

Synthesis, photophysical and photochemical properties of poly(oxyethylene)-substituted zinc phthalocyanines†

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The synthesis, photophysical and photochemical properties of the tetra- and octa-poly(oxyethylene)substituted zinc (II) phthalocyanines are reported for the first time. The new compounds have been characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy, electronic spectroscopy and mass spectra. General trends are described for photodegradation, singlet oxygen, triplet state and fluorescence quantum yields, and triplet and fluorescence lifetimes of these compounds in dimethylsulfoxide (DMSO). Photophysical and photochemical properties of phthalocyanine complexes are very useful for PDT applications. The effects of the substituents on the photophysical and photochemical parameters of the zinc(II) phthalocyanines (**3a**, **5a** and **6a**) are also reported. The singlet oxygen quantum yields (Φ_{Δ}), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.60 to 0.72. Thus, these complexes show potential as Type II photosensitizers. The fluorescence of the complexes was quenched by benzoquinone (BQ).

Introduction

Phthalocyanines (Pcs) play a major role in modern photochemistry. Complexation of phthalocyanines with metal ions has an influence on their photophysical properties. These compounds are used as catalysts as well as photoreceptors in electrographic printing.^{1,2} Pcs have found applications as photosensitizers in photodynamic therapy of cancer (PDT).^{3,4} All these applications require compounds of various solubility and a high degree of purity. Porphyrin derivatives such as hematoporphyrin derivatives and Photofrin[®] have been used as photosensitizers for PDT.^{5,6} Aluminium and zinc phthalocyanine derivatives have, in particular, found use as photosensitizers for PDT.^{6–13}

In PDT, singlet oxygen is produced through transfer of energy from the excited triplet state of the photosensitizer to the ground state (triplet) of oxygen.¹⁴ Singlet oxygen does not only cause tumor necrosis¹⁵ but it also induces several biological reactions.^{16,17} It has been found that phthalocyanines are better photosensitizers for PDT than porphyrins, since the former exhibit effective tissue penetration¹⁸ due to their chemical stability, photodynamic activity, and efficient light absorption in the red region of the electromagnetic radiation.¹⁵ Phthalocyanines have long triplet lifetimes, and high singlet oxygen quantum yields.¹⁹ Aggregation in phthalocyanines has a strong influence on the bioavailability, the *in vivo* distribution and singlet oxygen production efficiency.²⁰

In spite of the above properties of phthalocyanines, there are fewer reports involving their use as photosensitizers for PDT (in comparison with porphyrins) because of their low level of solubility in common organic solvents. Naturally, there has

been considerable research on the syntheses of soluble metal phthalocyanine derivatives.² In order to be soluble in an aqueous media, sulfo groups are introduced on to the MPc ring.^{2,21–23} For example, sulfonated chloroaluminium and zinc phthalocyanine derivatives have been studied as potential sensitizers for PDT.^{21–23}

The great interest in the development of these macromolecules has led us to investigate the synthesis and properties of phthalocyanines substituted with amphiphilic groups in order to evaluate their influence on the solubility and photophysical properties. Thiol-derivatized metallophthalocyanine complexes show rich spectroscopic and photochemical properties. For example, they are known to absorb at longer wavelengths^{24–28} than other substituted metallophthalocyanine complexes, which is a very useful feature for application in PDT, optoelectronics and near-IR devices. In addition to this feature, the function of the poly(oxyethylene) groups is to enhance the solubility of the phthalocyanines in water, rendering them easier to administer in medical applications. Thus, in this work we describe the synthesis of new sterically hindered thia-bridged tetra- and octa-poly(oxyethylene)-substituted zinc(II) phthalocyanine derivatives (Fig. 1). The influence of the presence of the thia bridges in the poly(oxyethylene) side chains on the photophysical and photochemical properties is presented.

