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Photophysical and photochemical studies of long chain-substituted zinc phthalocyanines

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Abstract

Photochemical and photophysical measurements were conducted on peripheral and non-peripheral tetra(13,17-dioxanonacosane-15-hydroxy)-substituted zinc phthalocyanines (**1**, **2**). General trends are described for quantum yields of photodegradation, fluorescence yields, triplet lifetimes and triplet quantum yields as well as singlet quantum yields of these compounds in dimethylformamide (DMF) and toluene. The effects of the solvents on the photophysical and photochemical parameters of the zinc(II) phthalocyanines (**1**, **2**) are reported.

Keywords: Phthalocyanine; Quantum yields; Singlet oxygen; Triplet; Photodegradation

1. Introduction

Phthalocyanines and metallophthalocyanines have been investigated in detail for many years because of their wide applications in many fields, including use in chemical sensors, liquid crystals, Langmuir–Blodgett films, non-linear optics, optical data storage and as carrier generation materials in near-IR devices. Substituted derivatives can also be used for photodynamic cancer therapy and other processes driven by visible light [1,2]. A decisive disadvantage of phthalocyanine and metal phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework [3]. Because of their lower degree of order in solid state, tetra-substituted phthalocyanines are more soluble than the corresponding octa-substituted ones. In contrast to octa-substituted systems tetra-substituted phthalocyanines are obtained as a mixture of constitutional isomers by statistical synthesis starting from mono-substituted phthalonitriles or corresponding diiminoisoindolines. Depending on their substituent positions two types (non-peripherally and peripherally substituted) of tetra-substituted macrocycles, which show significant differences in their chemical and physical behaviour, can be distinguished.

For photodynamic therapy (PDT), a combination of a photosensitizing drug and light in the presence of molecular oxygen is used to obtain a therapeutic effect, and has been proposed as an alternative treatment to complement conventional protocols in the management of malignant tumors and many other non-oncologic diseases [4]. The use of photosensitizing agents for inactivation of several cancer cells has been widely studied [5].

Many groups of compounds have been shown to possess photosensitizing tendencies. Metallophthalocyanines (MPcs), in particular, have proved to be highly promising in this respect, due to their intense absorption in the red region of visible light. High triplet state quantum yields and long lifetimes are required for efficient sensitization and these criteria may be fulfilled by the incorporation of a diamagnetic metal such as zinc, aluminum or silicon into the phthalocyanine macrocycle.

Zinc phthalocyanine complexes have attracted much interest because of their appreciably long triplet lifetimes [6–8]. Such long lifetimes constitute a great advantage since the number of diffusional encounters between the triplet excited state and ground state molecular oxygen increases with the lifetime of the excited state. The introduction of peripheral and non-peripheral substituents onto the MPc ring is expected to affect

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both the triplet quantum yield and lifetime, hence it is desirable to carry out studies on the effects of substituents on these parameters.

In this work, we report on the effects of peripheral and non-peripheral ring substituents on the photophysical and photochemical parameters of zinc phthalocyanine derivatives. Aggregation behaviour, photophysical (triplet state lifetimes and quantum yields, and fluorescence quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties were investigated. Since PDT activity is mainly based on singlet oxygen, its production was determined by the dye-sensitised photooxidation of 1,3-diphenylisobenzofuran (DPBF), a specific scavenger of this toxic species [9]. Studies of the photostability of MPcs during photosensitized reactions is also of immense importance. The effects of peripheral or non-peripheral substitution by 13,17-dioxanonacosane-15-hydroxy on the photochemical and photophysical properties of the phthalocyanine ring are also investigated.

2. Experimental

2.1. Materials and equipment

2(3),9(10),16(17),23(24)-[13,17-Dioxanonacosane-15-oxy] phthalocyaninato zinc(II) (**1**) and 1(4),8(11),15(18),22(25)-[13,17-dioxanonacosane-15-oxy]phthalocyaninato zinc(II) (**2**) were prepared, purified and characterised according to literature procedures [10] (Fig. 1). Zinc phthalocyanine (ZnPc) was obtained from Aldrich. Zinc tetrasulphophthalocyanine (ZnTSPc) was synthesized according to the method reported by Weber and Busch [11]. All other reagents and solvents with reagent-grade quality were obtained from commercial suppliers and dried as described in Perrin and Armarego [12] before use. 1,3-Diphenylisobenzofuran (DPBF) was obtained from Aldrich.

