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SUPPLEMENTARY INFORMATION

Peptide-substituted phthalocyanine photosensitizers: design, synthesis, photophysicochemical and photobiological studies

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Chemicals and materials

All solvents were reagent-grade quality and obtained from commercial suppliers. Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and preparative thin layer chromatography (TLC) was performed on silica gel 60 P F_{254}. 1,3-diphenylisobenzofuran (DPBF) was obtained from Fluka. Zinc phthalocyanine used as standard for photophysical and photochemical measurements was purchased from Aldrich. All reactions were monitored by TLC using 0.25 mm silica gel plates with UV indicator ($60F_{254}$).

Equipments

Elemental analyses were obtained from Thermo Finnigan Flash 1112 Instrument. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 spectrophotometer. Electronic absorption spectra were measured on a Shimadzu 2101 UV-Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvette at room temperature. ^{1}H and ^{13}C NMR spectra with TMS as the internal standard were recorded on a Varian 500 MHz spectrometer. The mass spectra were recorded on a MALDI (Matrix Assisted Laser Desorption Ionization) BRUKER Microflex LT using a 2,5-dihydroxybenzoic acid (DHB) as matrix.

Photophysical parameters

Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) are determined in DMSO by the comparative method using by equation 1 [1, 2],

$$\Phi_F = \Phi_F(\text{Std})\frac{F \,.\, A_{Std} \,.\, n^2}{F_{Std} \,.\, A \,.\, n^2_{Std}} \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**2**, **5**, **6**, **7**, **8**, and **9**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (Φ_F = 0.20) [3] was employed as the standard in DMSO. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative life times (τ_0) are determined using PhotochemCAD program [4] which uses the Strickler-Berg equation. The fluorescence lifetimes (τ_F) are calculated using equation 2.

$$\Phi_F = \frac{\tau_F}{\tau_0} \qquad (2)$$

Photochemical parameters

Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations are carried out using the experimental set-up described in literature [6] in DMSO. Typically, a 3 mL portion of the respective unsubstituted or tetra-substituted zinc (II) phthalocyanine solutions (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 [6]. Φ_Δ values were determined in air using the relative method with ZnPc (in DMSO) as standards. DPBF was used as chemical quenchers for singlet oxygen in DMSO. Equation 3 was employed for the determination of Φ_Δ values:

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \frac{R \,.\, I_{abs}^{Std}}{R^{Std} \,.\, I_{abs}} \qquad (3)$$

where Φ_{Δ}^{Std} is the singlet oxygen quantum yields for the standards ZnPc (Φ_{Δ}^{Std} = 0.67 in DMSO) [7], R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**2**, **5**, **6**, **7**, **8**, and **9**) and standards, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples (**2**, **5**, **6**, **7**, **8**, and **9**) and standards, respectively. To avoid chain reactions induced by quencher (DPBF) in the presence of singlet oxygen, the concentration of quenchers (DPBF) was lowered to ~$3x10^{-5}$ M [8]. Solutions of sensitizer (absorbance = 1 at the irradiation wavelength) containing quencher (DPBF) were prepared in the dark and irradiated in the Q band region. DPBF degradation at 417 nm was monitored. The light intensity $6.21x10^{15}$ photons s^{-1} cm^{-2} was used for Φ_{Δ} determinations.

Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations are carried out using the experimental set-up described in literature [6]. Photodegradation quantum yields were determined using equation 4 in both DMSO.

$$\Phi_d = \frac{(C_0 - C_t) \,.\, V \,.\, N_A}{I_{abs} \,.\, S \,.\, t} \qquad (4)$$

where C_0 and C_t are the samples concentrations before and after irradiation, respectively. 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 2.17x 10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

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