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Photophysical and photochemical studies of sulphonated non-transition metal phthalocyanines in aqueous and non-aqueous media

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Abstract

The photophysical and photochemical parameters for mixed sulphonated metallophthalocyanine complexes ($AlPcS_{mix}$, $SiPcS_{mix}$, $GePcS_{mix}$, $SnPcS_{mix}$, and $ZnPcS_{mix}$) are reported in phosphate buffer saline (PBS, pH 7.4), PBS containing the surfactant Triton X-100, and in dimethylsulphoxide (DMSO). The ground state spectra of $SiPcS_{mix}$, $GePcS_{mix}$ and $SnPcS_{mix}$ show splitting of the Q-band in DMSO, but the fluorescence spectra have only one band, suggesting that only some components of the mixed complexes fluoresce. In general the quantum yields of fluorescence (Φ_F) were smaller in DMSO compared to the aqueous solvents, while quantum yields of triplet state (Φ_T) were larger in DMSO. Triplet lifetimes were much lower in aqueous solutions (compared to DMSO) due to the fact that water absorbs strongly around 1108 nm, which corresponds to the triplet energy of a metallophthalocyanine complex. The $MPcS_{mix}$ complexes quenched hydroquinone, and the Stern–Volmer constants follow the order: $AlPcS_{mix} > SiPcS_{mix} > GePcS_{mix} > ZnPcS_{mix} > SnPcS_{mix}$ which is the order of the extinction coefficients (of the low energy band for complexes with split Q-band) of these molecules. The rate constants for fluorescence, intersystem crossing, internal conversion, and photodegradation were determined from the hydroquinone quenching data.

Keywords: Hydroquinone; Quenching; Sulphonated metallophthalocyanine; Fluorescence lifetime; Triplet quantum yield; Triplet lifetime

1. Introduction

Metallophthalocyanines (MPcs) have found use as conventional dyes and catalysts. In recent times, many MPc derivatives have been synthesized which exhibit properties that make them appropriate for use in optical data storage [1–3], Langmuir–Blodgett films [4,5], chemical sensors [6,7], non-linear optics [8,9] and as photoconducting materials in laser printers [10]. The use of MPcs in visible light-driven processes cannot be over-emphasized; they are being used as photosensitizers in photodynamic therapy (PDT) [11–16] and as active components in light harvesting devices (solar, photoelectrochemical and photovoltaic cells) [17,18].

Attempts to mimic photosynthetic energy capture and electron transfer has been well documented [19–21]. Photosynthesis is a process by which light energy is captured by absorbing pigments and converted into chemical energy. In general, these pigments consist of chlorophylls, quinones and other materials; it is supposed that chlorophyll acts as the absorber while quinone acts as an electron carrier. The thrust behind the electron transfer functions of quinones (e.g. benzoquinone, BQ and hydroquinone, HQ) is their ease of oxidation and reduction, as well as the formation of resonance-stabilized aromatic systems, which make the formation of charge-transfer complexes between them and the excited porphyrin analogues possible.

For efficient light harvesting, it is desirable that the absorbing species be intrinsically highly fluorescent, as it is the supposed fluorescence energy that is converted into chemical energy. Sulphonated non-transition metallophthalocyanines are successful candidates for this application because the central ions do not possess partially filled d-orbitals, which could quench the excited states as soon as they are formed.

The use of MPcs in these light-driven processes provides a justification for the photophysical and photochemical studies

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on these compounds; such studies serve as tools to estimating the photocatalytic abilities of MPc derivatives. This work investigates the photophysics, photochemistry and fluorescence quenching of sulphonated phthalocyanine complexes of Al, Si, Ge, Sn and Zn. The effects of changing the central ions are also considered.

2. Experimental

2.1. Materials

Sulphonated phthalocyanine complexes (containing mixtures of differently substituted derivatives, Fig. 1) of aluminium ($AlPcS_{mix}$), silicon ($SiPcS_{mix}$), germanium ($GePcS_{mix}$), tin ($SnPcS_{mix}$) and zinc ($ZnPcS_{mix}$) were synthesised from the ClAlPc, $(OH)_2SiPc$, $(OH)_2GePc$, $(OH)_2SnPc$ and ZnPc, respectively using fuming sulphuric acid (30% SO_3) in accordance with the method reported in literature for $AlPcS_{mix}$ [22–24]. The starting materials, $(OH)_2SiPc$, $(OH)_2GePc$, $(OH)_2SnPc$ were prepared, purified and characterised according to literature procedures [25]. ZnPc and ClAlPc complexes were obtained from Aldrich. Singlet oxygen quenchers: tetrasodium anthracene-9,10-bis-methylmalonate (ADMA) was a gift from Dr. N. Kuznetsova, and 1,3-diphenyl*iso*benzofuran (DPBF) was purchased from Aldrich. Phosphate buffer saline (PBS, pH 7.4) and DMSO (SAARCHEM) were used as solvents. The surfactant, Triton X-100 and hydroquinone (HQ) were obtained from Aldrich and May and Baker, respectively.

2.2. Equipment

Absorption spectra were recorded on a Varian Cary 500 UV–vis–NIR spectrophotometer. Fluorescence excitation and emission spectra, were recorded on a Varian Eclipse spectrofluorometer. Photo-irradiations were done using a General electric Quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 20 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter. Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Nd:YAG laser (Quanta-Ray, 1.5 J/8 ns) pumping a tunable dye laser (Lambda Physic FL 3002, Pyridine 1 dye in methanol). The analysing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses.

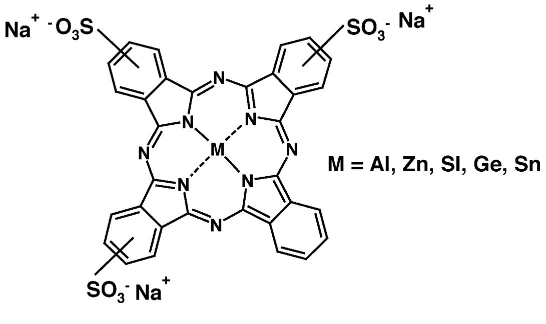

Fig. 1. Molecular structure of sulphonated metallophthalocyanines, showing three sulpho groups.