Absorption spectra in the UV–vis region were recorded with an Shimadzu 2001 UV Pc spectrophotometer and Varian 500 UV-Vis/NIR spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path-length cuvettes at room temperature.

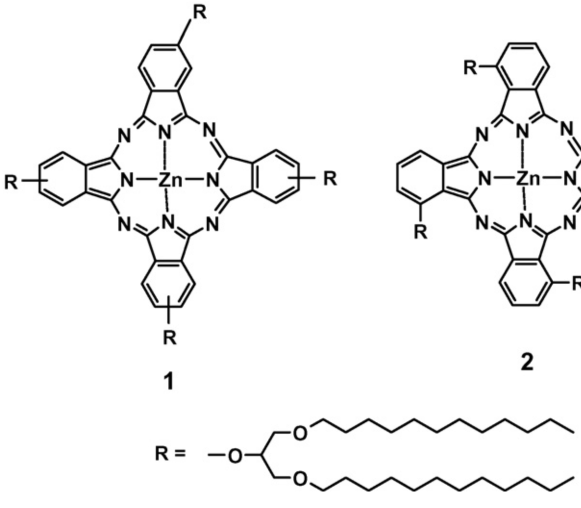

Fig. 1. Structure of zinc(II) phthalocyanine derivatives.

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 40 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–triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were 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 (Pyridine 1 dye in methanol). Single pulse energy was 2 mJ. The analyzing 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 16 laser pulses.

2.2. Photophysical parameters

2.2.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by the comparative method [13,14]:

$$\Phi_F = \Phi_{F_{std}} \frac{F A_{std}\, \eta^2}{F_{std}\, A\, \eta_{std}^2} \tag{1}$$

where F and F_{std} are the areas under the fluorescence emission curves of the samples (**1** or **2**) and the standard, respectively. A and A_{std} are the respective absorbances of the samples and standard at the excitation wavelength, respectively, and η and η_{std} are the refractive indexes of solvents ($\eta_{toluene} = 1.50$; $\eta_{DMSO} = 1.48$; $\eta_{DMF} = 1.44$) used for the samples and standard, respectively. The refractive indices of the solvents were employed in calculating fluorescence quantum yields in different solvents. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.18$) [15] was employed as the standard. Both the samples and standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05. Fluorescence life times (τ_F) were determined using PhotochemCAD Program which uses the Strickler–Berg equation [14]. Using the τ_F values, rate constants for fluorescence (k_f), intersystem crossing (k_{ISC}), internal conversion (k_{IC}) and photodegradation (k_d) were estimated.

2.2.2. Triplet quantum yields and lifetimes

The deaerated solutions of the respective peripheral and non-peripheral tetra-substituted ZnPc (**1** and **2**) complexes were introduced into a 1 cm path-length spectrophotometric cell and irradiated at the Q band maxima with the laser system described above. Triplet quantum yields (Φ_T) were determined by a comparative method using triplet decay [16]:

$$\Phi_T^{sample} = \Phi_T^{std} \frac{\Delta A_T^{sample}\, \varepsilon_T^{std}}{\Delta A_T^{std}\, \varepsilon_T^{sample}} \tag{2}$$

where $\Delta A_{\mathrm{T}}^{\mathrm{sample}}$ and $\Delta A_{\mathrm{T}}^{\mathrm{std}}$ are the changes in the triplet state absorbances of the samples (**1** or **2**) and standard, respectively; $\varepsilon_{\mathrm{T}}^{\mathrm{sample}}$ and $\varepsilon_{\mathrm{T}}^{\mathrm{std}}$ are the triplet state extinction coefficients for the samples (**1** or **2**) and standard, respectively. The triplet quantum yield ($\Phi_{\mathrm{T}}^{\mathrm{std}}$) for the ZnPc standard is $\Phi_{\mathrm{T}}^{\mathrm{std}} = 0.65$ in toluene [8] and 0.56 [17] for ZnTSPc standard in DMF.