Experimental

Materials

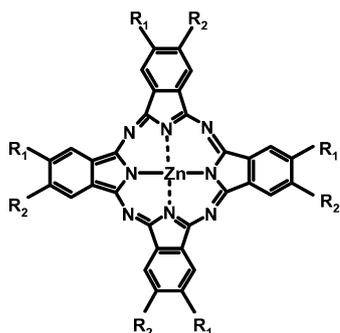
All solvents were purified as described in Perrin and Armarego.²⁹ 1,3-Di[2-(2-ethoxyethoxy)ethoxy]-2-propanethiol (**1**),³⁰ 4-nitro-phthalonitrile (**2**),³¹ 4-{2-[2-(2-ethoxyethoxy) ethoxy]-1-[2-(2-ethoxyethoxy)) ethoxymethyl] ethylsulfanyl} phthalonitrile (**3**),³² 1,2-dichloro-4,5-dicyano benzene(**4**),³³ 4-chloro-5{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy) ethoxy] ethoxymethyl] ethylsulfanyl} phthalonitrile (**5**)³² and 4,5-di{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-((2-ethoxy ethoxy) ethoxy)ethoxymethyl]ethyl sulfanyl} phthalonitrile (**6**)³² were prepared

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† The HTML version of this article has been enhanced with colour images.



Compound	R ₁	R ₂
3a	SCH[(CH ₂ O(CH ₂ CH ₂ O) ₂ C ₂ H ₅) ₂]	H
5a	SCH[(CH ₂ O(CH ₂ CH ₂ O) ₂ C ₂ H ₅) ₂]	Cl
6a	SCH[(CH ₂ O(CH ₂ CH ₂ O) ₂ C ₂ H ₅) ₂]	SCH[(CH ₂ O(CH ₂ CH ₂ O) ₂ C ₂ H ₅) ₂]

Fig. 1 Structure of the substituted zinc(II) phthalocyanines.

according to the reported procedures. Benzoquinone and 1,3-diphenylisobenzofuran (DPBF) were purchased from Aldrich. All other reagents and solvents were of reagent grade quality.

Equipment

Elemental analyses were obtained from a Carlo Erba 1106 Instrument. Infrared spectrum in a KBr pellet was recorded on a Perkin-Elmer 983 spectrophotometer. Absorption spectra in the UV-visible region were recorded with a 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 pathlength cuvettes at room temperature. Mass spectra were recorded using a VG Zab-Spec GC-MS spectrometer by fast atom bombardment techniques using *m*-nitrobenzyl alcohol (MNBA) as the matrix. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions on a Bruker 200 MHz and Varian 500 MHz spectrometers using TMS as an internal reference.

Photo-irradiations were performed 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 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 256 laser pulses.

Photophysical parameters

Fluorescence quantum yields. Fluorescence quantum yields (Φ_F) were determined by the comparative method (eqn 1),^{34,35}

$$\Phi_F = \Phi_F(\text{Std}) \frac{FA_{\text{Std}}\eta^2}{F_{\text{Std}}A\eta_{\text{Std}}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of the samples (**3a**, **5a** and **6a**) and the standard respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths (absorbance ~ 0.05), and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc in DMSO ($\Phi_F = 0.18$)³⁶ was employed as the standard. Both the sample and standard were excited at the same wavelength.

Fluorescence (τ_F) and natural radiative (τ_0) life times were determined using PhotochemCAD Program³⁷ which uses the Strickler–Berg equation.³⁷

Triplet quantum yields and lifetimes

The de-aerated solutions of the respective octa and tetra substituted ZnPc complexes (**3a**, **5a** and **6a**) were introduced into a 1 cm pathlength 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,³⁸ eqn 2:

$$\Phi_T^{\text{Sample}} = \Phi_T^{\text{Std}} \frac{\Delta A_T^{\text{Sample}} \epsilon_T^{\text{Std}}}{\Delta A_T^{\text{Std}} \epsilon_T^{\text{Sample}}} \quad (2)$$

where $\Delta A_T^{\text{Sample}}$ and ΔA_T^{Std} are the changes in the triplet state absorbances of the samples (**3a**, **5a** and **6a**) and standard, respectively. $\epsilon_T^{\text{Sample}}$ and ϵ_T^{Std} are the triplet state extinction coefficients for the samples (**3a**, **5a** and **6a**) and standard, respectively. The standard employed was zinc phthalocyanine (ZnPc) in DMSO. The triplet quantum yield (Φ_T^{Std}) for the standard is $\Phi_T^{\text{Std}} = 0.65$ for ZnPc³⁹ in DMSO.

