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Photophysicochemical and fluorescence quenching studies of tetra- and octa-carboxy substituted silicon and germanium phthalocyanines

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ABSTRACT

Spectral, photophysical and photochemical properties of tetra- and octa-carboxy substituted metallophthalocyanines containing silicon and germanium as central metals ($(OH)_2$GeTCPc, $(OH)_2$SiTCPc, $(OH)_2$GeOCPc and $(OH)_2$SiOCPc) have been studied in dimethylsulfoxide (DMSO) and the trends in triplet, fluorescence, singlet oxygen quantum yields and triplet lifetimes are described for these compounds. The GePc derivatives exhibited high triplet quantum yields ($\Phi_T = 0.79$ for $(OH)_2$GeOCPc and 0.82 for $(OH)_2$GeTCPc compared to $\Phi_T = 0.66$ for $(OH)_2$SiTCPc and 0.48 for $(OH)_2$SiOCPc) due to the spin–orbit coupling induced by Ge(IV). The triplet lifetimes were higher for MOCPc ($\tau_T = 760$ µs for $(OH)_2$SiOCPc and 480 µs for $(OH)_2$GeOCPc compared to $\tau_T = 210$ µs for $(OH)_2$SiTCPc and 260 µs for $(OH)_2$GeTCPc). The fluorescent states of the metallophthalocyanine (MPc) complexes were effectively quenched by benzoquinone (BQ) and the quenching course was found to follow a diffusion-controlled (dynamic) bimolecular mechanism. Theoretical values of bimolecular rate constant for the interaction of the complexes with BQ were determined using the Stokes–Einstein–Smoluchowski model, and values together with the Stern–Volmer quenching constants were used in calculating the fluorescence lifetimes of the complexes.

1. Introduction

The applications of porphyrin-type compounds such as metallophthalocyanines (MPcs) in photochemical and photobiological reactions are well established [1,2]. The applications of MPcs in photodynamic therapy (PDT) of cancer [3–5] have been made possible by their high triplet quantum yields and long triplet lifetimes, followed by oxygen quenching of their triplet states to produce singlet oxygen, which is the cytotoxic species. MPc complexes containing central metals with filled d-orbitals have been found to result in these high triplet yields and long lifetimes, which are required for efficient photosensitization [6–8]. MPcs are known for their light harvesting capability and their ability to undergo excited state charge transfer with ease [9,10] which makes them suitable in mimicking the photosynthetic process. Such excited state charge transfer have been favoured between some MPcs singlet excited state and quinones [9–14]. Charge transfer between benzoquinone (BQ) and $MPcS_{mix}$ complexes, containing a mixture of differently sulfonated derivatives and M = Ge, Si, Sn, Zn and Al [11] as well as tetra-carboxy (MTCPc) and octa-carboxy (MOCPc) derivatives containing Al and Zn as central metals [12] have been reported. When ZnPc containing benzyloxyphenoxy ligands was employed for charge transfer studies with benzoquinone, loss of symmetry due to protonation was observed [13]. The differences in molecular volume were proposed to be responsible for the trends in the variation of quenching constants, whereby the greater the molecular volume of the fluorophore, the more efficient the apparent static quenching [11].

Thus, in this work, we present a study of the light harvesting and energy transducing tendencies of tetra- and octa-carboxy substituted silicon and germanium metal phthalocyanines in the presence of 1,4-benzoquinone. It is important for light harvesters to possess appreciable photoactivity. Photophysicochemical studies on some phthalocyanine carboxylates have been documented [12,15–17] and they have shown to be promising candidates for photosensitization reactions. MPc derivatives incorporated with silicon or germanium metals show efficient intersystem crossing to the triplet state resulting in high triplet state yields, which are required for photosensitized reactions [9,18]. Silicon and germanium tetracarboxy phthalocyanines are not known, though their octa-carboxy counterparts have been reported [19]. However, their energy transducing tendencies have not been reported. Systematic investigation of the photophysical and photochemical properties of these carboxy substituted silicon and germanium phthalocyanine derivatives in dimethylsulfoxide (DMSO) is carried out in this work. Solvent reorganization energy during processes of charge transfer is also examined since sensitivity of reorganization energy to solvent is a major concern in electron transfer processes [20].