Quantum yields of internal conversion (Φ_{IC}) were obtained from Eq. (3), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of peripheral and non-peripheral tetra-substituted ZnPc complexes.

$$\Phi_{\mathrm{IC}} = 1 - (\Phi_{\mathrm{F}} + \Phi_{\mathrm{T}}) \tag{3}$$

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

2.3. 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 before [18,19]. Typically, a 2 ml portion of the respective peripheral and non-peripheral tetra-substituted ZnPc (**1** and **2**) solutions (absorbance ~1 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described above. Φ_{Δ} values were determined in air using the relative method with DPBF as singlet oxygen chemical quencher in DMF and toluene:

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

where $\Phi_{\Delta}^{\mathrm{std}}$ is the singlet oxygen quantum yield for the standards ($\Phi_{\Delta}^{\mathrm{std}} = 0.56$ for ZnPc in DMF [20] and 0.58 for ZnPc in toluene [21]). R and R_{std} are the DPBF photobleaching rates in the presence of the respective (**1** or **2**) and standard, respectively; I_{abs} and $I_{\mathrm{abs}}^{\mathrm{std}}$ are the rates of light absorption by the samples (**1** or **2**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [22], the concentration of DPBF was lowered to $\sim 3 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$. Solution of sensitizer (absorbance below 1 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm was monitored. The light intensity used for Φ_{Δ} determinations was found to be 8.5×10^{16} photons $\mathrm{s^{-1}\,cm^{-2}}$. The error in the determination of Φ_{Δ} was ~10% (determined from several Φ_{Δ} values). Photodegradation quantum yields were determined using the following equation:

$$\Phi_{\mathrm{d}} = \frac{(C_0 - C_t) V N_{\mathrm{A}}}{I_{\mathrm{abs}} S t} \tag{5}$$

where C_0 and C_{t} are the sample (**1** or **2**) concentrations before and after irradiation respectively; V the reaction volume; N_{A} the Avogadro's constant; S the irradiated cell area; t the irradiation time; I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**1** or **2**). A light intensity of 2.83×10^{17} photons $\mathrm{s^{-1}\,cm^{-2}}$ was employed for Φ_{d} determinations.

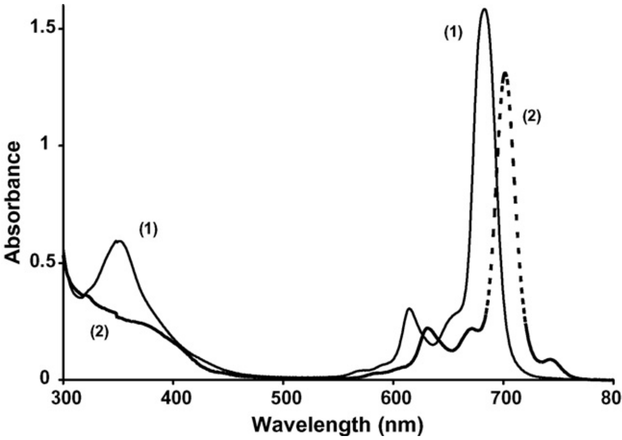

Fig. 2. Absorption spectra of the compound **1** and **2** in toluene. Concentration: $\sim 1.4 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$.

3. Results and discussion

3.1. Spectroscopic studies

The electronic spectra of the tetra-substituted phthalocyanine derivatives (**1** and **2**) showed intense Q absorption bands around 700 nm, Fig. 2. Although the peripherally substituted complex (**1**) has a typical spectral pattern in the visible region for the phthalocyanines, the non-peripheral complex (**2**) showed a new absorption band in chloroform at 744 nm in addition to the main Q band, Fig. 3. This new absorption band also appeared in dichloromethane or in toluene as shoulder, but did not appear in more polar solvents, such as ethanol, acetone or DMF, Fig. 3.

Substitution of the phthalocyanine at non-peripheral positions are known to cause a bathochromic shift of the Q band [23–26]. When the results of the UV–vis measurements of non-peripheral (**2**) and peripheral (**1**) tetra-substituted phthalocyanines are compared, it is found out that non-peripheral-substituted phthalocyanine (**2**) have approximately 20 nm higher wavelength values than the corresponding peripheral-substituted phthalocyanine (**1**), Fig. 2.