High-pressure liquid chromatography (HPLC) was performed on Quad-Gradient HPLC system, Agilent 1100 Series; fitted with an analytical column, μBondapak C18 (390 × 3.00 mm) and connected to a variable wavelength UV–vis detector (set at $\lambda = 365$ nm). The mobile phase comprised of 50:50 methanol:water mixture, with a flow rate of 1 ml min^{-1} and sample injection volume of 20 μl.

2.3. Photophysical parameters

Fluorescence quantum yields: Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [26,27]:

$$\Phi_F = \Phi_F(\mathrm{Std}) \frac{F A_{\mathrm{Std}} \eta^2}{F_{\mathrm{Std}} A \eta_{\mathrm{Std}}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence curves of the $MPcS_{mix}$ and the standard, respectively. A and A_{Std} are the respective absorbances of the sample and standard at the excitation wavelengths (which was ∼0.05 in all solvents used), and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Chlorophyll *a* in ether ($\Phi_F = 0.32$) [28], was employed as the standard. Both the sample and standard were excited at the same wavelength.

Triplet quantum yields and lifetimes: The de-aerated solutions of the respective $MPcS_{mix}$ complexes were introduced into a 2 mm × 10 mm spectrophotometric cell and irradiated at the Q-band maxima with the laser system described above. Triplet quantum yields (Φ_T) were determined by the singlet depletion method [29,30]. A comparative method [29,30], Eq. (2), was employed for the calculations.

$$\Phi_T^{\mathrm{Sample}} = \Phi_T^{\mathrm{Std}} \frac{\Delta A_S^{\mathrm{Sample}} \varepsilon_S^{\mathrm{Std}}}{\Delta A_S^{\mathrm{Std}} \varepsilon_S^{\mathrm{Sample}}} \tag{2}$$

where $\Delta A_S^{\mathrm{Sample}}$ and $\Delta A_S^{\mathrm{Std}}$ are the changes in the singlet state absorbances of the $MPcS_{mix}$ complex and standard, respectively; $\varepsilon_S^{\mathrm{Sample}}$ and $\varepsilon_S^{\mathrm{Std}}$, the singlet state extinction coefficients for the $MPcS_{mix}$ complex and standard, respectively. Extinction coefficient values are for the low energy component of the Q-band where this band is split. Irradiation was also carried out at the low energy component of the Q-band. The standards employed were tetrasulphozinc phthalocyanine ($ZnPcS_4$) in aqueous solutions and zinc phthalocyanine

(ZnPc) in DMSO. The triplet quantum yields (Φ_T^{Std}) for the standards are $\Phi_T^{Std} = 0.56$ for ZnPcS$_4$ [31] in aqueous solution and $\Phi_T^{Std} = 0.65$ for ZnPc [32] in DMSO.

Quantum yields of internal conversion were obtained from Eq. (3), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly de-activate the excited singlet state of an MPcS$_{mix}$ complex.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \tag{3}$$

Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

2.4. Singlet oxygen and photodegradation quantum yields

Singlet oxygen (Φ_Δ) and photodegradation (Φ_d) quantum yield determinations were carried out using the experimental set-up described in detail elsewhere [29,33,34]. Typically, a 2 ml portion of the respective MPcS$_{mix}$ solution (absorbance ~0.2 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 29,33,34. Φ_Δ values were determined in air using the relative method with ADMA and DPBF as singlet oxygen chemical quenchers in aqueous solution and DMSO, respectively (Eq. (4)):

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R I_{abs}^{Std}}{R^{Std} I_{abs}} \tag{4}$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard (ZnPcS$_{mix}$, $\Phi_\Delta^{Std} = 0.45$ in aqueous solution) [35] and ZnPc ($\Phi_\Delta^{Std} = 0.67$ in DMSO [29]); R and R^{Std} are the ADMA or DPBF photobleaching rates in the presence of the respective MPcS$_{mix}$ and standard, respectively; I_{abs} and I_{abs}^{Std} are the rates of light absorption by the MPcS$_{mix}$ and standard, respectively. The concentrations of ADMA and DPBF in the solutions were calculated using the determined values of $\log \varepsilon = 4.1$ at 380 nm (ADMA in aqueous solution) and $\log \varepsilon = 4.36$ at 417 nm (DPBF in DMSO). The light intensity used for Φ_Δ determinations was found to be 5.35×10^{15} photons s^{-1} cm^{-2}. The error in the determination of Φ_Δ was ~10% (determined from several Φ_Δ values). Photodegradation quantum yields were determined using Eq. (5),

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

where C_0 and C_t are the MPcS$_{mix}$ concentrations before and after irradiation respectively, V 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 MPcS$_{mix}$. A light intensity of 4.82×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.5. Fluorescence quenching by hydroquinone

Fluorescence quenching experiments on the various MPcS$_{mix}$ complexes were carried out by the addition of different concentrations of HQ to a fixed concentration of the complex, and the concentrations of HQ in the resulting mixtures were 0, 0.008, 0.024, 0.032, 0.040 and 0.048 M. The fluorescence spectra of MPcS$_{mix}$ complexes at each HQ concentration were recorded, and the changes in fluorescence intensity related to HQ concentration by the Stern–Volmer (SV) equation [36]:

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \tag{6}$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively; $[Q]$ the concentration of the quencher, and K_{SV} is the Stern–Volmer constant; and is the product of the bimolecular quenching constant (k_Q) and the fluorescence lifetime τ_F, i.e.

$$K_{SV} = k_Q \tau_F \tag{7}$$

The ratios I_0/I were calculated and plotted against $[Q]$ according to Eq. (6), and K_{S-V} determined from the slope.

The bimolecular rate constant for diffusion-controlled reactions (k_D) is related to the bimolecular quenching constant (k_Q) by Eq. (8) [37]:

$$k_Q = f k_D \tag{8}$$

where f is the quenching efficiency.

The bimolecular rate constant (k_D) can be obtained from the Einsten–Smoluchowski relationship:

$$k_D = \frac{4\pi N_A (D_f + D_q)(r_f + r_q)}{1000} \tag{9}$$

where N_A is the Avogadro's number; D_f and D_q, the diffusion coefficients of the fluorophore and quencher, respectively and r_f and r_q are the radii of fluorophore and quencher, respectively.