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2. Experimental and methods

2.1. Materials

1,4-Benzoquinone, cremophore EL (CEL) and 3-diphenylisobenzofuran (DPBF) were purchased from Aldrich and dimethylsulfoxide (DMSO, SAARCHEM) was dried before use. All other reagents were obtained from commercial supplies and used as received. Silicon ($(OH)_2SiOCPc$) and germanium ($(OH)_2GeOCPc$) octacarboxylphthalocyanines were synthesized, purified and characterized according to literature methods [21] while silicon ($(OH)_2SiTCPc$) and germanium ($(OH)_2GeTCPc$) tetracarboxylphthalocyanines were synthesized, purified and characterized according to literature methods (for the corresponding CuTCPc, FeTCPc and CoTCPc) with slight modification [17,22].

Briefly, finely ground mixture of trimellitic acid anhydride (4.8 g, 25 mmol), urea (15 g, 250 mmol) ammonium chloride (0.27 g, 0.5 mmol), ammonium molybdate (0.6 g, 0.5 mmol) and metal salt (15 mmol) ($SiCl_4$ for $(OH)_2SiTCPc$ and $GeCl_4$ for $(OH)_2GeTCPc$) was heated under reflux at 185 °C for 4 h. The dark coloured solid was filtered off and washed with methanol and dried overnight at 100 °C to yield the tetraamide complex. The solid was then boiled with 275 ml of 1 mol dm^{-3} HCl saturated with NaCl. The residue was collected by filtration and washed with boiling water. A small portion of the product was dissolved in warm 1 mol dm^{-3} NaOH solution and filtered by suction. The tetracarboxy complexes were precipitated from the sodium salt solution by addition of 1 mol dm^{-3} HCl. The complex was filtered and washed several times with boiling water until no more chloride was detected. The product was Soxhlet extracted with absolute ethanol and dried in vacuo.

$(OH)_2SiTCPc$: Yield: 36%. UV/vis (DMSO): λ_{max} (nm) ($\log\varepsilon$) 368 (4.62), 614 (4.33), 681 (4.61). IR [(KBr) ν_{max} (cm^{-1})]: 3350 (O–H), 1702 (C=O), 1313, 1289, 1237 (C–O). Calcd for $(OH)_2$ ($C_{36}H_{16}N_8O_8Si$): C 57.44, H 2.15; Found: C 56.93, H 3.85.

$(OH)_2GeTCPc$: Yield: 28 %. UV/vis (DMSO): λ_{max} (nm) ($\log\varepsilon$) 367 (4.58), 615 (4.11), 689 (4.99). IR [(KBr) ν_{max} (cm^{-1})]: 3402 (O–H), 1710 (C=O), 1484, 1399, 1255 (C–O). Calcd for $(OH)_2$ ($C_{36}H_{16}N_8O_8Ge$): C 54.37, H 2.28; Found: C 54.27, H 3.68.

2.2. Equipment

Ground state electronic absorption spectra were recorded on a Varian 500 UV-Vis/NIR spectrophotometer, fluorescence excitation and emission spectra recorded on a Varian Eclipse spectrofluorimeter. Laser flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd:YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye (Pyridin 1 dye in methanol). Single pulse energy ranged from 2 to 7 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360) and kinetic curves were averaged over 256 laser pulses. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software. Solutions for triplet yield and lifetime determinations were purged of oxygen (by bubbling with Argon) before laser irradiations. Photo-irradiations for singlet oxygen determination were performed using a General electric Quartz line lamp (300 W). A 600-nm glass cut off filter (Schott) and water were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 700 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and was found to be 1.78×10^{16} photons s^{-1} cm^{-2}.

2.3. Photophysical and photochemical studies

Fluorescence quantum yields (Φ_F) were determined by comparative method [23] (Eq. (1)):

$$\Phi_F = \Phi_{F(Std)}\frac{FA_{Std}n^2}{F_{Std}An^2_{Std}} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence curves of the MPc derivatives and the reference, respectively. A and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, and n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc in DMSO was used as a standard, $\Phi_F = 0.20$ [24]. At least three independent experiments were performed for the quantum yield determinations. Both the sample and the standard were excited at the same relevant wavelength.

