolute radiative power detection with a calibrated solar cell detector. Based on the construction plans generously offered by these authors, our system was slightly modified with a turning wheel for rapid switching between four different permanently installed high-power LED light sources covering the visible spectral range for photolysis experiments.

The spectral output of the actually built-in high-power LEDs (470, 525, 592 and 623 nm) [5] used for visible-light illumination experiments is shown below:

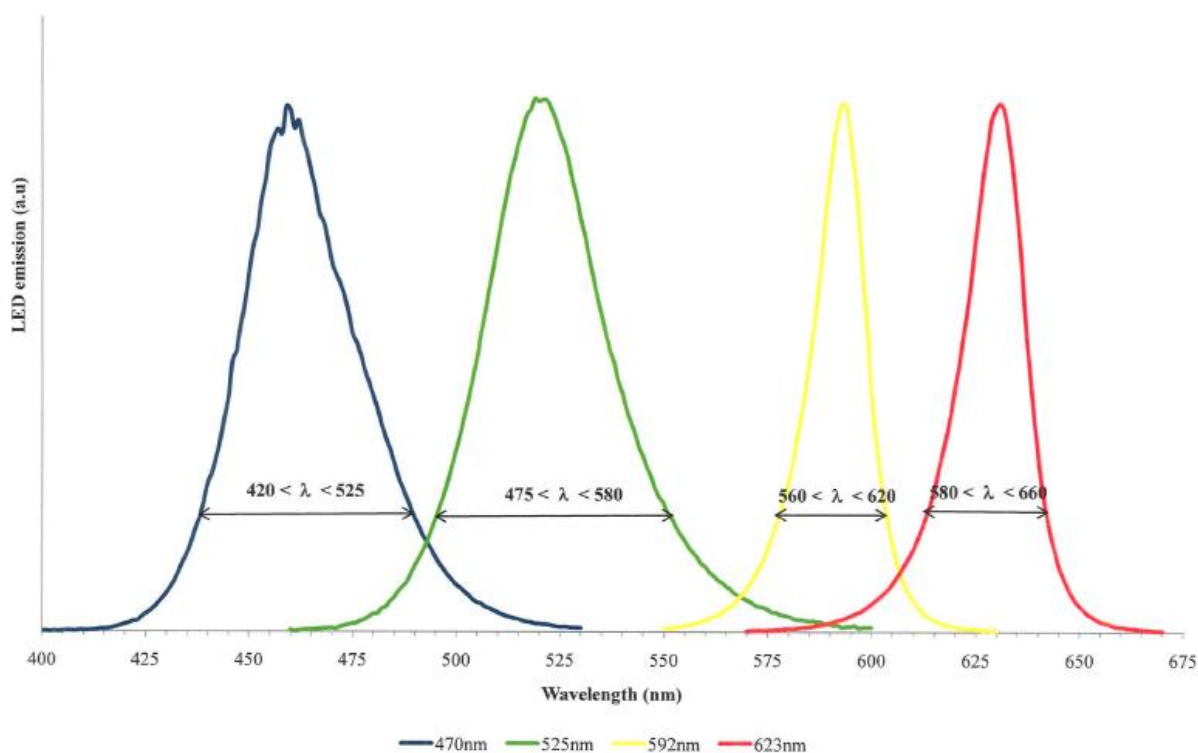


Fig. S2: Emission spectra of the high-power LEDs used

Calibration of the home-built system was carried out by applying classical chemical actinometry with Reinecke's salt in dilute acidic solution according to the recommended standard procedures [6] (0.01M: $\phi = 0.31$ at 470nm; 0.04M: $\phi = 0.29$ at 525nm; 0.01M: $\phi = 0.27$ at 592nm; 0.025M: $\phi = 0.29$ at 623nm).

Photophysical and Photochemical Experiments:

1) Characterization of the T_1 -state of SiPc:

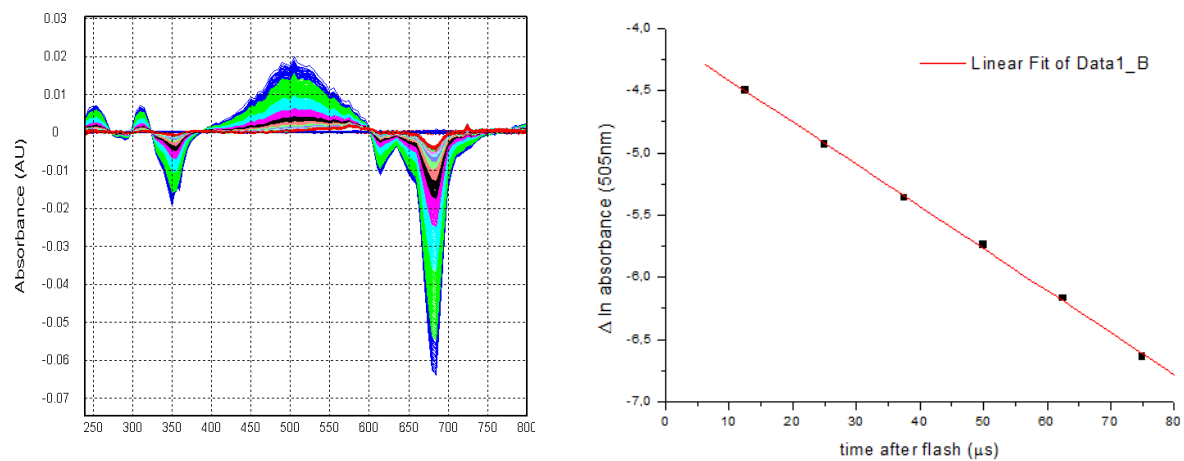


Fig. S3: Regeneration of SiPc ground state absorption and decay of triplet state absorption bands after nanosecond laser flash (355nm excitation).

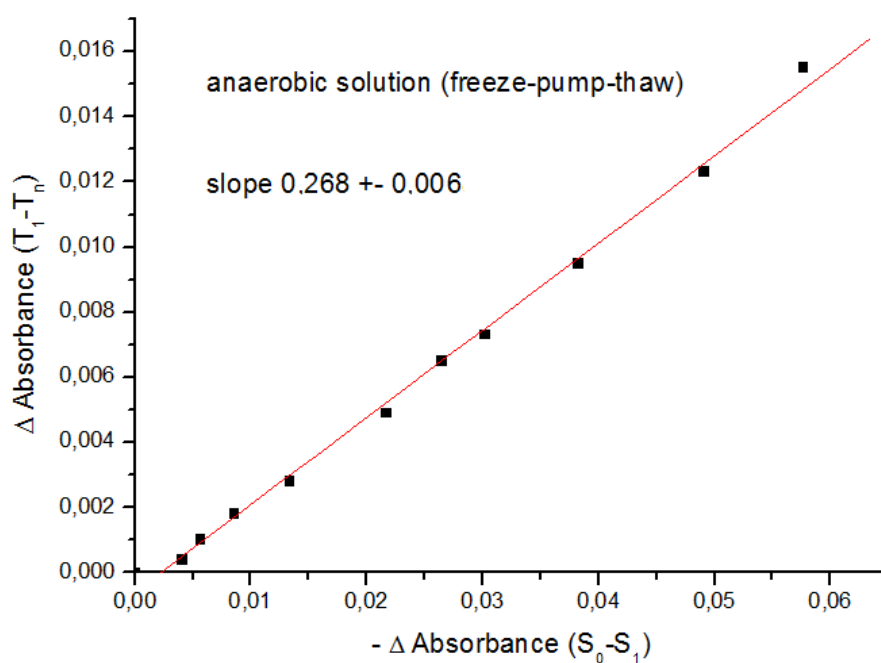
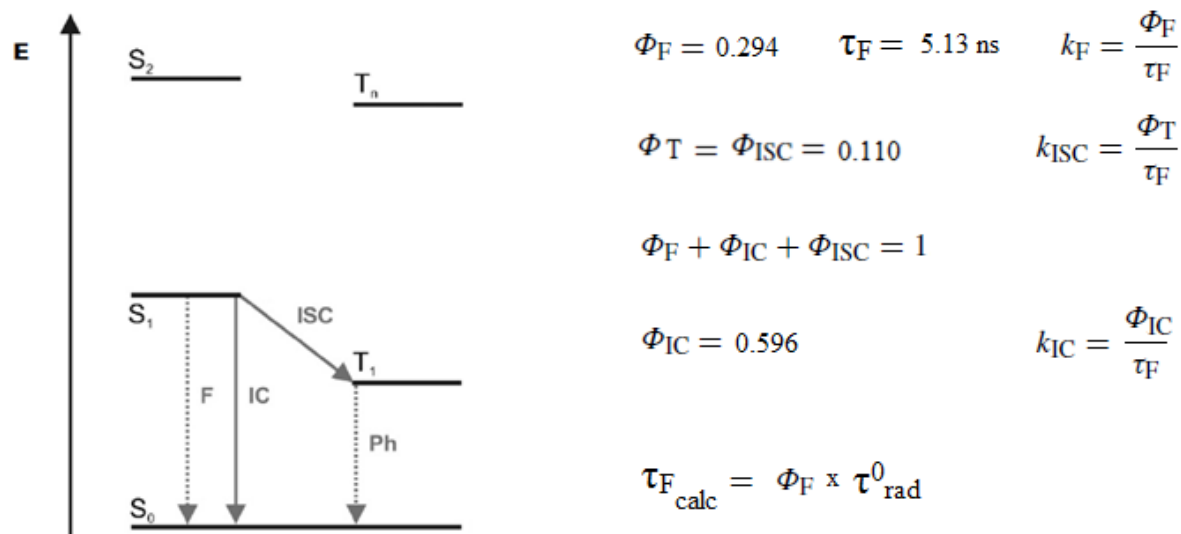


Fig. S4: Ratio of singlet and triplet state absorption in aqueous solution at 298K.

