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### Supplementary data for

# Magnesium(II) 1-(1-adamantylsulfanyl)phthalocyanine - synthesis, photochemical and electrochemical properties

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#### Synthethic procedures

All reactions were conducted in oven dried glassware under argon. All solvents were rotary evaporated at or below 50 °C. Solvents and all reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Dry flash column chromatography was carried out on Merck silica gel 60, particle size 40-63  $\mu$ m and Fluka silica gel 90 C18 – reversed phase. Thin layer chromatography (TLC) was performed on silica gel Merck Kieselgel 60 F254 and DC Kieselgel 60 RP-18 F254 plates and visualized with UV ( $\lambda_{max}$  254 nm).

<sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded using a Bruker 400 spectrometer. Chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) and are referred to a residual solvent peak. Coupling constants (J) are quoted in Hertz (Hz). The abbreviations s, b, m and pq refer to singlet, broad, multiplet, and pseudoquartet respectively. Mass spectra (ES, MALDI TOF) and elementary analysis were carried out by an Advanced Chemical Equipment and Instrumentation Facility at the Faculty of Chemistry, Adam Mickiewicz University in Poznan.

#### Photochemical and solvent effects studies

The UV-Vis spectra for solvent effects evaluation and quantitative spectra were recorded in the range of 300-900 nm using a Hitachi U-1900 spectrophotometer.

All solvents were obtained from commercial suppliers and used without further purification with exception of acetone, ethyl acetate, methanol, ethanol, *n*-hexane, dichloromethane, which were distilled prior to measurements. The quantum yields of singlet oxygen photogeneration were determined in DMSO and DMF solutions (3.0 mL, no oxygen bubbled) using the relative method with zinc(II) phthalocyanine (ZnPc, Sigma – Aldrich) as a reference and 1,3-diphenylisobenzofuran (DPBF) as a chemical quencher for singlet oxygen, following recently presented methodologies [34-36]. Solutions of **5** or ZnPc in DMF and DMSO in the presence of DPBF were irradiated in a 1 cm path length quartz cell with monochromatic light by a 150 W high-pressure xenon lamp (Optel) through a monochromator M250/1200/U. The irradiation wavelengths were adjusted to the maximum of the absorption peaks at the Q-bands characteristic of each compound - phthalocyanines absorbance ~ 0.5, wavelengths: DMF: **5** – 685 nm, ZnPc – 670; DMSO: **5** – 688 nm, ZnPc – 672 nm. The concentration of DPBF was set at ~  $3 \times 10^{-5}$  mol L<sup>-1</sup> in order to avoid chain reactions induced by DPBF in the presence of singlet oxygen. UV-Vis spectra were recorded on a Shimadzu UV-160A spectrophotometer with PC 160 PLUS manual. The light intensity was set to 0.5 mW cm<sup>-2</sup> (Radiometer RD 0.2/2

with TD probe, Optel). All the experiments were performed in the dark at ambient temperature.

Steady state fluorescence quantum yields were measured in solutions, using 1cm-thick-cell. Absorbance of the solution was kept below 0.1 at the maximum of Q-band, in order to avoid reabsorption of the emitted fluorescence.



**Fig. S1.** <sup>1</sup>H NMR spectrum of **5**. Symbols #, \* and \$ indicate the residual peaks of pyridine, water and tetrahydrofuran respectively. Closely spaced signals are expanded in the boxes above.



**Fig. S2.** <sup>13</sup>C NMR spectrum of **5**. Symbols \* and \$ indicate the residual peaks of pyridine and tetrahydrofuran. Closely spaced signals are expanded in the boxes above.



Fig. S3. 1H-1H COSY NMR spectrum of 5, aliphatic region is expanded.



Fig. S4. MALDI-TOF MS of 5. C<sub>42</sub>H<sub>30</sub>MgN<sub>8</sub>S requires *m/z* 702.2 [M]<sup>+</sup>, found 702.5.

## HPLC analysis of 5

The chromatographic analysis was done using an octadecylsilane coated column, 150 mm  $\times$  4.6 mm, 5  $\mu$ m (Eclipse XDB-C18, Agilent), using isocratic elution conditions at a flow rate of 1.0 mL/min, eluent: MeOH 90%, DCM 5%, THF 5%. Assay was established to be 97.5%.



Fig. S5. Chromatogram and UV-vis spectrum of phthalocyanine 5.



**Fig. S6**. The absorption spectra in the range of the Q-band of phthalocyanine **5** in different solvents.



**Fig. S7.** Pseudo first-order plots of oxidation of diphenylisobenzofuran (DPBF) during irradiation of mixture of DPBF and phthalocyanine **5** and in DMF solution.



**Fig. S8.** Pseudo first-order plots of oxidation of diphenylisobenzofuran (DPBF) during irradiation of mixture of DPBF and phthalocyanine **5** and in DMSO solution.



**Fig. S9.** Changes in the UV–vis spectra of DPBF and **5** in DMSO during irradiation at Q-band.



**Fig. S10.** Cyclic voltammogram of magnesium(II) phthalocyanine recorded in 0.1 TBAP/DCM at 50 mV s<sup>-1</sup>.

References cited in the Supplementary info:

- Goslinski T, Osmalek T, Mielcarek J. Photochemical and spectral characterization of peripherally modified porphyrazines. Polyhedron 2009;28:3839–43.
- 35. Seotsanyana-Mokhosi I, Kuznetsova N, Nyokong T. Photochemical studies of tetra-2, 3pyridinoporphyrazines. J. Photochem. Photobiol. A 2001;140:215–22.
- Spiller W, Kliesch H, Woehrle D, Hackbarth S, Roeder B, Schnurpfeil G. Singlet oxygen quantum yields of different photosensitizers in polar solvents and micellar solutions. J. Porphyr. Phthalocyanines 1998;2:145–58.