The diffusion coefficient D is given by the Stokes' equation (Eq. (10)) [37].

$$D = \frac{kT}{6\pi\eta r} \tag{10}$$

where k is the Boltzmann constant; T the absolute temperature; η the solvent's viscosity and r the fluorophore or quencher radius.

k_Q values may be determined from Eq. (8) using the calculated k_D value, provided that f is known. From the values of k_Q, the values of τ_F can then be calculated using Eq. (7).

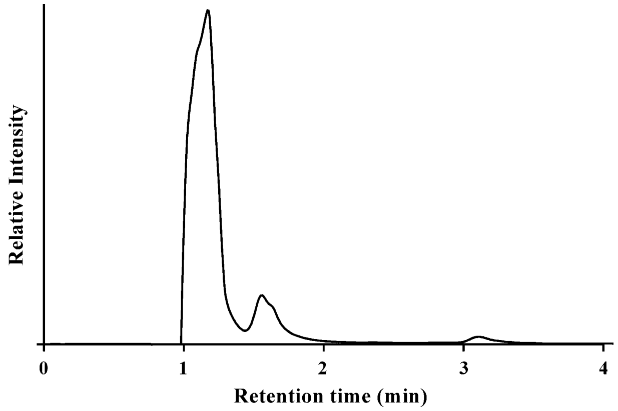

Fig. 2. HPLC trace for $GePcS_{mix}$.

3. Results and discussion

3.1. HPLC studies

$MPcS_{mix}$ complexes containing a mixture of sulphonated (mono-, di-, tri- and tetra-) are important to study (as mixtures) since $AlPcS_{mix}$ for example, is already in use for PDT. However, the composition of the prepared $MPcS_{mix}$ complexes may vary from batch to batch. For the studies presented in this work, the same batch of each complex was employed. In an attempt to characterise the mixture in these complexes HPLC was employed (Figs. 2 and 3). The component fractions in an $MPcS_{mix}$ preparation are known to possess different degrees of sulphonation. It is expected that the most highly sulphonated (most soluble) would be the first to be eluted from the chromatographic column, and so give the lowest retention time and that the monosulphonated fractions give the highest retention times [24]. For the five $MPcS_{mix}$ samples, the HPLC signals with the lowest retention times (~1 min) are assigned to the tetrasulphonated fractions, using tetrasulphozinc phthalocyanine (ZnTSPc) as reference, Figs. 2 and 3.

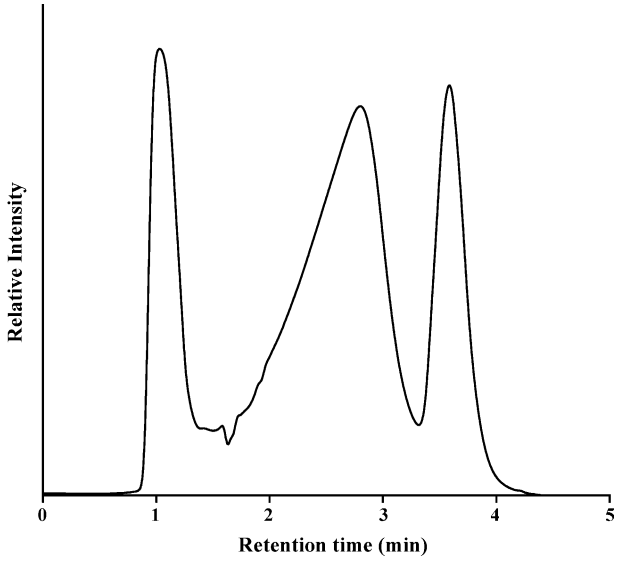

Fig. 3. HPLC trace for $ZnPcS_{mix}$.

$AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$, gave similar HPLC traces (Fig. 2) which consisted of a cluster of signals in the low-retention-time part of the HPLC traces (Fig. 2). This implies the prevalence of fractions with higher degree of sulphonation in these species. $ZnPcS_{mix}$ and $SnPcS_{mix}$ gave similar traces (Fig. 3), with appreciable signals in the relatively high retention time regions of the HPLC traces. These observations suggest the prevalence of the highly sulphonated fractions in $AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$, while in $ZnPcS_{mix}$ and $SnPcS_{mix}$, the less sulphonated fractions are prevalent. The degree of aggregation in PBS increases with lipophilicity hence the prevalence of the less sulphonated fractions in solution is expected to increase aggregation.

3.2. Spectrophotometric studies

Fig. 4 shows the ground state electronic absorption spectra of the $MPcS_{mix}$ complexes in PBS 7.4. Fig. 4a shows a broad spectra for $SnPcS_{mix}$ and $ZnPcS_{mix}$ complexes. $SiPcS_{mix}$ (as well as $GePcS_{mix}$) shows a split Q-band (Fig. 4b), which may suggest that this species is aggregated in aqueous solution.

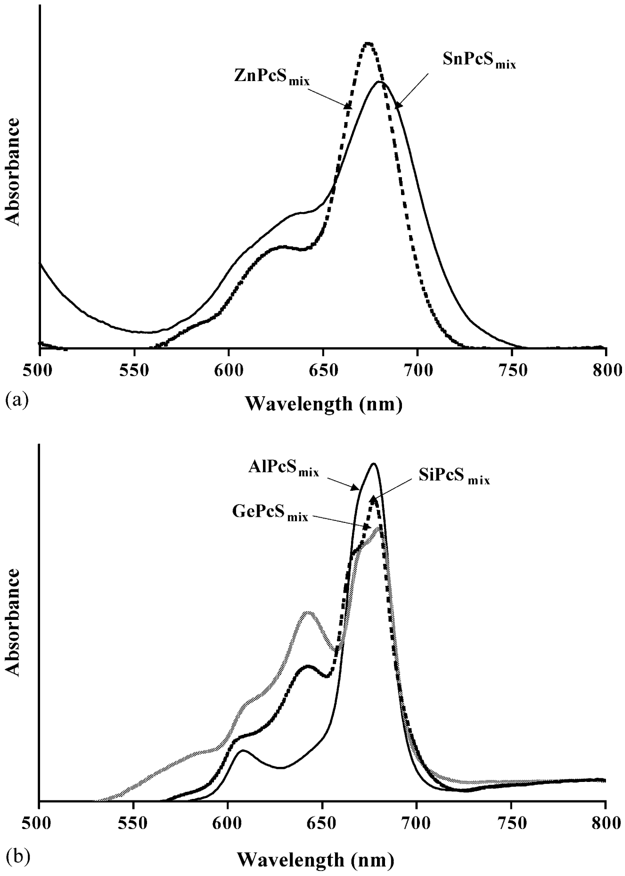

Fig. 4. Ground state electronic absorption spectra of: (a) the aggregated complexes: $ZnPcS_{mix}$ and $SnPcS_{mix}$, and (b) the non-aggregated complexes: $AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$ in PBS 7.4. Concentrations ~ 8.0×10^{-6} mol dm^{-3}.