2) Assumptions for calculating photophysical parameters of the S₁-state of **SiPc** :



3) S₁-Fluorescence quenching studies of **SiPc**:

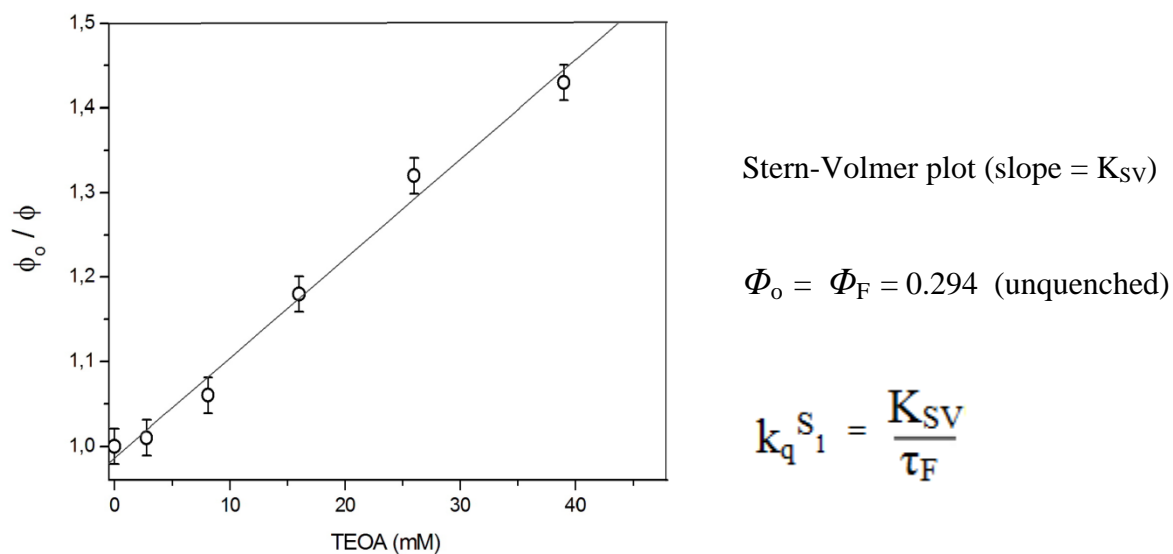


Fig. S5: Example of a linear Stern-Volmer plot in water containing increasing amounts of TEOA.

4) Photoreduction and full re-oxidation of **SiPc** with red LED-light excitation in the Q-band:

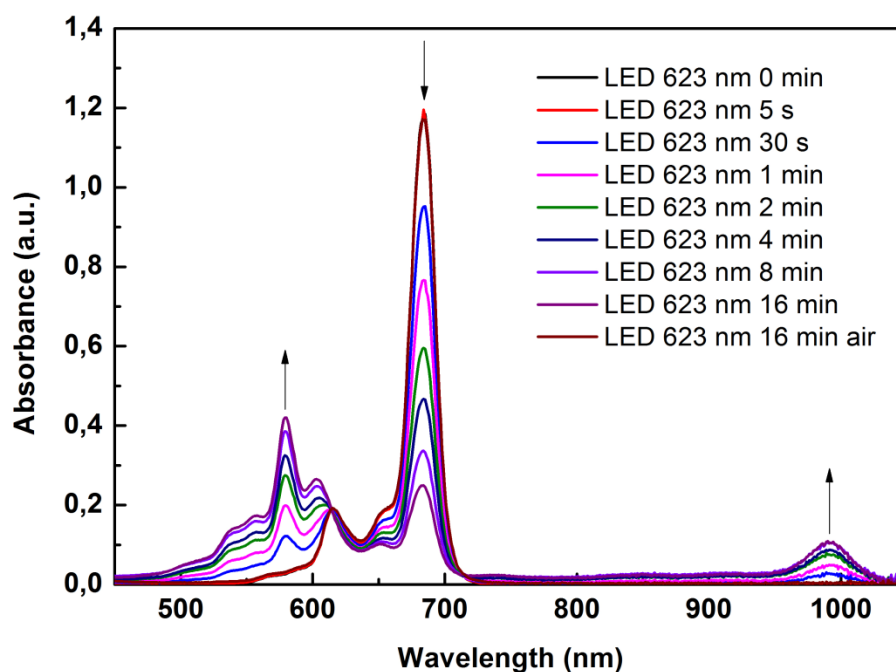


Fig. S6: Photolysis of ca. 1.3×10^{-5} M **SiPc** in Ar-saturated water at 298K in the presence of a large excess of amine (1M TEOA) acting as an electron donor. Dioxygen from air rapidly restores the initial spectrum of the photocatalyst after 16 min of irradiation.