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

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

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

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 above.^{40,41} Typically, a 2 ml portion of the respective octa and tetra substituted ZnPc (**3a**, **5a** and **6a**) 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 in references.^{40,41} Φ_Δ values were determined in air using the relative method with 1,3-diphenylisobenzofuran (DPBF) as singlet oxygen chemical quencher in DMSO (eqn 4):

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{RI_{\text{abs}}^{\text{Std}}}{R_{\text{Std}}^{\text{Std}} I_{\text{abs}}} \quad (4)$$

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_{\Delta}^{\text{Std}} = 0.67$ in DMSO⁴²). R and R^{Std} are the DPBF photobleaching rates in the presence of the respective (**3a**, **5a** and **6a**) and standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples (**3a**, **5a** and **6a**) and standard, respectively. The concentrations of DPBF in the solutions were calculated using the determined values of $\log \epsilon = 4.36$ at 417 nm (DPBF in DMSO). The light intensity used for Φ_{Δ} determinations was found to be 9.27×10^{15} photons $\text{s}^{-1} \text{cm}^{-2}$. The error in the determination of Φ_{Δ} was $\sim 10\%$ (determined from several Φ_{Δ} values).

Photodegradation quantum yields were determined using eqn 5,

$$\Phi_{\text{d}} = \frac{(C_0 - C_1) V N_{\text{A}}}{I_{\text{abs}} S t} \quad (5)$$

where C_0 and C_1 are the concentrations of complexes **3a**, **5a** and **6a** before and after irradiation respectively, V is the reaction volume, N_{A} the Avogadro's constant, S the irradiated cell area and t the irradiation time. I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**3a**, **5a** and **6a**). A light intensity of 3.09×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$ was employed for Φ_{d} determinations.

Fluorescence quenching by benzoquinone (BQ)

Fluorescence quenching experiments on the tetra- and octasubstituted zinc phthalocyanine complexes (**3a**, **5a** or **6a**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complex, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032, 0.040 and 0.048 mol dm^{-3} . The fluorescence spectra of tetra- and octasubstituted zinc phthalocyanine complexes (**3a**, **5a** or **6a**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) equation:⁴³

$$\frac{I_0}{I} = 1 + K_{\text{SV}}[Q] \quad (6)$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. 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.*

$$K_{\text{SV}} = k_{\text{q}} \cdot \tau_{\text{F}} \quad (7)$$

The ratios I_0/I were calculated and plotted against [BQ] according to eqn 6, and K_{SV} determined from the slope.

Synthesis

Tetrakis {2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl] ethylsulfanyl} phthalocyaninato zinc (II) (3a). A mixture of 4-{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl] ethylsulfanyl} phthalonitrile (**3**) (0.326, 0.7 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.10 ml, 0.7 mmol) and anhydrous zinc acetate (0.044 g, 0.24 mmol) in 1-hexanol (2 ml) were refluxed under an argon atmosphere for 48 h. Then 1-hexanol was removed under reduced pressure and finally the crude product was purified by column chromatography over Al_2O_3 using a mixture of CH_2Cl_2 : MeOH/100 : 1 ($R_{\text{F}} = 0.80$) as eluent. Furthermore, this product was purified with preparative TLC (silica gel) using CH_2Cl_2 : MeOH/20 : 1 solvent