Triplet quantum yields were determined using a comparative method based on triplet decay, using Eq. (2):

$$\Phi_T^{Sample} = \Phi_T^{Std}\frac{\Delta A^{Sample}\varepsilon^{Std}}{\Delta A^{Std}\varepsilon^{Sample}} \tag{2}$$

where A_T^{Sample} and A_T^{Std} are the changes in the triplet state absorbance of the sample and the standard, respectively. ε_T^{Sample} and ε_T^{Std} are the triplet state extinction coefficients for the sample and standard, respectively. Φ_T^{Std} is the triplet state quantum yield for the standard. ZnPc ($\Phi_T^{Std} = 0.65$ in DMSO [25]) was used as a standard. Quantum yields of internal conversion were obtained using Eq. (3) which assumes that only three processes (fluorescence, intersystem crossing and internal conversion); jointly deactivate the excited singlet states of the complexes:

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

Eq. (4) was employed for calculating singlet oxygen quantum yields:

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

where Φ_T^{Std} is the singlet oxygen quantum yield for the standard, ZnPc ($\Phi_T^{Std} = 0.67$ in DMSO [26]). R and R^{Std} are the DPBF photobleaching rates in the presence of the respective MPcs under investigation and the standard, respectively. I_{abs} and I^{Std}_{abs} are the rates of light absorption by the MPcs and the standard, respectively. To avoid chain reactions, the concentration of DPBF was kept at $\sim3\times10^{-5}$ mol l^{-1}. Solutions of the MPcs with an absorbance of 0.2 at the irradiation wavelength were prepared in the dark and irradiated at the Q band region. DPBF degradation was monitored at 417 nm. The error was ~10% from several values of Φ_Δ.

2.4. Fluorescence quenching by benzoquinone

Fluorescence quenching experiments on the various MPc complexes were carried out by the addition of increasing concentrations of BQ to a fixed concentration of the respective MPc complexes, and the concentrations of BQ in the resulting mixtures were 0, 0.0028, 0.0056, 0.0084, 0.0112 and 0.0140 M. The respective MPc fluorescence spectra were recorded in the absence and presence of the various BQ concentrations and the changes in fluorescence intensity of MPc with quencher concentration was analysed by the Stern–Volmer equation (Eq. (5)) [27]:

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \tag{5}$$

where I_0 and I are the fluorescence intensities of the fluorophore (MPc) in the absence and presence of quencher, BQ, respec-

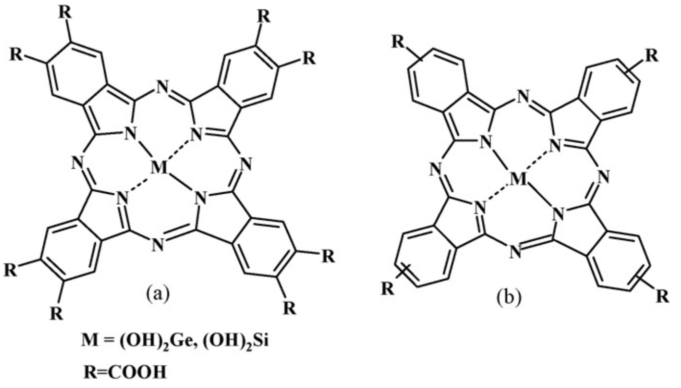

Fig. 1. Chemical structures of (a) octa-carboxy substituted and (b) tetra-carboxy substituted silicon and germanium phthalocyanine.

tively; [BQ] is the concentration of the quencher and K_{SV} is the Stern–Volmer constant.

K_{SV} is the product of the bimolecular quenching constant (k_Q) and the fluorescence lifetime, τ_F as shown by Eq. (6):

$$K_{SV} = k_Q \tau_F \quad (6)$$

and can be determined from the slope of the plot of the calculated ratios I_0/I against [BQ] according to Eq. (5).

3. Results and discussion

3.1. Ground state electronic absorption and fluorescence spectra

Tetra- and octa-carboxy metallophthalocyanine (MTCPc and MOCPc, respectively) complexes Fig. 1 are known and gave satisfactory analyses similar to literature [15–17,21,22]. The (OH)$_2$SiTCPc, (OH)$_2$GeTCPc complexes gave satisfactory spectroscopic and elemental analyses as outlined in Section 2.