However, addition of a surfactant, Triton X-100 to the solution of $SiPcS_{mix}$ (or $GePcS_{mix}$) brought about no observable change in both spectral intensity and position, implying that the complex is essentially monomeric. The splitting in Q-bands of $SiPcS_{mix}$ and $GePcS_{mix}$ was attributed [22] to the presence of a mixture of compounds with varying extents of sulphonation, with the different components absorbing at different wavelengths. $AlPcS_{mix}$ is monomeric even at concentrations as high as 10^{-4} mol dm^{-3}, as judged by lack of deviation from Beer's law. Also addition of Triton X-100 had no effect on the spectra of $AlPcS_{mix}$ in PBS 7.4. However, the Q-band for $AlPcS_{mix}$ is slightly broadened as has been observed before [38]; again this may be attributed to differently absorbing components of the mixture. Addition of Triton X-100 to aqueous solutions of $SnPcS_{mix}$ and $ZnPcS_{mix}$ brought about the narrowing and increase in the intensity of the band due to the monomeric species (Fig. 5). These spectral changes are consistent with monomerization [22], confirming the presence of aggregates in these complexes in aqueous solutions.

Thus the lack of aggregation in $AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$ could be due to the prevalence of fractions with higher degree of sulphonation. This was attested by HPLC results above, which showed the presence of mainly the highly sulphonated derivatives in the mixture for $AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$. It is known [39] that sulphonated aluminium phthalocyanine containing three sulphonate substituents is not aggregated in solution.

In DMSO, all five $MPcS_{mix}$ complexes show monomeric behaviour at concentrations up to 10^{-5} mol dm^{-3}, in that Beer's law was obeyed. It is known that MPc complexes show monomeric behaviour in DMSO and other organic solvents [40]. $AlPcS_{mix}$ (Fig. 6a) still showed slight broadening in DMSO consistent with the presence of mixtures absorbing at different wavelengths. However, the spectra for $SiPcS_{mix}$, $GePcS_{mix}$ and $SnPcS_{mix}$ (Fig. 6b), still showed split behaviour in DMSO, attributed to the presence of differently absorbing substituted fractions in solution.

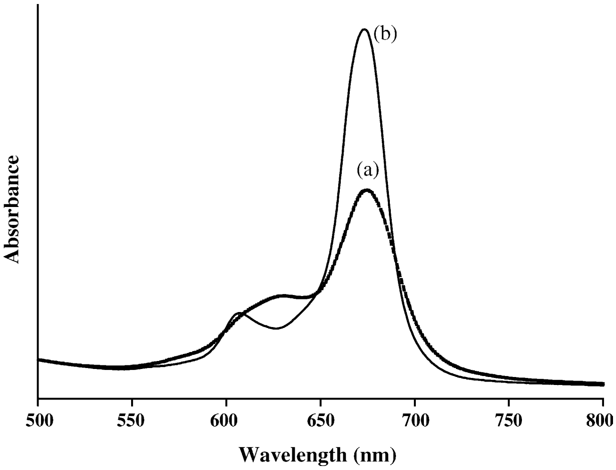

Fig. 5. Electronic absorption spectra of $ZnPcS_{mix}$ in PBS 7.4 (a) and in the presence of Triton X-100 (b). Concentration of $ZnPcS_{mix}$ = 5×10^{-6} M and for Triton X-100 = 0.02 M.

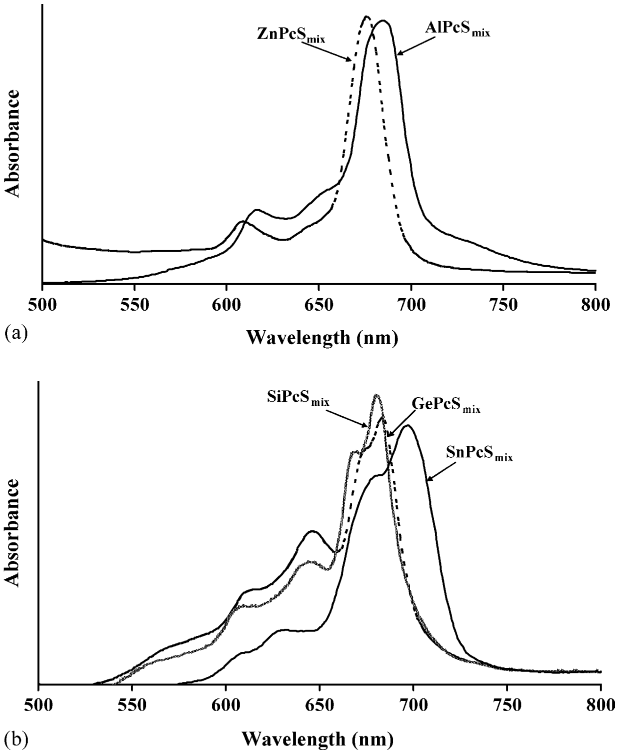

Fig. 6. Ground state electronic absorption spectra of (a) $AlPcS_{mix}$ and $ZnPcS_{mix}$, and (b) $SnPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$ in DMSO concentrations ~ 4.0×10^{-6} mol dm^{-3}).

