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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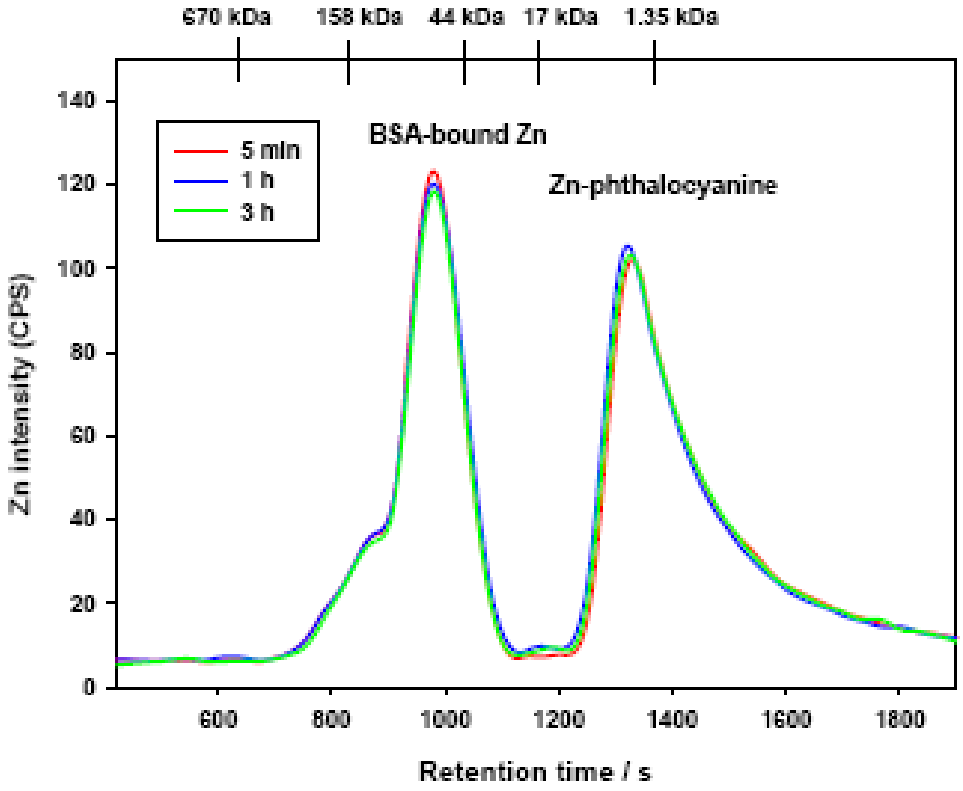

Fig. S1. Representative Zn-specific chromatograms that were obtained for the analysis of **1** spiked BSA (50 mg/mL in PBS) after incubation at 37°C, on a Superdex 200 10/300 GL SEC column (30 x 1.0 cm I.D., 13 µm particle size). Mobile phase: PBS-buffer (0.15 M, pH 7.4), Flow-rate: 1.0 mL/min, Injection 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_F) were determined by the comparative method (Equation 2)[1]

$$\Phi_F = \Phi_F(\text{Std}) \frac{F \cdot A_{Std} \cdot n^2}{F_{Std} \cdot A \cdot n^2_{Std}} \quad (2)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths. n^2 and n^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (Φ_F = 0.18 in DMSO)[2] 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_0) were determined using PhotochemCAD program which uses the Strickler-Berg equation[3]. The fluorescence lifetimes (τ_F) were evaluated using equation 3.

$$\Phi_F = \frac{\tau_F}{\tau_0} \quad (3)$$

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature[4]. 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.[4] Φ_Δ values were determined in air using the relative method, with ZnPc (in DMSO) or $ZnPcS_{mix}$ (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:

$$\Phi_\Delta = \Phi^{Std}_\Delta \frac{R \cdot I^{Std}_{abs}}{R^{Std} \cdot I_{abs}} \quad (4)$$

where Φ^{Std}_Δ is the singlet oxygen quantum yields for the standard ZnPc (Φ^{Std}_Δ = 0.67 in DMSO)[5] and $ZnPcS_{mix}$ (Φ^{Std}_Δ = 0.45 in aqueous media)[4b], R and R_{Std} are the DPBF (or ADMA) photobleaching rates in the presence of the respective samples and standards, respectively. I_{abs} and I^{Std}_{abs} 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[6], the concentration of quenchers (DPBF or ADMA) was lowered to ~3×10^{-5} 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 6.60×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

Photodegredation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature.[4] Φ_d values were determined using equation 5,

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{abs} \cdot S \cdot t} \quad (5)$$

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_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples. A light intensity of 2.20×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

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