The solubility of the MPc carboxy substituted complexes was achieved in aqueous medium due to the presence of the ionic charge on their substituents, though for the MTCPcs, complete dissolution only occurred at pH 10. The ground state electronic absorption spectra of the MOCPc complexes showed monomeric behaviour evidenced by a single Q band, typical of metallated phthalocyanine complexes [28] (Fig. 2). The MTCPcs were highly aggregated in aqueous solution as seen from the broadness of their spectra in Fig. 2. The spectra showed the monomer peaks near 700 nm and the peak due to the aggregates near 630 nm. Interestingly, the maxima of their monomeric bands were red-shifted compared to their MOCPcs. The exciton coupling theory explains that aggregation of symmetrically substituted Pcs gives rise to pronounced spectral changes that extend from broadening to splitting of the Q band [29], indicating the presence of additional electronic levels of the aggregates. In these additional electronic levels, transitions are formally allowed only to the upper energy pairs of states (represented as ^{1}Eu). However, transitions to the lower energy pairs of states (^{1}Eg) (LUMO) though symmetry forbidden, may still occur to a small extent, resulting in a broad absorption spectrum or red-shifting of the spectrum [30]. This may explain the behaviour of these MTCPcs.

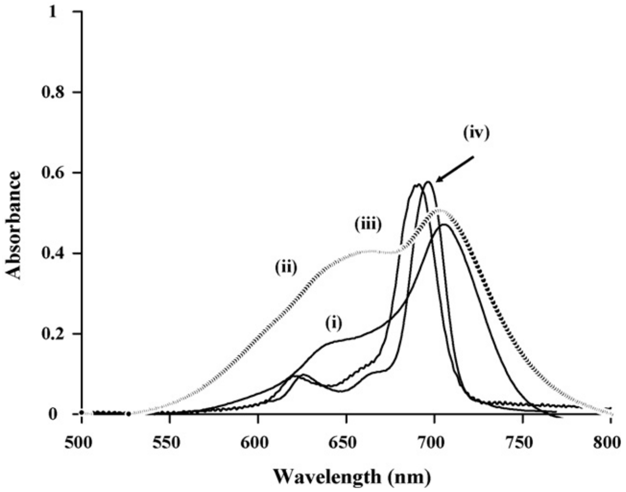

Fig. 2. Electronic absorption spectra of (OH)$_2$SiTCPc (i), (OH)$_2$GeTCPc (ii), (OH)$_2$SiOCPc (iii) and (OH)$_2$GeOCPc (iv) complexes in aqueous medium (~10^{-6} mol dm^{-3}). pH 10 for MTCPc and pH 7.4 for MOCPc.

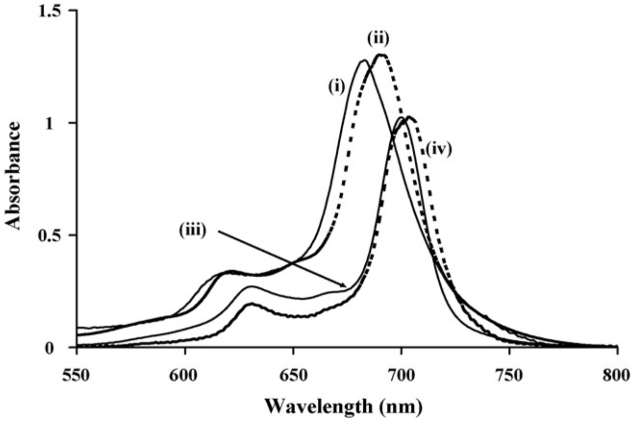

Fig. 3. Electronic absorption spectra of (OH)$_2$SiTCPc (i), (OH)$_2$GeTCPc (ii), (OH)$_2$SiOCPc (iii) and (OH)$_2$GeOCPc (iv) complexes in DMSO (~1×10^{-6} mol dm^{-3}).