For $SiPcS_{mix}$ and $GePcS_{mix}$, absorption and fluorescence excitation spectra are similar, but not mirror images of the fluorescence emission spectrum, Fig. 7, in PBS 7.4. Fig. 8 shows the UV–vis absorption, fluorescence and excitation spectra of $ZnPcS_{mix}$ in PBS 7.4. Obviously, there is a lack of agreement between the absorption and fluorescence excitation spectra. The band around 630 nm, associated with the dimer is not seen in the fluorescence excitation spectrum; which suggests

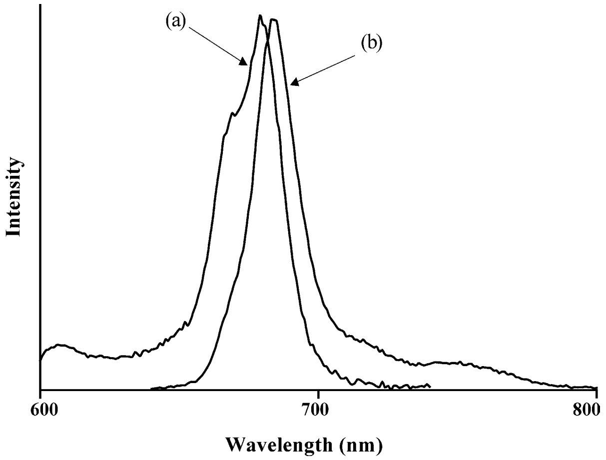

Fig. 7. Normalized fluorescence excitation (a) and emission (b) spectra of $SiPcS_{mix}$ in PBS 7.4.

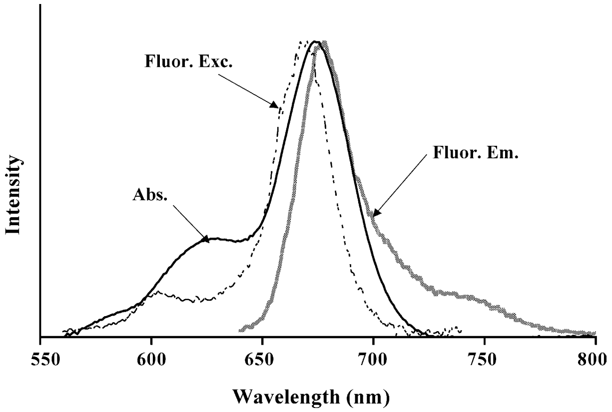

Fig. 8. Normalized absorption and fluorescence spectra of ZnPcS$_{mix}$ in PBS 7.4.

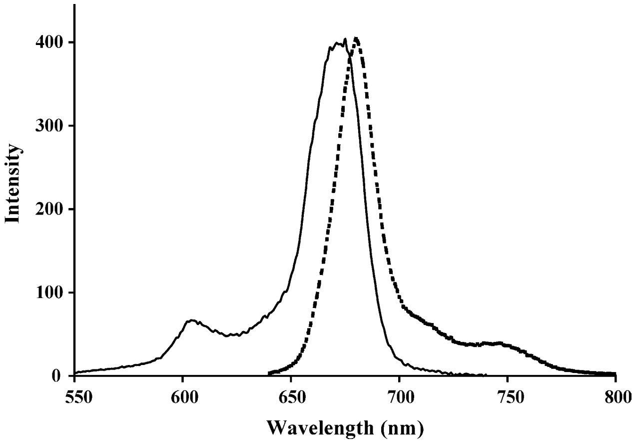

Fig. 9. Fluorescence excitation (a) and emission (b) spectra of AlPcS$_{mix}$ in PBS 7.4.

that it is only the monomer that fluoresces. A similar behaviour was observed for SnPcS$_{mix}$. In both cases, the λ_{max} of absorption are different from those of fluorescence excitation, which implies that the absorbing species are somewhat different from the fluorescing species. For AlPcS$_{mix}$ (in PBS 7.4) the absorption and fluorescence excitation spectra are in close agreement, suggesting that the absorbing species is also the fluorescing species, and the fluorescence emission spectrum of AlPcS$_{mix}$ is a mirror image of its excitation spectrum, Fig. 9.

In DMSO, the absorption and fluorescence excitation spectra of AlPcS$_{mix}$ and ZnPcS$_{mix}$ are similar and are mirror images of their emission spectra. However, for SiPcS$_{mix}$, GePcS$_{mix}$ and SnPcS$_{mix}$, single Q-bands were observed in the fluorescence excitation spectra, in contrast with the split Q-bands in these complexes' absorption spectra (Fig. 6); probably suggesting that not all components of each mixture are equally fluorescent.

3.3. Fluorescence, triplet quantum yields and triplet lifetimes

The general photophysical and photochemical parameters of the MPcS$_{mix}$ complexes are listed in Table 1. Solvent parameters such as polarity, viscosity refractive index and the presence of heavy atoms in the solvent molecule, are widely known to influence the yield of fluorescence. It is important to state that since the MPcS$_{mix}$ are a mixture of sulphonated MPc complexes, the determined photochemical and photochemical parameters are an average for each mixture. The Φ_F values in Table 1 demonstrate the influence of the environment of the fluorescing molecules on their fluorescence efficiency. In a particular solvent (PBS 7.4 or DMSO), fluorescence quantum yield (Φ_F) values are larger for MPc complexes containing lighter atoms (e.g. Al), and smaller for those MPc complexes containing heavier atoms (e.g. Ge and Zn); this is attributed to the heavy atom effect, which results in

Table 1
Photophysical and photochemical parameters of MPcS$_{mix}$ in aqueous and non-aqueous media

	Solvent	λ_Q (nm) (log ε)[a,b]	λ_F (nm)	τ_T ((s)	Φ_F[c]	Φ_T[c]	Φ_{IC}	Φ_d[c] ($\times 10^5$)	Φ_Δ[c]	S_Δ[c]
AlPcs$_{mix}$	PBS	674 (5.18)	677	2.93	0.44	0.44	0.12	0.40	0.42	0.95
	DMSO	685 (5.23)	690	800	0.39	0.52	0.09	5.79	0.48	0.92
SiPcS$_{mix}$	PBS	678 (5.11)	682	2.90	0.34	0.45	0.21	0.71	0.49	1.09
	DMSO	680 (5.07)	685	430	0.29	0.58	0.13	7.35	0.52	0.90
GePcS$_{mix}$	PBS	680 (5.01)	686	2.76	0.30	0.67	0.03	0.45	0.68	1.01
	DMSO	685 (5.03)	692	760	0.21	0.79	0.01	9.74	0.78	0.99
SnPcS$_{mix}$	PBS	688 (4.57)	699	2.52	0.05	0.59	0.36	1.59	0.42	0.71
	PBS/TX[d]	680	684,700	2.32	0.19	0.68	0.13	4.13	0.52	0.77
	DMSO	696 (4.95)	684,701	120	0.13	0.87	0.01	14.01	0.65	0.75
ZnPcS$_{mix}$	PBS	673 (4.89)	677	2.95	0.16	0.53	0.31	3.65	0.45	0.85
	PBS/TX[d]	673	683	2.37	0.21	0.61	0.18	7.02	0.54	0.89
	DMSO	675 (5.14)	682	530	0.14	0.86	0.01	13.65	0.72	0.84

The values are average for the mixed complexes.