5) Characterization of dioxygen-dependent photoreactions of **SiPc** using model substrates:

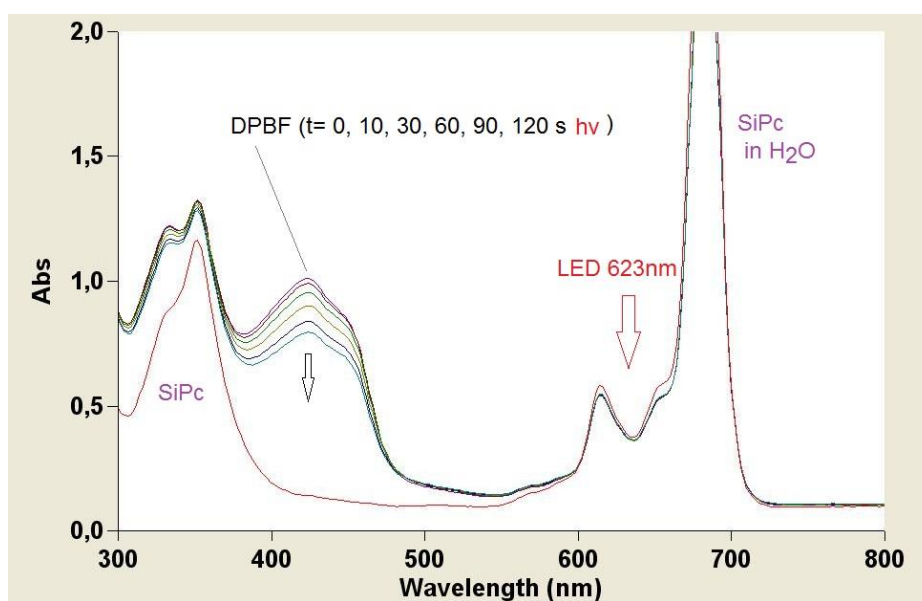


Fig. S7: Degradation of DPBF in the presence of air (**SiPc** in DMSO/water, 298K, 623 nm excitation)

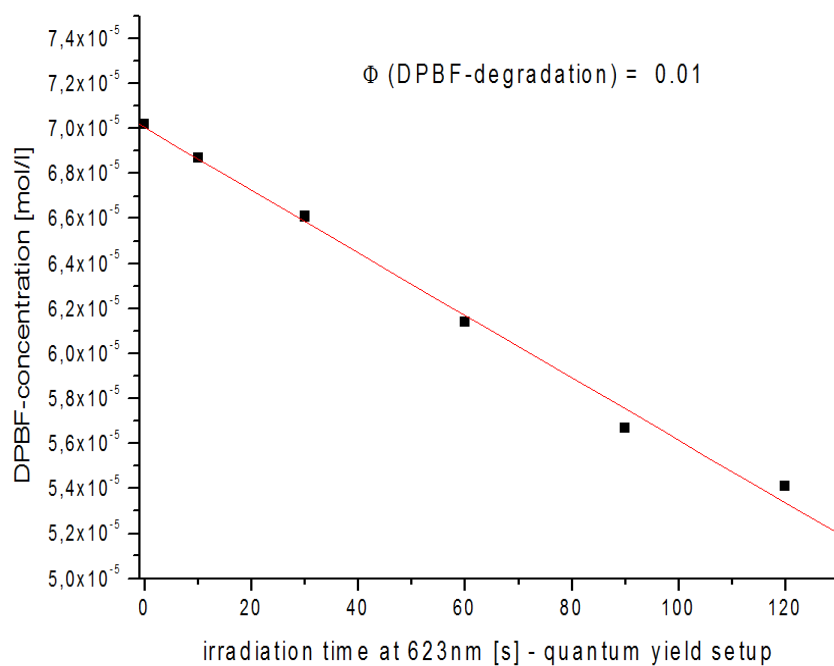


Fig. S8: Absolute quantum yield of DBPF degradation by photoexcited **SiPc** in the presence of air
(DMSO/water, 298K, 623 nm excitation)