Also, tetrasubstituted MPcs are known to be a mixture of constitutional isomers [31], whereas octasubstituted derivatives are isomerically pure and the plurality of the substituents may also result in monomerization [32]. Addition of a neutral surfactant cremophore EL (CEL), to the aqueous solutions of the MTCPcs resulted in no noticeable change in the shape and intensity of their spectra, suggesting that the broadness of their spectra may be due to distortion of symmetry, the presence of isomers, or strong aggregation which cannot be broken down by CEL. When the MTCPcs were dissolved in an organic solvent, dimethylsulfoxide they exhibited monomeric behaviour (Fig. 3 and Table 1). There was however, still some broadness existing in both (OH)$_2$SiTCPc and (OH)$_2$GeTCPc complexes. The monomerization in DMSO is not unexpected since organic solvents are known to break aggregation [9,33]. The small broadness still observed in DMSO is probably due to isomers or

Table 1
Spectral and photophysical parameters for MPc complexes in DMSO.

Complex	λ_Q (nm)	λ_F (nm)	λ_{Exc} (nm)	Φ_F	Φ_T	Φ_{IC}	Φ_Δ	$^aS_\Delta$	τ_T (μs)
(OH)$_2$SiTCPc	681	699	694	0.14	0.66	0.16	0.17	0.26	210
(OH)$_2$GeTCPc	689	697	689	0.17	0.82	0.01	0.73	0.89	260
(OH)$_2$SiOCPc	700	720	704	0.27	0.48	0.25	0.33	0.69	760
(OH)$_2$GeOCPc	703	713	704	0.19	0.79	0.02	0.63	0.80	480

[a] $S_\Delta = \Phi_\Delta / \Phi_T$.

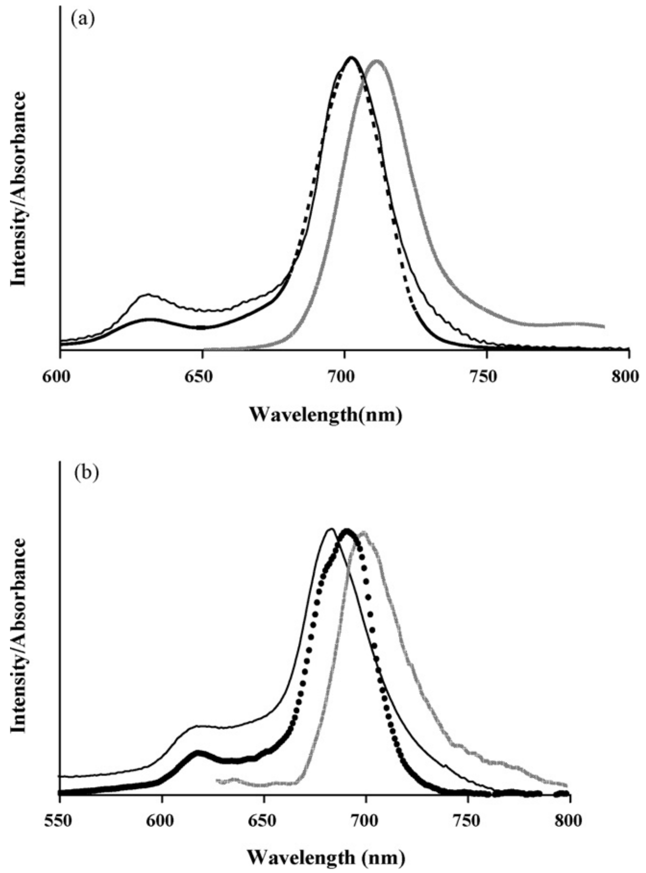

Fig. 4. Absorption (solid line), excitation (dotted line) and emission (blurred line) spectra of $(OH)_2GeOCPc$ (a) and $(OH)_2SiTCPc$ (b). Solvent = DMSO (λ_{Exc} = 625 and 615 nm, respectively).

incomplete disaggregation. Beer's law was however, obeyed up to ~1×10^{-5} mol dm^{-3} in DMSO. It can therefore be inferred that strong aggregation that cannot be easily broken by a neutral surfactant such as CEL exists in $(OH)_2SiTCPc$ and $(OH)_2GeTCPc$ complexes in aqueous media. It has been documented that aggregation is accompanied by a reduction of photochemical activity in processes involving phthalocyanine excited states [34,35], hence for proper comparison between the tetra and octasubstituted MPcs in this work, further studies hereafter are carried out in DMSO.