[a] Q-band maxima shown for the low energy band only where bands are split.

[b] The log ε values are for the low energy band where there are more than two bands.

[c] Values in PBS 7.4 have been reported before [22].

[d] TX = Triton X-100.

intersystem crossing for the heavier atoms hence, less fluorescence, as observed before [22] in PBS solutions. Aggregation in the fluorescing molecules also exerts a major influence on the fluorescence quantum yield. In aqueous solutions, where they form aggregates, $SnPcS_{mix}$ and $ZnPcS_{mix}$ show significantly lower Φ_F values than the non-aggregated complexes. Aggregation dissipates the electronic energy of the excited singlet state, thereby lowering the likelihood of fluorescence. Any procedure that results in the monomerization of aggregates will ultimately give rise to an enhanced fluorescence. This is seen in the notable increase in Φ_F values of $SnPcS_{mix}$ and $ZnPcS_{mix}$ (in PBS 7.4) in the presence of Triton X-100. However, Triton X-100 had no effect on the Φ_F values for the Ge, Si and Al complexes. Contrary to what might be expected on grounds of DMSO's higher viscosity than water, Φ_F values were found to be lower in DMSO than in PBS 7.4, except for $SnPcS_{mix}$. This observation may be attributed to the presence of relatively heavier atoms in DMSO than in water, which would tend to favour intersystem crossing rather than fluorescence. As will be seen shortly, quantum yields of triplet formation are consistently higher in DMSO than in PBS 7.4.

Φ_T values depended on the heavy atom effect as well as on aggregation. In PBS 7.4 where they are aggregated, $SnPcS_{mix}$ and $ZnPcS_{mix}$ have lower Φ_T values than are expected on the premise of heavy atom effect; this is expressed by the lower Φ_T value for $SnPcS_{mix}$ than for $GePcS_{mix}$ (Table 1). However, in DMSO, $SnPcS_{mix}$ gave the highest Φ_T value, as it showed no aggregation in this solvent. In both solvents, the Φ_T values for $AlPcS_{mix}$ and $SiPcS_{mix}$ are consistently lower than for others; this observation is indicative of the smaller atomic masses of Al and Si compared to Ge Sn and Zn. Comparing Φ_T values in different media, higher values were obtained in DMSO than in PBS 7.4 (or PBS 7.4 plus Triton X-100); this observation reinforces our earlier proposition that intersystem crossing is favoured in DMSO than in aqueous solution. As expected, the presence of Triton X-100 gave increased Φ_T values for the hitherto aggregated $SnPcS_{mix}$ and $ZnPcS_{mix}$ in aqueous solutions; monomers have greater tendencies to undergo intersystem crossing because less energy is lost through internal conversion.

The determination of Φ_F and Φ_T values for the $MPcS_{mix}$ complexes paved the way for the calculation of internal conversion quantum yield (Φ_{IC}), Eq. (3). Table 1 shows that in PBS 7.4, Φ_{IC} values are higher for the aggregated species than for the monomeric ones, which is due to the dissipation of electronic energy by the aggregates. As earlier stated, aggregation hinders fluorescence and intersystem crossing; hence most of the electronic energy of the excited singlet state is lost through internal conversion to the ground singlet state. Φ_{IC} values are higher in PBS 7.4 (or PBS 7.4 plus Triton X-100) than in DMSO, which suggests that the molecules are more photoactive in DMSO than in aqueous solutions. Φ_{IC} is drastically reduced for $SnPcS_{mix}$ and $ZnPcS_{mix}$ in PBS 7.4 in the presence of Triton X-100, due to the monomerizing effect of this surfactant. In DMSO, Φ_{IC} values for the heavier atom $MPcS_{mix}$ (M = Ge, Sn and Zn) are close to zero.

Triplet lifetimes (τ_T) among the $MPcS_{mix}$ complexes do not vary in a well-defined fashion in Table 1. Ordinarily, one would expect lower τ_T values for complexes containing heavy metals or metalloids; although this is manifested to some extent in DMSO (Table 1), with $AlPcS_{mix}$ (800 μs) showing the highest and $SnPcS_{mix}$ (120 μs) showing the lowest τ_T values, the observed trend among the five species does not strictly conform to that predicted on the basis of heavy atom effect.

There is a striking increase in τ_T values on going from PBS 7.4 (or PBS 7.4 plus Triton X-100) to DMSO among all the complexes. Also, triplet lifetimes for $SnPcS_{mix}$ and $ZnPcS_{mix}$ are slightly lower in the presence of Triton X-100, in spite of monomerization. It is possible that molecular vibrations in Triton X-100 could accelerate triplet quenching, suggesting that solvent effect in this case overrides that of monomerization by Triton X-100. These observations demonstrate that the effect of solvents on the triplet lifetimes of MPc complexes cannot be overstressed. We recently discussed the effects of solvent on the triplet lifetime of $ZnPcS_{mix}$ in terms of the near IR absorption of the various solvents [29]. The energy of the triplet states of most MPc derivatives is ~1.12 eV (~1108 nm) [29], where water has a very broad and intense absorption. This implies that water would ordinarily quench the triplet states of MPc derivatives, and this is responsible for the short triplet lifetimes in aqueous solutions. The absorption of DMSO at ~1108 nm is not as broad and intense as that of water; hence longer triplet lifetimes are predicted in DMSO. In PBS 7.4, triplet lifetimes ranged from 2.52 nm ($SnPcS_{mix}$) to 2.95 nm ($ZnPcS_{mix}$); there is no particular trend in the variation of τ_T values (in PBS 7.4) among the five complexes. We think that the triplet quenching of these complexes is PBS 7.4 is so severe that the heavy atom effect on intersystem crossing (from the triplet state to the ground singlet state) becomes insignificant in this solvent.

