SUPPLEMENTARY INFORMATION

Investigation of photophysical and photochemical properties of peripherally tetra-substituted water-soluble zwitterionic and cationic zinc(II) phthalocyanines

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1. Materials and Equipments

DMSO, DMF, DCM, CHCl₃, methanol, H₂O₂ (30%) and methyl iodide were purchased from Merck, 1,3-propanesultone, triethylamine, ethylchloroformate, N,N′-dimethyl-1,3-propanediamine, zinc (II) acetate, dimethylethanolamine (DMAE) and sodiumchloroacetate were purchased from Sigma Aldrich. 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), 9,10-antracenediyl-bis(methylene)dimalonoic acid (ADMA) and 1,3-diphenylisobenzofuran (DPBF) were purchased from Fluka. All reagents and solvents obtained from commercial suppliers were reagent grade quality. Solvents were dried via an A3 molecular sieve and stored in the presence of it.

4-(4-carboxyphenoxy)phthalodinitrile,¹⁻³ 4-nitrophthalonitrile,⁴ were synthesized and purified according to the previously studies.

2. Photophysical parameters

2.1. Fluorescence quantum yields

Fluorescence quantum yields (Φₘ) were determined by a comparative method⁵ using equation 1.

\[
\Phi_F = \Phi_{F_{\text{Std}}} \frac{F \cdot A_{\text{Std}} \cdot n^2_{\text{Std}}}{F_{\text{Std}} \cdot A \cdot n^2}\]

where F and Fₘ are the areas under the fluorescence curves of the phthalocyanine samples and the reference, respectively. A and Aₘ are the absorbances of the samples and reference at the excitation wavelength. n and nₘ are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc was used as a standard (Φₘ = 0.20 in DMSO⁶) for the determination of fluorescence quantum yields. The sample and the standard were both excited at the same relevant wavelength.

3. Photochemical parameters

3.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φₙ) determinations were carried out using the experimental set-up described in literature.⁷,⁸ Typically, a 3 mL portion of the respective substituted non-ionic and ionic phthalocyanine (2-6) solutions (C=1.0x10⁻⁵ M) containing the singlet oxygen
quencher was irradiated in the Q band region with the photo-irradiation set-up described in references.\textsuperscript{7,8} $\Phi_\Delta$ values were determined in air using the relative method and unsubstituted ZnPc in DMSO or ZnPcS\textsubscript{mix} in aqueous media were used as references. DPBF and ADMA were used as chemical quenchers for singlet oxygen in DMSO and aqueous media, respectively. Equation 2 was employed for the calculations:

\[
\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{R \cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot I_{\text{abs}}} 
\]

(2)

where $\Phi_\Delta^{\text{Std}}$ is the singlet oxygen quantum yields for the standard unsubstituted ZnPc ($\Phi_\Delta^{\text{Std}} = 0.67$ in DMSO)$^9$ and ZnPcS\textsubscript{mix} ($\Phi_\Delta^{\text{Std}} = 0.45$ in aqueous media),$^8$ $R$ and $R^{\text{Std}}$ are the DPBF (or ADMA) photobleaching rates in the presence of the respective samples and standards, respectively. $I_{\text{abs}}$ and $I_{\text{abs}}^{\text{Std}}$ 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,$^{10}$ the concentration of quenchers (DPBF or ADMA) was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (C=$1.0 \times 10^{-5}$ M) 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 $6.54 \times 10^{15}$ photons s$^{-1}$ cm$^{-2}$ was used for $\Phi_\Delta$ determinations.

4. Binding of ionic zinc (II) phthalocyanine complexes to BSA

The binding of the ionic zinc(II) phthalocyanine complexes (3-6) to BSA protein were studied by spectrofluorometry at room temperature. An aqueous solution of BSA (fixed concentration) was titrated with varying concentrations of the respective ionic zinc(II) phthalocyanine (3-6) solutions. BSA was excited at 280 nm and fluorescence recorded between 290 nm and 500 nm. The steady diminution in BSA fluorescence with increase in ionic zinc(II) phthalocyanine (3-6) concentrations was noted and used in the determination of the binding constants and the number of binding sites on BSA, according to equation 3.$^{11-13}$

\[
\log \left[ \frac{(F - F_a)}{(F - F_{\infty})} \right] = \log K_a + n \log [\text{Pc}] 
\]

(3)
where $F_0$ and $F$ are the fluorescence intensities of BSA in the absence and presence of ionic zinc(II) phthalocyanines (3-6) respectively; $F_\infty$, the fluorescence intensity of BSA saturated with ionic zinc(II) phthalocyanine complexes; $K_b$, the binding constant; $n$, the number of binding sites on a BSA molecule; and $[Pc]$ the concentration of ionic zinc(II) phthalocyanine complexes. Plots of $\log\left(\frac{(F_0-F)}{(F-F_\infty)}\right)$ against $\log[Pc]$ would provide the values of $n$ (from the slope) and $K_b$ (from the intercept).

The changes in BSA fluorescence intensity were related to ionic zinc(II) phthalocyanine concentrations by the Stern-Volmer relationship (Equation 4):

$$\frac{F_0^{BSA}}{F_{BSA}} = 1 + K_{SV}^{BSA} [Pc]$$  \hspace{1cm} (4)

and $K_{SV}^{BSA}$ is given by equation 5:

$$K_{SV}^{BSA} = k_q \tau_{F(BSA)}$$  \hspace{1cm} (5)

where $F_0^{BSA}$ and $F^{BSA}$ are the fluorescence intensities of BSA in the absence and presence of ionic zinc(II) phthalocyanine complexes (3-6) respectively; $K_{SV}^{BSA}$ is the Stern-Volmer quenching constant; $k_q$ is the bimolecular quenching constant; and $\tau_{F(BSA)}$ is the fluorescence lifetime of BSA. $\tau_{F(BSA)}$ is known to be 10 ns,$^{14-16}$ thus from the values of $K_{SV}^{BSA}$ obtained from the plots of $\frac{F_0^{BSA}}{F^{BSA}}$ versus $[Pc]$, the value of $k_q$ may be determined (Equation 5).

References


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