$(OH)_2SiOCPc$ and $(OH)_2GeOCPc$ maintained monomeric behaviour in DMSO and are red-shifted by 19 and 14 nm, respectively, when compared to their corresponding tetrasubstituted complex.

Absorption and fluorescence excitation spectra of MPcs are expected to be similar and mirror images of their emission spectrum and this was the case with the GePc derivatives ($(OH)_2GeTCPc$ and $(OH)_2GeOCPc$) complexes (Fig. 4a). For the SiPc derivatives ($(OH)_2SiTCPc$ and $(OH)_2SiOCPc$), the Q band maxima of the absorption and excitation spectra are different (Fig. 4b), especially for $(OH)_2SiTCPc$ with differences of 4 and 13 nm for $(OH)_2SiOCPc$ and $(OH)_2SiTCPc$, respectively, Table 1, suggesting a difference in the nuclear configuration of the ground and excited states, most likely due to partial demetalation, such behaviour has been observed before for some MPc complexes [36]. There was also enhanced splitting of the Q band of the excitation spectra for $(OH)_2SiTCPc$ (Fig. 4b). For $(OH)_2SiOCPc$ the fluorescence spectrum was a mirror image of the absorption spectrum. Stokes' shifts were ~8–20 nm, typical of MPc complexes, the Stokes shift are also larger for the SiPc complexes compared to the corresponding GePc derivatives. The smaller Stokes' shifts values for the GePc complexes imply rigidity of the environment and possibility of very little arrangement while the larger Stokes' shifts in the SiPc complexes, allows for greater rearrangement of the molecule at the excited state. Large Stokes' shifts may be an advantage in that fluorescent signals from the molecules may be easily separated from scattered excited light.

3.2. Photophysical studies

The values obtained for photophysical parameters of $(OH)_2SiTCPc$, $(OH)_2GeTCPc$, $(OH)_2SiOCPc$ and $(OH)_2GeOCPc$ in DMSO are shown in Table 1. Fluorescence quantum yields (Φ_F) are lower for the tetrasubstituted derivatives $(OH)_2SiTCPc$, $(OH)_2GeTCPc$ compared to their corresponding octasubstituted ones, $(OH)_2SiOCPc$ and $(OH)_2GeOCPc$. Φ_F value for $(OH)_2GeOCPc$ is lower compared to $(OH)_2SiOCPc$, this is expected on the basis of spin–orbit coupling (SOC), since Ge(IV) as an heavier atom will induce a stronger SOC than Si(IV), thereby enhancing the likelihood of the spin-forbidden transition and reducing spin-allowed fluorescence. The MTCPcs, however, behaved differently, with the $(OH)_2GeTCPc$ having a higher Φ_F value than $(OH)_2SiTCPc$ this may be due to aggregation effects.

An opposite trend was observed for the triplet quantum yield values (Φ_T, Table 1) when compared with Φ_F. Φ_T values are higher for the tetrasubstituted derivatives compared to corresponding octasubstituted derivatives, implying that most of the non-fluorescing molecules in the tetrasubstituted derivatives undergo intersystem crossing to the excited triplet state, this corresponds to the low Φ_F values of the tetrasubstituted derivatives. For both the tetra and octasubstituted complexes, Φ_T values are higher for the germanium Pc complexes than for the silicon Pc complexes, which is attributed to the larger size of Ge(IV) ion compared to Si(IV) ion. Triplet lifetimes (τ_T) are longer for the MOCPcs compared to the MTCPcs, corresponding to the lower Φ_T values for the former. $(OH)_2SiTCPc$ has the shortest τ_T amongst the complexes. $(OH)_2SiTCPc$ would be expected to have a longer lifetime than its $(OH)_2GeTCPc$ counterpart as it is the case with the MOCPcs, the difference could be due to difference in the extent of aggregation. The lifetimes are long enough for photosensitized reactions to occur.

Quantum yields of internal conversion (Φ_{IC}, Table 1) are higher for the silicon Pc derivatives than for the germanium Pc derivatives. The difference in the nuclear configuration of the ground and excited states, exhibited by the silicon complexes may provide pathways through which excitation energy can "leak out" non-radiatively via internal conversion.

Table 2
Fluorescence quenching and kinetic data for MPc complexes in DMSO.