3.4. Singlet oxygen and photodegradation quantum yields

Singlet oxygen is most commonly produced by photosensitization from the triplet state of photosensitizers. Consequently, singlet oxygen quantum yield (Φ_Δ) should depend on the triplet quantum yield and lifetime of the photosensitizer. In fact, it is expected that the trend in variation of Φ_Δ within an array of photosensitizers should be parallel to variations in their Φ_T and τ_T values. Among the $MPcS_{mix}$ complexes studied, the trend observed for Φ_Δ variation is almost the same as that observed for Φ_T; e.g. $GePcS_{mix}$ has the largest Φ_T and Φ_Δ values in PBS 7.4, while these values are the lowest for $AlPcS_{mix}$ in the same solvent. Hence the explanations made for Φ_T variation among the complexes should also be also valid for Φ_Δ variation. As expected, for $ZnPcS_{mix}$ and $SnPcS_{mix}$, Φ_Δ values are lower in PBS 7.4 than in DMSO, and values in the presence of Triton X-100 are also higher than those in PBS 7.4 alone.

The efficiency of energy transfer from the triplet state of a photosensitizer to ground state molecular oxygen is quantified by S_Δ. S_Δ is the fraction of the triplet state quenched by ground state molecular oxygen, and the values for the $\mathrm{MPcS_{mix}}$ complexes are listed in Table 1. From the table we can conclude that S_Δ values do not depend significantly on the solvent, but depend largely on aggregation. In PBS 7.4, S_Δ values are conspicuously lower for the aggregated species ($\mathrm{SnPcS_{mix}}$ and $\mathrm{ZnPcS_{mix}}$) than for the other three as discussed before [22]. Definitely, some electronic energy must have been lost to the aggregates rather than being quenched by oxygen. The composition of the respective $\mathrm{MPcS_{mix}}$ complexes could also influence the values of S_Δ. For all three monomeric $\mathrm{MPcS_{mix}}$ complexes ($\mathrm{AlPcS_{mix}}$, $\mathrm{SiPcS_{mix}}$ and $\mathrm{GePcS_{mix}}$), S_Δ values are >0.9, implying efficient photosensitization.

Photodegradation (photobleaching) quantum yield (Φ_d) is a measure of the stability of a molecule under photoirradiation. It is supposed [41] that photobleaching is a singlet oxygen-mediated process; hence its efficiency should depend on the value of Φ_Δ. However, Φ_d values are higher (considering the same solvent) for $\mathrm{SnPcS_{mix}}$ and $\mathrm{ZnPcS_{mix}}$ which have lower Φ_Δ values than $\mathrm{GePcS_{mix}}$; this implies that $\mathrm{MPcS_{mix}}$ photodegradation is probably not initiated by singlet oxygen alone. The excited triplet state of a photosensitizer is sufficiently long lived to intercept other species in solution, thus photobleaching is most likely to have taken place in the triplet state. It therefore follows that Φ_d values should also depend on the values of Φ_T. Φ_d values are higher in DMSO than in PBS 7.4 and also higher in the presence of Triton X-100 for the aggregated species ($\mathrm{SnPcS_{mix}}$ and $\mathrm{ZnPcS_{mix}}$).

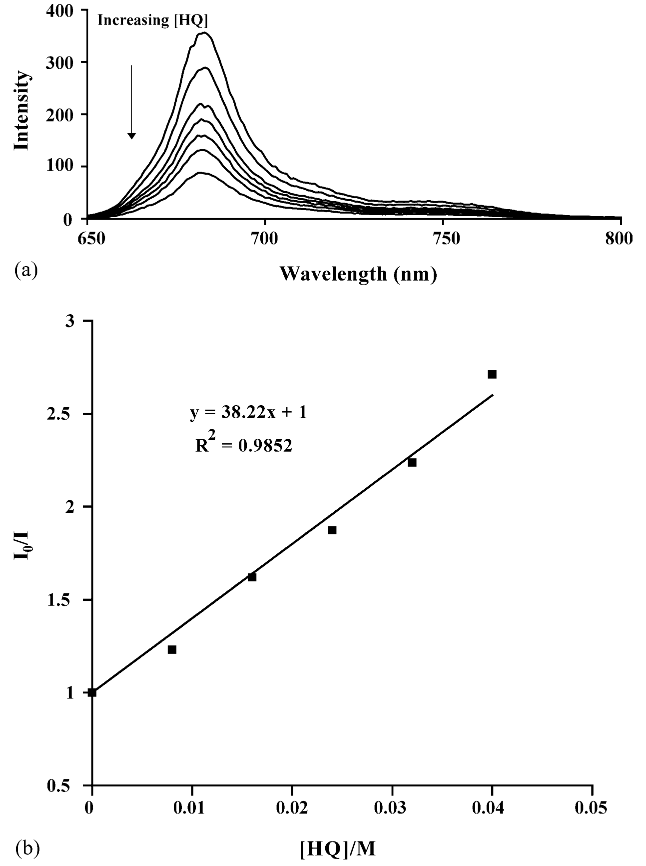

Fig. 10. (a) Fluorescence emission spectral changes of $\mathrm{SiPcS_{mix}}$ (3.12×10^{-6} mol dm^{-3}) on addition of increasing concentrations of HQ. [HQ] = 0.008, 0.016, 0.024, 0.032, 0.040, 0.048 mol dm^{-3}. (b) Stern–Volmer plot for HQ quenching of $\mathrm{SiPcS_{mix}}$.

3.5. Fluorescence quenching by hydroquinone

In the presence of HQ quencher, a reaction takes place between the excited $\mathrm{MPcS_{mix}}$ and the HQ molecules. According to Darwent et al. [38], the following mechanism holds for the reaction:

$$\mathrm{MPcS}^{*}_{\mathrm{mix}} + \mathrm{BQH_2} \rightarrow (\mathrm{MPcS_{mix}}{}^{\bullet-} \cdots \mathrm{BQ}^{\bullet-}) + 2\mathrm{H}^{+} \qquad (15)$$

(HQ could also be represented as $\mathrm{BQH_2}$, where BQ is benzoquinone).