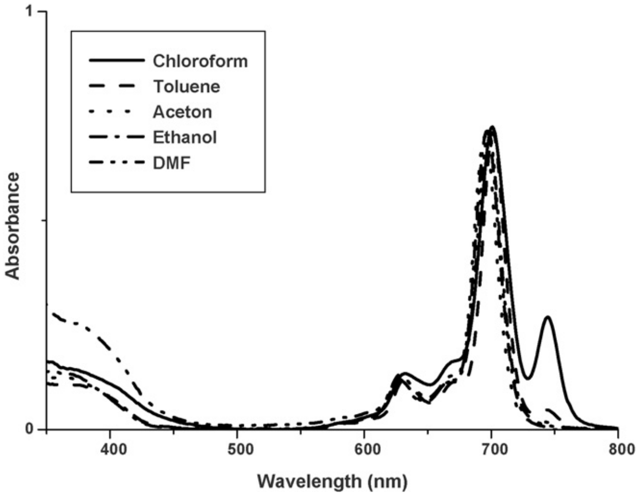

Fig. 3. UV–vis absorption spectrum of **2** in different solvents. Concentration: $\sim 1.4 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$.

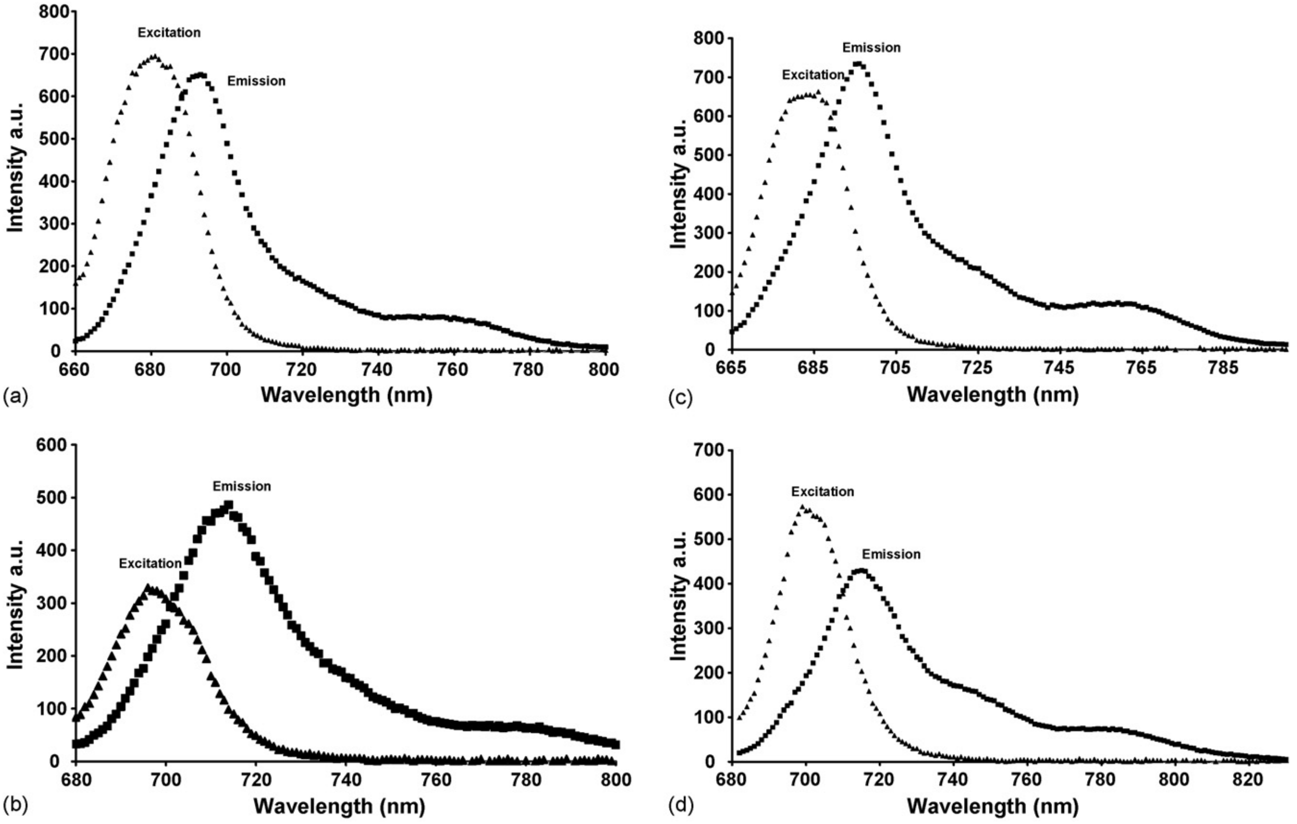

Fig. 4. Fluorescence excitation and emission spectra of (a) **1** in DMF: excitation; λ = 650 nm; (b) **2** in DMF: excitation λ = 670 nm; (c) **1** in toluene: excitation λ = 685 nm; (d) **2** in toluene: excitation λ = 670 nm. For excitation spectra, emission wavelengths were set at the values for fluorescence Q band maxima for each complex.