Complex	K_{SV} (dm^3 mol^{-1})	k_Q (dm^3 mol^{-1} s^{-1} × 10^9)	$\tau_{F\,(MPc)}$ (ns)	$^a k_F$ (s^{-1} × 10^7)	$^a k_{ISC}$ (s^{-1} × 10^8)	$^a k_{IC}$ (s^{-1} × 10^7)
$(OH)_2SiTCPc$	13.49	4.85	2.78	5.04	2.37	5.76
$(OH)_2GeTCPc$	18.35	5.03	3.65	4.66	2.25	0.27
$(OH)_2SiOCPc$	17.62	5.08	3.46	7.80	1.39	7.23
$(OH)_2GeOCPc$	11.44	5.10	2.24	8.48	3.53	0.89

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$; k_{ISC} is the rate constant for intersystem crossing. Values calculated using $k_{ISC} = \Phi_T/\tau_F$; k_{IC} is the rate constant for internal conversion. Values calculated using $k_{IC} = \Phi_{IC}/\tau_F$.

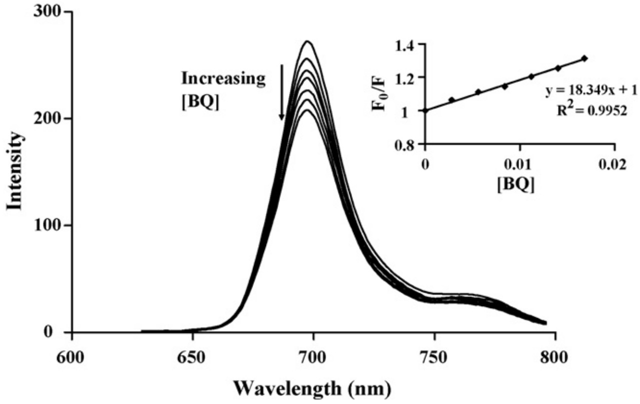

Fig. 5. Effect of BQ ((0 to 1.10×10^{-5}) mol dm^{-3}) on fluorescence spectrum of $(OH)_2$GeTCPc (1.24×10^{-5} mol dm^{-3}). Inset: Stern–Volmer plot for BQ quenching of $(OH)_2$GeTCPc. Excitation wavelength = 615 nm.

Rate constants for the intrinsic processes deactivating the excited singlet state (k_F, k_{ISC} and k_{IC}) are shown in Table 2. These values follow the same trends as their respective quantum yield values. The rate constants of internal conversion were higher for the silicon Pc complexes compared to the germanium Pc complexes following the trend of Φ_{IC}, showing that there is a higher rate of quenching of the singlet excited state in the silicon Pc derivatives. Larger rate constants for fluorescence (k_F) were observed for the MOCPc complexes compared to the MTCPcs, indicating a greater fluorescing ability of the former which may be due to their monomeric and isomeric nature. All the complexes exhibited large rate constants for intersystem crossing (k_{ISC}) indicating their high intersystem crossing ability to the triplet state.

3.3. Singlet oxygen quantum yield

Energy transfer between the triplet state of photosensitizers and ground state molecular oxygen leads to the production of singlet oxygen, Φ_Δ, which is the cytotoxic species in PDT. There is a necessity of high efficiency of transfer of energy between excited triplet state of MPc and ground state of oxygen to generate large amounts of singlet oxygen for photochemical reactions. The Φ_Δ values (Table 1) are high for GePc complexes corresponding to their triplet state quantum yields. $(OH)_2$SiTCPc showed a low Φ_Δ and a relatively short triplet lifetime, the latter may be a reason for its low production of Φ_Δ since efficient energy transfer from its triplet state to ground state molecular oxygen may not have been plausible within the short triplet lifetime. Singlet oxygen ($^1O_2$), is one of the reactive oxygen species, that plays an important role in many photosensitization reactions. The observed Φ_Δ values of these germanium and silicon phthalocyanine complexes shows that the complexes will be valuable for use in photochemical reactions involving singlet oxygen such as PDT. $S_\Delta = (\Phi_\Delta/\Phi_T)$ values, were near unity (Table 1) for the complexes (except $(OH)_2$SiTCPc) suggesting efficient quenching of the triplet state by singlet oxygen for these complexes.