system. Yield : 0.06 g (18%). (Found C 57.35, H 7.05, N 5.53%. $\text{C}_{92}\text{H}_{136}\text{N}_8\text{O}_{24}\text{S}_4\text{Zn}$ (1930) requires C 57.20, H 7.10, N 5.80%); IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr cell): 3040 (ArCH), 2980–2850 (CH_2), 1600 (ArC=C), 1529, 1450, 1400, 1381, 1350, 1310, 1260, 1240, 1120–1080 (C–O–C), 930, 880; MS (FAB) m/z (%): 1931(100) $[\text{M} + 1]^+$, 1624 (20) $[\text{M} - (\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$, 1315 (7) $[\text{M} - 2(\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$, 705 (5) $[\text{M} - 4(\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$.

Tetrakis (2, 9, 16, 23-{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl] ethylsulfanyl} 3,10,17,24-chloro) phthalocyaninato zinc (II) (5a). 4-Chloro-5{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxy] ethoxy methyl} ethylsulfanyl} phthalonitrile (**5**) (0.64 g, 1.27 mmol), DBU (0.19 g, 1.27 mmol), anhydrous zinc acetate (0.079 g, 0.43 mmol) and dried 1-hexanol (4 ml) were refluxed with stirring under an argon atmosphere for 48 h. Then 1-hexanol was removed under reduced pressure, and the crude green product was purified by column chromatography (Al_2O_3 , CH_2Cl_2 : methanol/100 : 1 ($R_{\text{F}} = 0.81$) as eluent). Furthermore, this product was purified with preparative TLC (silica gel) using CH_2Cl_2 : MeOH/20 : 1 solvent system. Yield: 0.120 g (18%). (Found C 53.80, H 6.22, N 5.60%. $\text{C}_{92}\text{Cl}_4\text{H}_{132}\text{N}_8\text{O}_{24}\text{S}_4\text{Zn}$ (2068) requires C 53.39, H 6.43, N 5.41%); IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr cell): 3040 (ArCH), 2980–2850 (CH_2), 1600(ArC=C), 1450, 1410, 1380, 1340, 1280, 1240, 1120–1080(C–O–C), 960, 880; MS (FAB) m/z (%): 2069 (75) $[\text{M} + 1]^+$, 1927 (10) $[\text{M} - \text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5]^+$, 1763 (35) $[\text{M} - (\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$, 1455 (8) $[\text{M} - 2(\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$, 842 (10) $[\text{M} - 4(\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$.

Octakis {2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl] ethylsulfanyl} phthalocyaninato zinc (II) (6a). A mixture of 4,5-di{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxy]ethoxymethyl}ethyl sulfanyl} phthalonitrile (**6**) (0.80 g, 1 mmol), DBU (0.15 g, 1 mmol), anhydrous zinc acetate (0.062 g, 0.34 mmol) and dried 1-hexanol (2 ml) were refluxed with stirring under an argon atmosphere for 48 h. Then 1-hexanol was removed under reduced pressure, and the crude green product was purified by column chromatography over Al_2O_3 with a mixture of dichloromethane : methanol/100 : 1 ($R_{\text{F}} = 0.31$) as eluent. Furthermore this product was purified with preparative TLC (silica gel) using CH_2Cl_2 : MeOH/20 : 1 solvent system. Yield: 0.110 g (13%). (Found C 55.72, H 7.71, N 3.14. $\text{C}_{152}\text{H}_{256}\text{N}_8\text{O}_{48}\text{S}_8\text{Zn}$ (3285) requires C 55.56, H 7.85, N 3.41%); IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr cell): 3040 (ArCH), 2980–2850 (CH_2), 1600 (ArC=C), 1520, 1450, 1410, 1380, 1340, 1280, 1240, 1120–1080(C–O–C), 960, 880, 780, 750, 710; MS (FAB) m/z (%): 3285 (100) $[\text{M}]^+$, 2977 (25) $[\text{M} - (\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$, 2670 (20) $[\text{M} - 2(\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$, 830 (15) $[\text{M} - 8(\text{CH}(\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5)_2)^+]$.