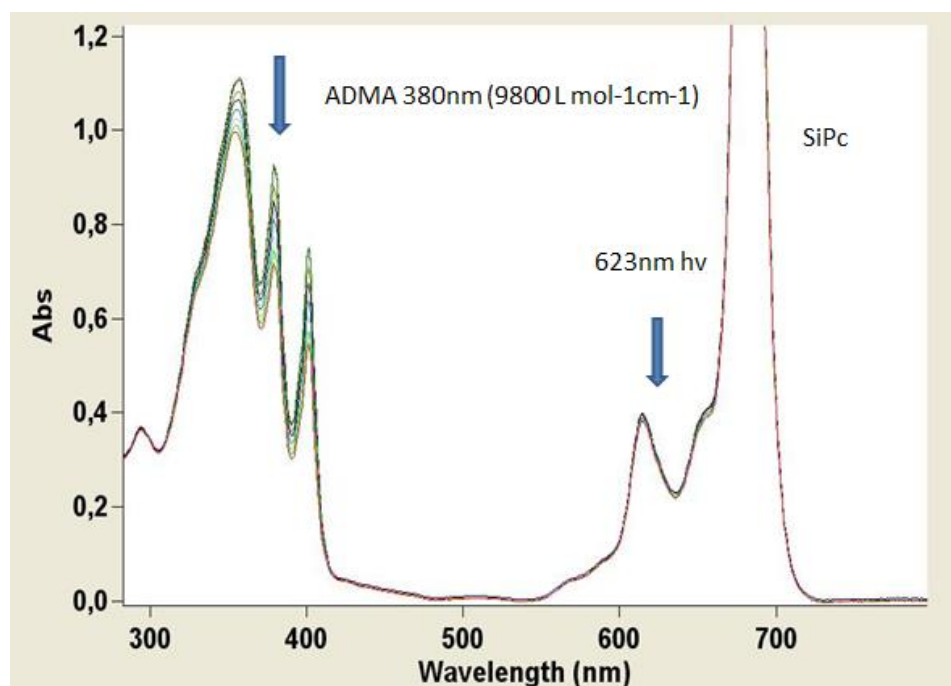


Fig. S9: Degradation of ADMA in the presence of air (**SiPc**, water, pH 7.0, 298K, 623 nm excitation)

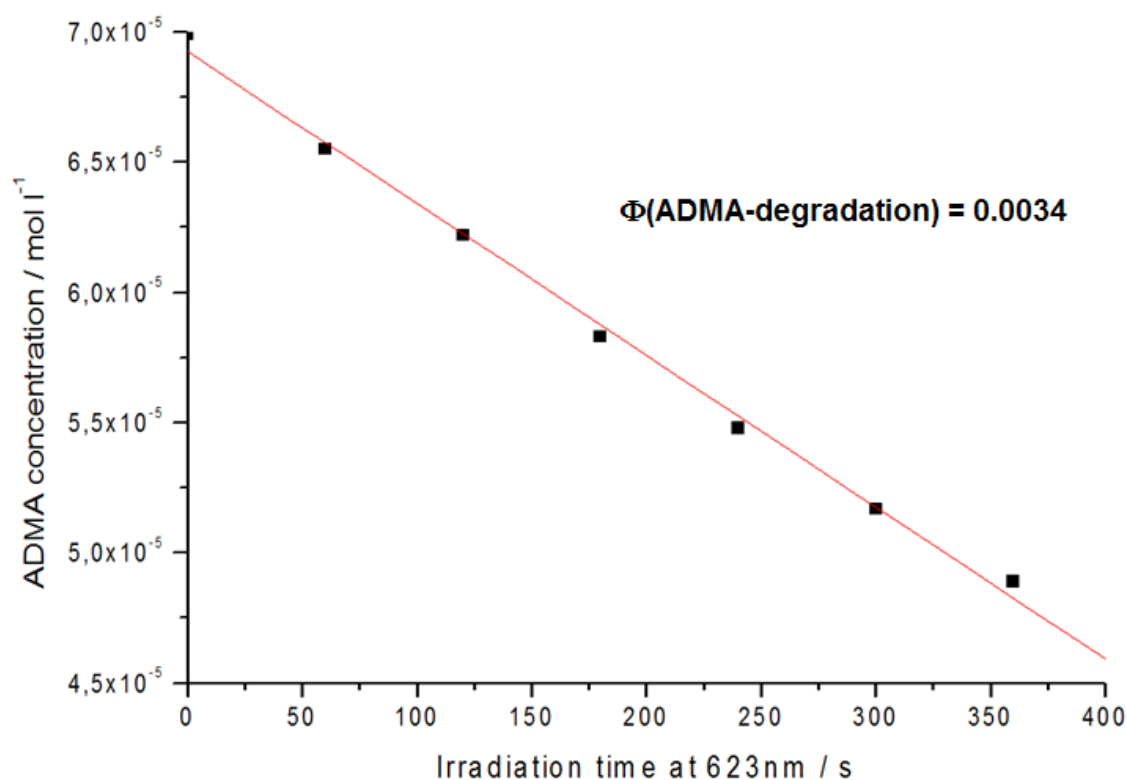


Fig. S10: Absolute quantum yield of ADMA degradation by photoexcited **SiPc**
(air saturated water, phosphate buffer pH 7, 298K, 623 nm excitation)

Determination of the Singlet Oxygen Formation Quantum Yield:

The singlet oxygen quantum yield Φ_{Δ} of **SiPc** in air saturated aqueous solution was measured relative to $[\text{Ru}(\text{bpy})_3]^{2+}$ as a standard ($\Phi_{\Delta, \text{ref}} = 0.18$ reported in [7]), using ADMA as the substrate. The degradation of ADMA by **SiPc** was followed both in the presence and in the absence of sodium azide known to act as an efficient singlet oxygen quencher. The gradual self-sensitized degradation of **SiPc** caused by the reaction with the singlet oxygen formed in water under ambient conditions was also studied without ADMA present in solution. All experiments were carried out with monochromatic light excitation at 355 nm absorbed by the Soret-band of the **SiPc** sensitizer or the $[\text{Ru}(\text{bpy})_3]^{2+}$ standard under otherwise identical conditions (solvent, temperature, optical pathlength and setup, sample absorbance at 355nm and ADMA concentration present in solution). The reported singlet oxygen quantum yield Φ_{Δ} of **SiPc** was corrected for the degree of singlet oxygen consumption by self-sensitization