An observation of two bands in the Q band region of MPc complexes is normally associated with the presence of monomeric and aggregated species. Occurrence of a red-shifted peak due to aggregated species is a result of formation of J-type aggregates in MPc complexes [27]. Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [28]. In the aggregated state, the electronic structure of the complexed phthalocyanine rings are perturbed resulting in alternation of the ground and excited state electronic structures [29]. Compounds **1** and **2** are readily soluble in toluene, chloroform, acetone, ethanol and DMF. The aggregation behaviour of the phthalocyanines are investigated in different solvents. The phthalocyanine derivative **1** is not aggregated in these solvents. But only non-peripherally substituted zinc phthalocyanine complex (**2**) showed a new absorption band in chloroform, dichloromethane and toluene at 744 nm (Fig. 3). The band at 744 nm was tentatively assigned to result of the formation of a face-to-face slipped dimer by a mutual interaction of two phthalocyanines through contact of the zinc(II) ion and the outer-bridged nitrogen atom [10]. The shift of the Q and Soret bands has been explained by excitation interactions [30]. Hence, it is likely that the face-to-face slipped dimer formation may occur in the case of Zn(II) complex. The presence of a split Q band could also be due to demetallation, but this was ruled out since the positions of the peaks are different from those of the unmetallated derivatives of the complexes. The presence of a weak red-shifted band could also be due to the oxidation of the Pc ring and the aggregation of the oxidized species. However, bands typical of ring oxidation in the 500 nm region were not observed.

3.2. Photophysical properties

For both complexes **1** and **2** in DMF (Fig. 4a and b) and complex **1** in toluene (Fig. 4c), excitation spectra were similar to absorption spectra, and both were mirror images of the fluorescence spectra. For complex **2** in toluene, the excitation spectra (Fig. 4d) was different from the absorption spectra in that the band at 744 nm was not observed for the former, suggesting that it is due to the aggregated species. Fig. 4d shows that it is the monomeric species, which fluoresces for **2** in toluene. Aggregated species do not normally fluoresce. The proximity of the wavelength of the Q band absorption to the Q band maxima of the excitation spectra for both complexes suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation. The Φ_F values and Stoke's shift for both complexes were similar and typical of MPc complexes, Table 1.

The radiative lifetimes (τ_F) were estimated using the Strickler–Berg equation, Table 2. Using this equation, a good correlation between experimentally determined fluorescence lifetimes and the theoretically determined lifetimes for the unag-

Table 1
Photophysical and photochemical parameters of peripheral- and non-peripheral-substituted phthalocyanines in DMF or toluene

Compound	Solvent	λ_Q (nm) (log ε)[a]	λ_F (nm)	τ_T (μs)	Φ_F	Φ_T	Φ_{IC}	Φ_d ($\times 10^{-3}$)	Φ_Δ	S_Δ
1	DMF	681 (5.19)	693	100	0.18	0.60	0.22	2.28	0.51	0.85
	Toluene	682 (5.03)	696	40	0.16	0.81	0.03	7.90	0.77	0.95
2	DMF	701 (5.20)	713	76	0.17	0.65	0.18	1.39	0.62	0.95
	Toluene	701 (5.20), 744 (4.13)	715	20	0.15	0.75	0.10	1.53	0.71	0.94
ZnPc	DMF			330 [20]					0.56 [20]	
	Toluene			340 [31]		0.65 [20]			0.58 [20]	

References in square brackets for literature values.

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

Table 2
Rate constants for various excited state deactivation processes of compounds **1** and **2** in DMF and toluene

Compound	Solvent	τ_F (ns)	k_F (s^{-1})[a]	k_{ISC} ($\times 10^8$ s^{-1})[b]	k_{IC} (s^{-1})[c]	k_d (s^{-1})[d]
1	DMF	1.7	1.06×10^8	3.55	1.30×10^8	22.8
	Toluene	2.8	7.39×10^7	2.85	1.05×10^7	197
2	DMF	1.7	9.86×10^7	3.77	1.04×10^8	48.3
	Toluene	1.6	9.28×10^7	4.65	6.20×10^7	76.5

[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 $k_d = \Phi_d/\tau_T$.

gregated molecules has been established before [14]. Thus, we believe that the values obtained using this equation are a good measure of fluorescence lifetimes for the unaggregated species. Thus, considering only the unaggregated complexes (**2** in DMF, and **1** in both DMF and toluene), τ_F values were found to be lower for the non-peripherally substituted complex **1** in DMF, suggesting more quenching by peripheral substitution when compared to non-peripheral. The τ_F values were within the range reported for MPc complexes [14]. The value for **2** in toluene will be affected by aggregation. The τ_F value for **1** was higher in toluene than in DMF.