Results and discussion

Synthesis and characterization

Depending on the reaction conditions, the syntheses of phthalocyanine derivatives from aromatic nitriles result in different yields. The reaction of substituted dinitriles in the presence of strong non-nucleophilic bases such as 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) either in

Table 1 ¹H-NMR spectral data for the phthalocyanine complexes in CDCl₃

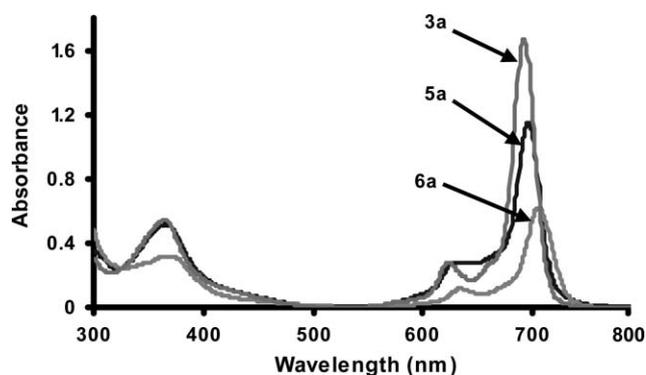
Compound	CH ₃	OCH ₂ and CH	Aromatic H
3a	1.07 (t, 24 H)	3.22–4.01 (m, 100H)	7.82–8.24 (br, m, 4H) 8.80–9.20 (br, m, 8H)
5a	1.06 (t, 24H)	3.29–4.14 (m, 100H)	8.31–9.05 (br, m, 8H)
6a	1.11 (t, 48H)	3.20–4.21 (m, 200H)	9.58 (s, 8H)

([M-307]⁺), 2{CH[CH₂O(CH₂CH₂O)₂C₂H₅]₂} ([M-614]⁺) and 8{CH[CH₂O(CH₂CH₂O)₂C₂H₅]₂} ([M-2455]⁺) were easily identified.

The IR spectra showed characteristic vibrations corresponding to ether groups (C–O–C) at 1120–1100 cm⁻¹ and CH₂ stretching at ca. 2950–2850 cm⁻¹, which are common for the phthalocyanine compounds (**3a**, **5a**, **6a**). NMR investigation of all compounds gave characteristic chemical shifts for the expected structures (Table 1 and 2).

Electronic absorption spectroscopic properties

The electronic spectra of the tetra- and octa-substituted phthalocyanine complexes (**3a**, **5a** and **6a**) showed intense Q absorption bands around 690–700 nm, Fig. 3. The spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes for **3a** and **6a** in DMSO.⁴⁸

**Fig. 3** Absorption spectra of substituted zinc phthalocyanine complexes (**3a**, **5a** and **6a**) in DMSO. Concentration = 4×10^{-6} mol dm⁻³.**Table 2** ¹³C-NMR spectral data for the phthalocyanine complexes in CDCl₃

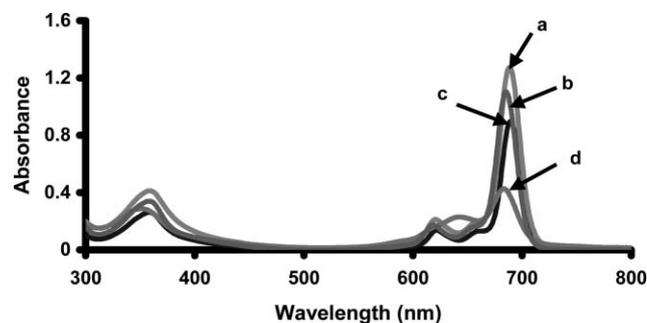
Compound	CH ₃	CH	OCH ₂	Aromatic CH	Aromatic C
3a	15.25	48.55 48.65	66.72, 69.98, 70.69 70.96, 71.05	122.41, 124.32 125.75	132.70, 136.15, 137.36 139.80 154.08
5a	15.32	49.40 50.20	66.59, 69.85, 70.82 71.15, 72.32	122.72, 125.13	136.47, 137.12 138.10, 152.73
6a	15.55	48.05	65.57, 68.89, 70.68 70.89, 71.09	126.60	136.72, 141.54, 152.55