(increasing the uncorrected Φ_{Δ} value by 0.02) and for the significant degree of ADMA degradation observed even in the presence of sodium azide (decreasing the uncorrected Φ_{Δ} value by 0.11 and tentatively attributed to a reaction from the first excited singlet state). Without both of these corrections, an apparently higher value of $\Phi_{\Delta} = 0.20$ relative to $\Phi_{\Delta, \text{ref}} = 0.18$ of the $[\text{Ru}(\text{bpy})_3]^{2+}$ reference was obtained by comparing the slopes of the corresponding ADMA degradation plots. This apparent value exceeds the experimental triplet quantum yield of Φ_{T} observed for 355 nm excitation. Taking into account the corrections properly, the $\Phi_{\Delta} = 0.11 \pm 0.01$ value of **SiPc** and the triplet quantum yield $\Phi_{\text{T}} = 0.11$ coincide.

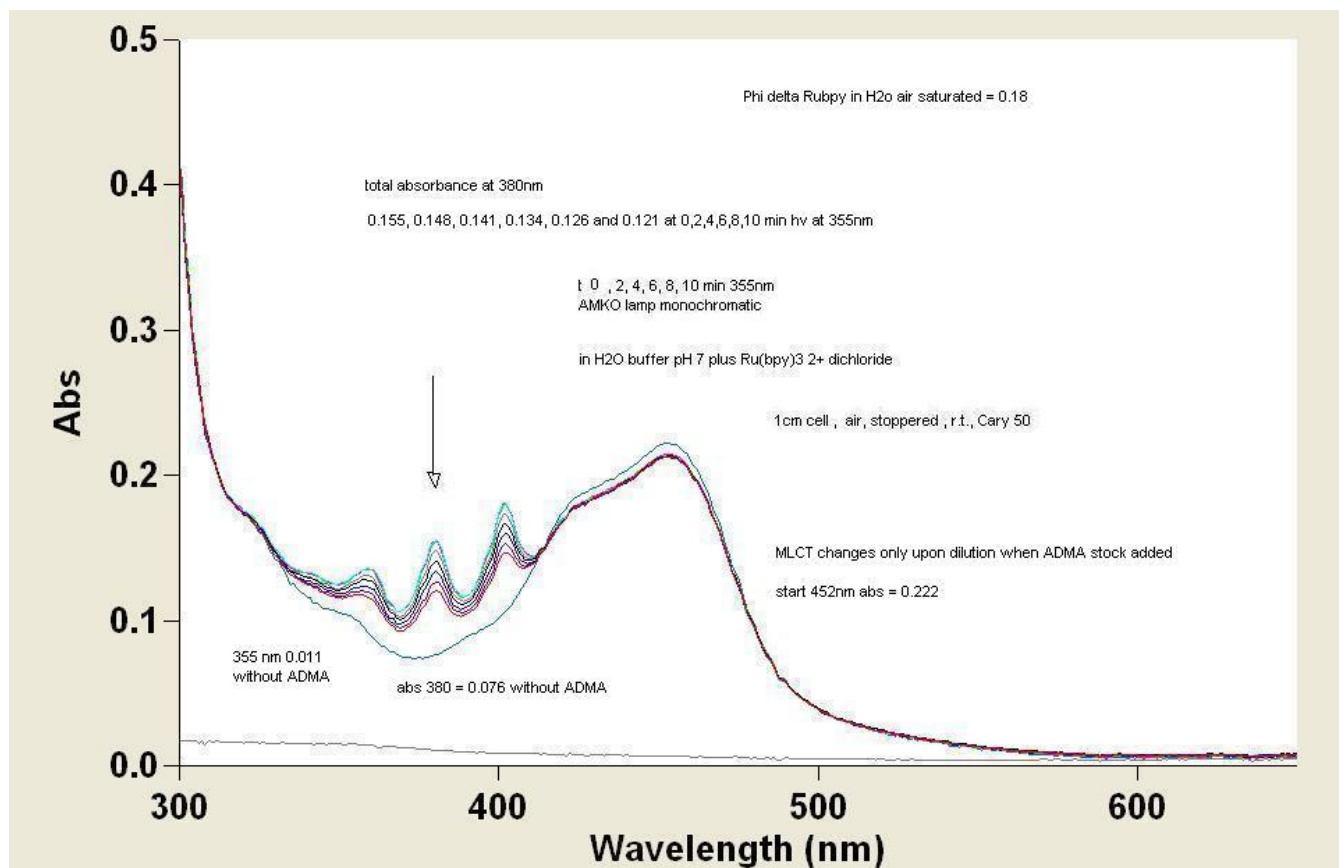


Fig. S11: Degradation of ADMA with $[\text{Ru}(\text{bpy})_3]^{2+}$ (water, pH=7.0, air, 298K, 355 nm excitation).

