Electronic supplementary information (ESI)

A set of highly water-soluble tetraethyleneglycol-substituted Zn(II) phthalocyanines: synthesis, photochemical and photophysical properties, interaction with plasma proteins and in vitro phototoxicity.

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Fig. S1. Representative Zn-specific chromatograms that were obtained for the analysis of I spiked BSA (50 mg/mL in PBS) after incubation at 37°C, on a Superdex 200 10/300 GL SEC column (30 x 1.0 cm I.D., 13 μm particle size). Mobile phase: PBS-buffer (0.15 M, pH 7.4), Flow-rate: 1.0 mL/min, Injection volume: 500 μL, Detector: ICP-AES at 213.856 nm (Zn). Abbreviations: BSA bovine serum albumin. The retention times of the molecular weight markers are depicted on top of the figure.
**Experiment details for the fluorescence, singlet oxygen and photodegradation quantum yields measurements**

**Fluorescence.** Fluorescence quantum yields (Φ<sub>F</sub>) were determined by the comparative method (Equation 2)<sup>1</sup>

\[
\Phi_F = \Phi_F(\text{Std}) \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2} \tag{2}
\]

where F and F<sub>Std</sub> are the areas under the fluorescence emission curves of the samples and the standard, respectively. A and A<sub>Std</sub> are the respective absorbances of the samples and standard at the excitation wavelengths. n<sup>2</sup> and n<sub>Std</sub><sup>2</sup> are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (Φ<sub>F</sub> = 0.18 in DMSO)<sup>2</sup> was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative life times (τ<sub>0</sub>) were determined using PhotochemCAD program which uses the Strickler-Berg equation<sup>3</sup>. The fluorescence lifetimes (τ<sub>F</sub>) were evaluated using equation 3.

\[
\Phi_F = \frac{\tau_F}{\tau_0} \tag{3}
\]

**Singlet oxygen quantum yield** (Φ<sub>α</sub>) determinations were carried out using the experimental set-up described in literature<sup>4</sup>. Typically, a 3 mL solution of the unsubstituted (ZnPc), and of substituted phthalocyanines 1, 2 and 3 (absorbance ~ 1.0 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references. <sup>4</sup> Φ<sub>α</sub> values were determined in air using the relative method, with ZnPc (in DMSO) or ZnPcS<sub>mix</sub> (in aqueous media) as references. DPBF and ADMA were used as chemical quenchers for singlet oxygen in DMSO and aqueous media, respectively. Equation 4 was employed for the calculations:

\[
\Phi_\alpha = \Phi_\alpha^\text{Std} \frac{R_{\text{Std}}}{R} \frac{I_{\text{abs}}^\text{Std}}{I_{\text{abs}}} \tag{4}
\]

where Φ<sub>α</sub><sup>Std</sup> is the singlet oxygen quantum yields for the standard ZnPc (Φ<sub>α</sub><sup>Std</sup> = 0.67 in DMSO)<sup>5</sup> and ZnPcS<sub>mix</sub> (Φ<sub>α</sub><sup>Std</sup> = 0.45 in aqueous media)<sup>6</sup>, R and R<sub>Std</sub> are the DPBF (or ADMA) photobleaching rates in the presence of the respective samples and standards, respectively. I<sub>abs</sub> and I<sub>abs</sub><sup>Std</sup> are the rates of light absorption by the samples and standards, respectively. To avoid chain reactions induced by DPBF (or ADMA) in the presence of singlet oxygen<sup>6</sup>, the concentration of quenchers (DPBF or ADMA) was lowered to ~3x10<sup>-5</sup> M. Solutions of sensitizer...
(absorbance = 1 at the irradiation wavelength) containing DPBF (or ADMA) were prepared in
the dark and irradiated in the Q band region using the setup described above. DPBF degradation
at 417 nm and ADMA degradation at 380 nm were monitored. The light intensity $6.60 \times 10^{15}$
photons s$^{-1}$ cm$^{-2}$ was used for $\Phi_d$ determinations.

**Photodegradation quantum yield** ($\Phi_d$) determinations were carried out using the
experimental set-up described in literature.$^4$ $\Phi_d$ values were determined using equation 5,

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{\text{abs}} \cdot S \cdot t}$$

where $C_0$ and $C_t$ are respectively the samples concentrations before and after irradiation, $V$ is the
reaction volume, $N_A$ the Avogadro’s constant, $S$ the irradiated cell area and $t$ the irradiation time,
$I_{\text{abs}}$ is the overlap integral of the radiation source light intensity and the absorption of the
samples. A light intensity of $2.20 \times 10^{16}$ photons s$^{-1}$ cm$^{-2}$ was employed for $\Phi_d$ determinations.

**References**

1. (a) S. Fery-Forgues and D. Lavabre, *J. Chem. Ed.*, 1999, **76**, 1260; (b) D. Maree, T. Nyokong,
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5. N. Kuznetsova, N. Gretsova, E. Kalmkova, E. Makarova, S. Dashkevich, V. Negrimovskii, O.