For the unaggregated complex **1**, the rate constants for fluorescence (k_F) were higher in DMF than in toluene and comparing complex **1** and **2** in DMF, shows a larger k_F value for the former. Similarly rate constants for intersystem crossing (k_{ISC}) and internal conversion (k_{IC}) were higher for **1** in DMF compared to toluene. The values for **2** in toluene will be affected by the aggregated nature of the complex as discussed above.

The triplet–triplet absorption spectrum for **2** in DMF is shown in Fig. 5, and shows a maximum at 500 nm, hence the triplet life times and yields were determined at this wavelength for both complexes. Fig. 6 shows a triplet decay curve of the complexes (using complex **1** as an example). The triplet life times (τ_T) for these complexes (**1** and **2**) are much lower than for unsubstituted ZnPc in the same solvents (Table 1). This suggests that the substituents quench the triplet state. The τ_T values are lower for **2** than **1** in corresponding solvents, suggesting more quenching by the substituents at the non-peripheral positions compared to peripheral. The τ_T values for both complexes were lower in toluene compared to DMF. This could be due to the deactivation of excited states by toluene. Alternatively, an increase in intersystem crossing (ISC) in toluene will result in low τ_T and large Φ_T as will be discussed below. The low values of τ_T for **2** in toluene could also be a result of aggregation as discussed above. Aggregation lowers the photoactivity of molecules through dissipation of energy by aggregates.

The triplet quantum yields (Φ_T) for **1** and **2** in both solvents are high compared to ZnPc standard in toluene ($\Phi_T = 0.65$) and ZnTSPc in DMF ($\Phi_T = 0.56$). The high values of Φ_T suggest efficient intersystem crossing (ISC) in the presence of the long chain substituents for **1** and **2**, resulting in high Φ_T and inevitably resulting in short triplet lifetimes. The Φ_T values are large in toluene corresponding to the low triplet lifetimes in this solvent for both complexes. This suggests that toluene encourages ISC to the triplet state. Aggregation in **2** would also result in low Φ_T values but this is not the case in Table 1, suggesting that it is the ISC in the presence of toluene is prominent. Both complexes showed low Φ_{IC}.

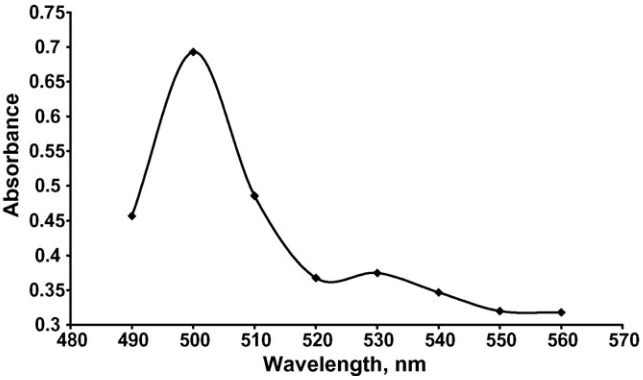

Fig. 5. The triplet–triplet absorption spectrum for ~1×10^{-5} mol L^{-1} of **2** in DMF. Excitation wavelength = 701 nm.

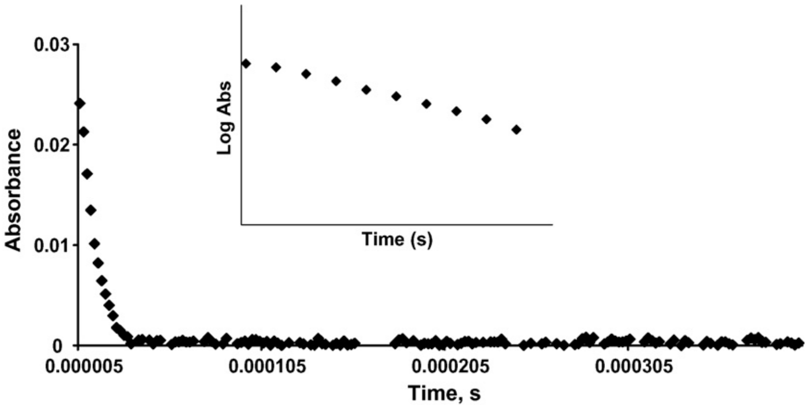

Fig. 6. Triplet decay curve of **1** in toluene. Wavelength = 500 nm.