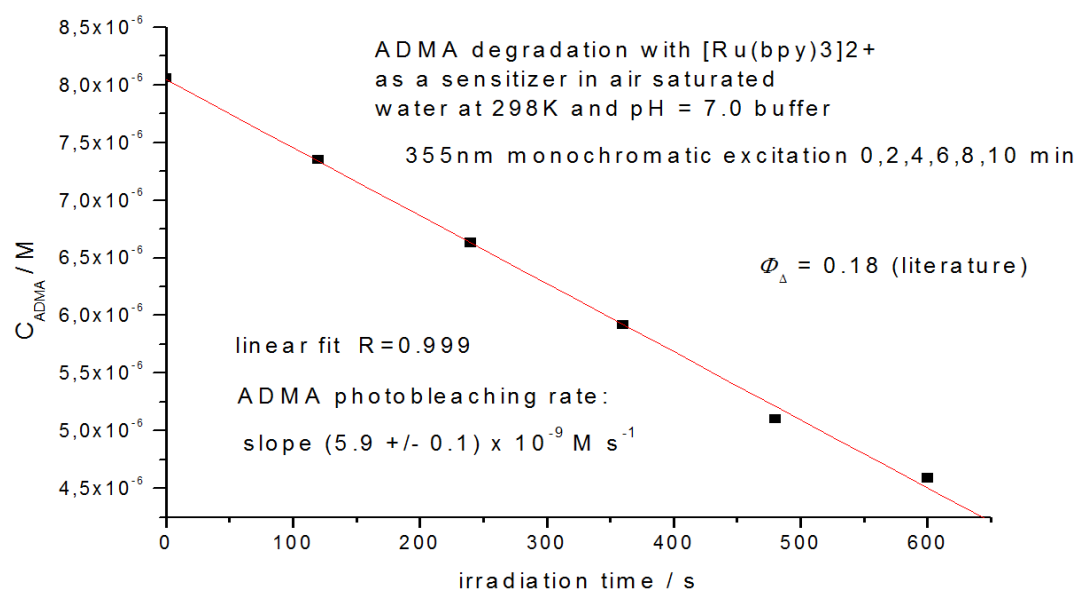


Fig. S12: Time-course of ADMA degradation by $[Ru(bpy)_3]^{2+}$ (water, pH=7.0, air, 298K, 355 nm).

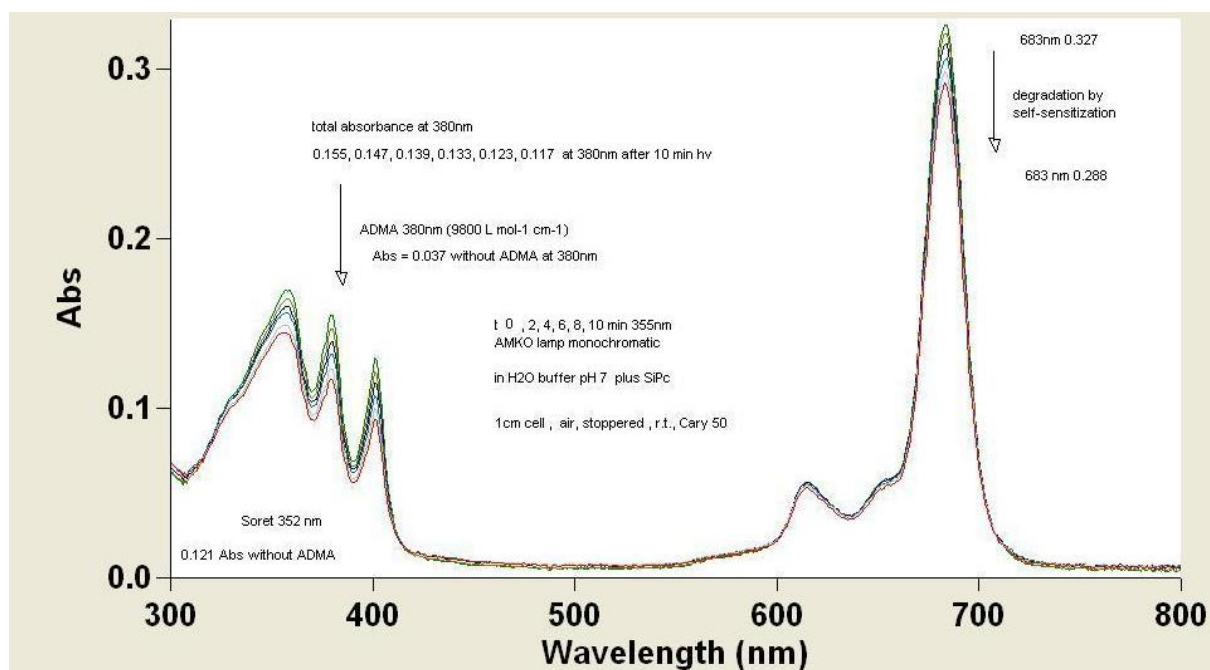


Fig. S13: Time-course of ADMA degradation by **SiPc** under conditions corresponding to the experiment shown in Fig. S11 above (water, pH=7.0, air, 298K, 355 nm).