The fluorescence quenching of $\mathrm{MPcS_{mix}}$ by hydroquinone (HQ) in PBS 7.4 was found to obey Stern–Volmer kinetics (Fig. 10), which is consistent with diffusion-controlled bimolecular reactions. Only the Stern–Volmer dependence of quenching of $\mathrm{AlPcS_{mix}}$ by HQ in aqueous solution has been reported before [38]. K_SV values for the HQ quenching of $\mathrm{MPcS_{mix}}$ are listed in Table 2. The observed order of the values is $\mathrm{AlPcS_{mix}} > \mathrm{SiPcS_{mix}} > \mathrm{GePcS_{mix}} > \mathrm{ZnPcS_{mix}} > \mathrm{SnPcS_{mix}}$. It is interesting to note that this is the exact order of molar extinction coefficients (in PBS 7.4, Table 1) of the respective complexes. The molar extinction coefficient value is an indication of the population of molecules in the excited singlet state of the sensitizer; and since the interaction of the excited molecules with HQ is diffusion-controlled, it follows from collision theory of reaction rates that the higher the number of molecules in the excited state, the higher the likelihood of collision; and the more collisions there are, the greater the quenching constant (K_SV). Aggregation, coupled with the relatively low molar extinction coefficients results in the low K_SV values for $\mathrm{SnPcS_{mix}}$ and $\mathrm{ZnPcS_{mix}}$.

The bimolecular quenching constant (k_Q) values for the complexes were calculated according to Eqs. (8)–(10), assuming that the efficiency (f) of $\mathrm{MPcS_{mix}}$-HQ collision is unity (HQ quenches the fluorescence of $\mathrm{MPcS_{mix}}$ complexes effectively) [38]. Using the values of $\sim 7.7 \times 10^{-10}$ m and 3.9×10^{-10} m for molecular radii of an MPc molecule [42] and HQ [43], respectively (assuming that a change of the central metal ion has little effect on the molecular radius of the MPc backbone); the bimolecular rate constant (k_D) value for the HQ-quenching of each $\mathrm{MPcS_{mix}}$ species was found to be 8.4×10^{9} M^{-1} s^{-1}. From the values of K_SV and k_Q, the fluorescence lifetimes (τ_F) could be calculated according to Eq. (7). The τ_F values obtained using this semi-empirical approach compares well with literature values for $\mathrm{AlPcS_{mix}}$ ($\tau_\mathrm{F} = 5.00$ ns [24,38]) and $\mathrm{ZnPcS_{mix}}$ ($\tau_\mathrm{F} = 2.90$ ns [31]).

Table 2
Rate constants for various excited state deactivation processes of MPcSmix complexes in PBS 7.4; $k_D = 8.4 \times 10^9$ M^{-1} s^{-1}

	K_{SV} (M^{-1})	τ_F (ns)	k_F (s^{-1})[a]	k_{ISC} (s^{-1})[b]	k_{IC} (s^{-1})[c]	k_d(s^{-1})[d]
$AlPcS_{mix}$	44.86	5.34 (5.00)[e]	8.24×10^7	8.24×10^7	2.25×10^7	1.37
$SiPcS_{mix}$	38.22	4.55	7.47×10^7	9.89×10^7	4.62×10^7	2.45
$GePcS_{mix}$	36.29	4.32	6.94×10^7	1.55×10^8	6.94×10^6	1.63
$SnPcS_{mix}$	17.05	2.03	2.46×10^7	2.91×10^8	1.77×10^8	6.31
$ZnPcS_{mix}$	23.35	2.78 (2.90)[f]	5.76×10^7	1.91×10^8	1.12×10^8	12.37

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] k_{ISC} is the rate constant for intersystem crossing. Values calculated using $k_{ISC} = \Phi_T/\tau_F$.
[c] k_{IC} is the rate constant for internal conversion. Values calculated using $k_{IC} = \Phi_{IC}/\tau_F$.
[d] k_d is the rate constant for photodegradation. Values calculated using $k_d = \Phi_d/\tau_T$.
[e] Literature values ([24,38].
[f] Literature values [31].

The determination of τ_F afforded the calculation of the rate constants for the intrinsic processes (k_F, k_{IC}, k_{ISC}) from quantum yield values of the respective processes (see legend to Table 2). The rate constant values of processes deactivating the excited states of the $MPcS_{mix}$ complexes are listed in Table 2. Rate constants for fluorescence (k_F) ranged from 2.46×10^7 s^{-1} ($SnPcS_{mix}$) to 8.24×10^7 s^{-1} ($AlPcS_{mix}$); while k_{ISC} values range from 8.24×10^7 s^{-1} ($AlPcS_{mix}$) to 2.91×10^8 s^{-1} ($SnPcS_{mix}$). These opposite orders emphasize the importance of heavy atom effect and aggregation on the rate constant values. k_{IC} values for $SnPcS_{mix}$ and $ZnPcS_{mix}$ are higher than those for their monomeric counterparts. Rate constants for photodegradation (k_d, Table 2) are larger for the aggregated species ($SnPcS_{mix}$ and $ZnPcS_{mix}$) than for the non-aggregated ones.

In conclusion, this work presents an insight into the photophysical and photochemical properties of mixed sulphonated metallophthalocyanine complexes of Al, Si, Ge, Sn and Zn, which were found to be greatly dependent on the central ions, as well as solvents. Since these $MPcS_{mix}$ complexes are a mixture of differently substituted derivatives, the determined photochemical and photophysical parameters are an average for the whole mixture. Triplet and singlet oxygen quantum yield values suggest that the $MPcS_{mix}$ complexes are potential candidates for photocatalytic applications in for example, PDT and photodegradation of pollutants. The appreciable quenching of $MPcS_{mix}$ fluorescence by hydroquinone can be exploited in the conversion and storage of solar energy, which makes these complexes equally applicable as light harvesters in molecular photonics. In-depth photophysical studies of photosensitizers are usually hampered by the non-availability of their fluorescence lifetime data; determination of fluorescence lifetimes involves the use of high-level equipment, which is beyond the reach of many researchers. This work provides a simple route to the determination of fluorescence lifetimes of photosensitizers from familiar fluorescence quenching experiments. The lifetime values obtained here compared well with typical literature values. The determined photochemical and photophysical parameters gives an idea as to how the different central ions compare in influencing these parameters. These studies have shown of $GePcS_{mix}$ has the best photosensitising abilities, and hence has a potential for future PDT applications.

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