3.3. Photochemical properties

Singlet oxygen quantum yield (Φ_Δ) values for complexes **1** and **2** were high in toluene corresponding to the high triplet yields. There was no change in the Q band intensity during the Φ_Δ determinations, Fig. 7, confirming that both complexes are not degraded during singlet oxygen studies. The magnitude of the $S_\Delta(=\Phi_\Delta/\Phi_T)$ represents the efficiency of quenching of the triplet excited state by singlet oxygen. Both complexes showed S_Δ of near unity (Table 1), suggesting efficient quenching of the triplet state by singlet oxygen.

Table 1 shows that complex **1** was marginally less stable than **2**, but both complexes were less stable to degradation compared to other substituted ZnPc derivatives [21]. Thus, the substitution of ZnPc with long chains seem to decrease the stability of the complexes. Photodegradation occurred with decrease in Q band absorption and increase in the absorption in B band area. The latter is due to the absorption of the degradation product of Pcs, which is phthalimide, Fig. 8. The rate constant for photodegradation (k_d) was higher in toluene than in DMF.

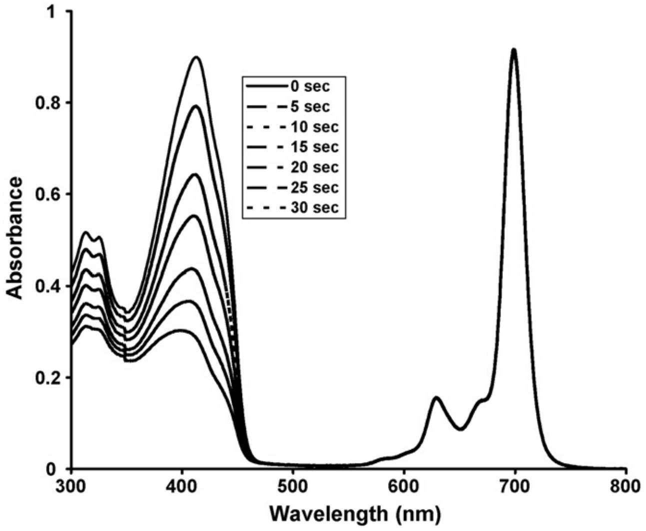

Fig. 7. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **2** in DMF at a concentration of 3×10^{-5} mol L^{-1}.

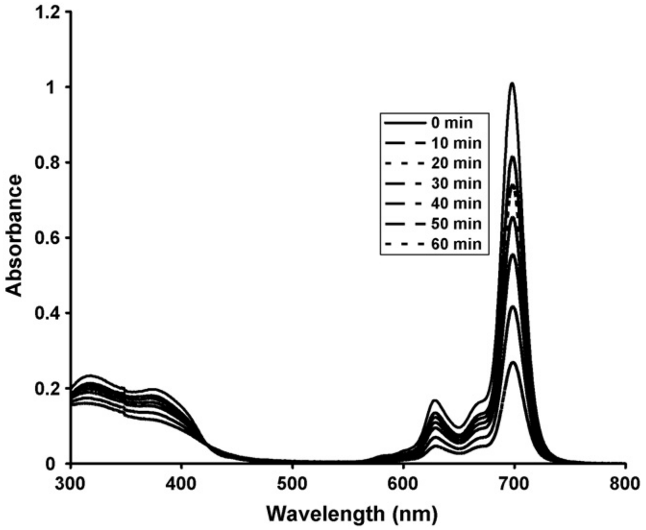

Fig. 8. The photodegradation of compound **2** in DMF showing the disappearance of the Q band at 10 min intervals.

4. Conclusion

Non-peripheral substitution of ZnPc with long chain substituents results in aggregation of complexes in toluene and other less polar solvents such as chloroform, but not in DMF. Non-peripheral substitution results in the decrease in triplet lifetime. The quantum yields of the triplet state are larger in toluene than in DMF, suggesting more efficient ISC crossing in the former solvent. Complex **1** containing peripheral substituents is less stable than the non-peripherally substituted **2**.

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