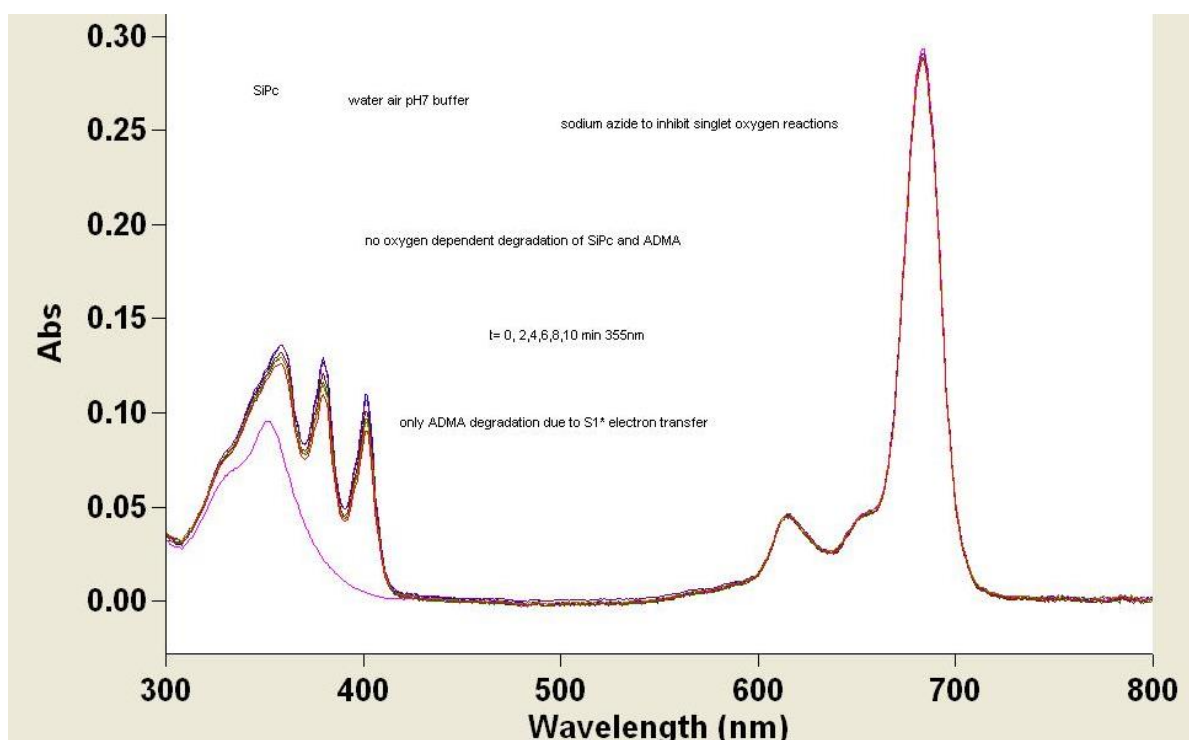


Fig. S14: Singlet oxygen independent degree of ADMA photodegradation sensitized by **SiPc** in the presence of sodium azide in excess (water, pH=7.0, air, 298K, 355 nm excitation). Note the lack of self-sensitized degradation of **SiPc** compared to the situation in Fig. S13.

References:

- [1] T. Nyokong and E. Antunes in: Handbook of Porphyrin Science, K. M. Kadish, K. M. Smith and R. Guilard, Eds., World Scientific, Singapore, 2010, Vol. 7, Chpt. 34, p. 273.
- [2] C. Uslan and B. Ş. Sesalan, *Inorg. Chim. Acta* 2013, **394**, 353.
- [3] B. Ş. Sesalan, A. Koca, A. Gül, *Monatsh. Chem.* 2000, **131**, 1191.
- [4] Megerle, U.; Lechner, R.; König, B.; Riedle, E. *Photochem. Photobiol. Sci.*, 2010, **9**, 1400. (see also: <http://www.rsc.org/suppdata/pp/c0/c0pp00195c/c0pp00195c.pdf>)
- [5] ALUSTAR 3W LED-Modules (LEDxON) commercially available (Conrad electronics) mounted with precise lens optics into an Al-case with 10° output angle were used. The ready-to-use system is based on the EDISON Opto® Edixeon® S single color high-power LED series. (<http://www.edison-opto.com.tw>).
- [6] Kuhn, H- J.; Braslavsky, S. E.; Schmidt, R. Chemical Actinometry, IUPAC Technical Report 2004 (<http://www.iupac.org/publications/pac/76/12/2105/pdf/>)
- [7] J- M. Wessels, C. S. Foote, W. E. Ford and M. J. Rodgers, *Photochem. Photobiol.* 1997, **65**, 96.