3.4. Fluorescence quenching by benzoquinone

Fig. 5 shows the spectral changes accompanying the fluorescence quenching of $(OH)_2$GeTCPc by BQ in DMSO, as well as the corresponding Stern–Volmer plot. All the other complexes in this work were also effectively quenched by BQ. The Stern–Volmer plots for all four complexes gave straight lines, depicting diffusion-controlled quenching mechanisms. No changes were observed in the absorption spectra of the complexes in the presence of BQ; hence the quenching mechanism can be said to be dynamic. Quinones have high electron affinities, and their involvement in electron transfer processes is well documented [11]. The energy of the lowest excited state for quinones is greater than the energy of the excited singlet state of MPc complexes [37], hence, energy transfer from the excited MPc to BQ is not likely to occur. Moreover, MPcs are known to be easily reduced [21]. Therefore MPc fluorescence quenching by BQ is via excited state electron transfer, from the MPc to the BQ.

Stern–Volmer constants (K_{SV}), Table 2, for fluorescence quenching by BQ did not follow a particular pattern but are relatively within the same range for the MPc complexes; probably due to the similar structure and chemical nature of the MPc complexes.

The bimolecular rate constant for diffusion-controlled reactions (k_D) is related to the bimolecular quenching constant (k_Q) (Eq. (6)) by Eq. (7) [38]:

$$k_Q = fk_D \tag{7}$$

where *f* is the collision efficiency.

k_D can be obtained from the Einstein–Smoluchowski relationship:

$$k_D = 4\pi N_A(D_f + D_q)(r_f + r_q) \tag{8}$$

where N_A is the Avogadro's number, D_f and D_q are 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. (9)) [38]:

$$D = \frac{kT}{6\pi\eta r} \tag{9}$$

where k is the Boltzman constant; T is the absolute temperature; η is the solvent's viscosity; and r is the fluorophore (or quencher) radius. The radii were determined using ACD/Chem Sketch program in comparison with literature [39,40].

k_Q values can be determined from Eq. (7) 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. (6).

The bimolecular quenching constants (k_Q), calculated (assuming that collision efficiency, *f*, is unity) for the MPc complexes range between 4.85×10^9 and 5.10×10^9 dm^3 mol^{-1} s^{-1}; these values are close to 10^{10} dm^3 mol^{-1} s^{-1}, which is in agreement with the Einstein–Smoluchowski approximation at room temperature for diffusion-controlled bimolecular interactions [40]. Fluorescence lifetimes, τ_F values (Eq. (6), Table 2), are within the expected range for MPc derivatives [34,37,41]. The fluorescence lifetimes range between 2.2 and 3.7 ns.

The solvent dependence on the rate of electron transfer was also examined and the solvent reorientation energies (λ_S) were calculated using the Marcus dielectric continuum formula [42] (Eq. (10)):

$$\lambda_s = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{n^2} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2R_A} + \frac{1}{2R_D} - \frac{1}{R_{AD}}\right) \tag{10}$$

where e is the electronic charge, ε_0 is the permittivity of vacuum; n and ε_s are the solvent's refractive index, and dielectric constant, respectively; R_A and R_D are the molecular radii of the electron acceptor and donor (MPc), respectively, while R_{AD} is the sum of R_A and R_D.

Marcus [42] suggested that a reorganization of the solvent molecules around the electron donor and acceptor occurs prior to the electron transfer process. The clustering of solvent molecules around the interacting species inhibits electron transfer; hence a solvent reorganization is essential for the electron transfer process so that a partial disengagement of solvent molecules attached to the donor and acceptor occurs, leading to an increase in entropy. Solvent reorganization energies were calculated according to Eq.

(10), and the values are basically the same for all the complexes (~0.66 eV); which is not unexpected, because the same solvent was employed in all cases.

4. Conclusions

The photophysical and photochemical properties of silicon and germanium tetra- and octa-carboxy phthalocyanines have been studied and reveal high yields of the metastable excited state which should make them find use in applications requiring photosensitizers. A difference in the nuclear configuration of the ground and excited states was observed in the silicon Pc omplexes. The effective quenching of the complexes' fluorescence by benzoquinone suggests that such systems that contain SiPc or GePc derivatives and quinones could serve well as good light harvesters and energy transducers.

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