Table 3 Absorption, excitation and emission spectral data for unsubstituted, tetra- and octasubstituted zinc phthalocyanine complexes in DMSO

Compound	Q band λ_{\max} /nm	log ϵ	Excitation λ_{Ex} /nm	Emission λ_{Em} /nm	Stokes shift Δ_{Stokes} /nm
ZnPc	672	5.14	672	682	10
3a	692	5.42	692	702	10
5a	696	5.21	697	707	11
6a	705	5.12	706	716	11

Complex **5a** showed a broad band around 650 nm due to the aggregation in DMSO. Complex **3a** was also aggregated in methanol. As expected, aggregation was not detectable for any complex in less polar tetrahydrofuran and carbon tetrachloride. In DMSO, the Q bands were observed at: 672 (**ZnPc**), 692 (**3a**), 696 (**5a**) and 705 (**6a**) nm, Table 3. Thus, substitution of the ZnPc with branched polyoxy substituents increased the wavelength of the Q band. The extinction coefficients of the substituted complexes (**3a**, **5a** and **6a**) decreased with increase in the number of substituents, Table 3.

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, peripheral substituents, complexed metal ions and temperature.^{49,50} In the aggregated state the electronic structure of the complexed phthalocyanine rings is perturbed, resulting in alternation of the ground and excited state electronic structure.⁵¹ In this study, the aggregation behaviour of the phthalocyanine complexes (**3a**, **5a** and **6a**) are investigated at different solvents (chloroform, THF, CCl₄ and MeOH) (Fig. 4 for complex **3a**).

**Fig. 4** UV-Vis Spectrum of **3a** in different solvents in: (a) chloroform, (b) THF, (c) CCl₄ (d) MeOH Concentration $\sim 3.5 \times 10^{-6}$ mol dm⁻³.

The aggregation behaviour of the phthalocyanine complexes (**3a** and **6a**) was investigated at different concentrations in DMSO (Fig. 5 for complex **3a**). As the concentration was increased, the intensity of the Q band absorption also increased and there were no new bands (normally blue shifted) associated with the aggregated species for complexes **3a** and **6a** (Fig. 5 for complex **3a**). Thus, the

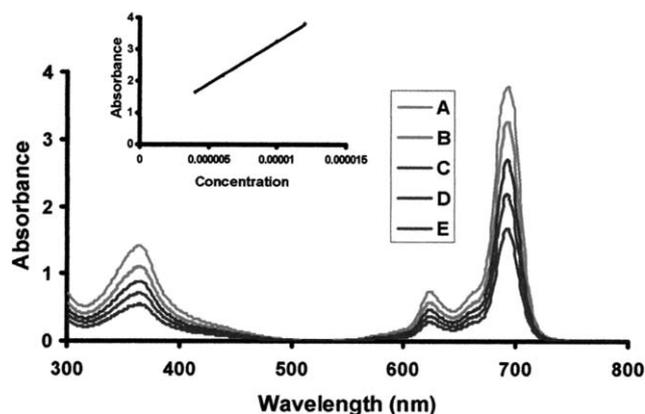


Fig. 5 Aggregation behaviour of **3a** in DMSO at different concentrations: 14×10^{-6} (A), 12×10^{-6} (B), 10×10^{-6} (C), 8×10^{-6} (D), 6×10^{-6} (E), 4×10^{-6} (F) mol dm⁻³.

phthalocyanine derivatives (**3a** and **6a**) did not show aggregation in DMSO at different concentrations. The Beer–Lambert law was obeyed for all of these compounds in concentrations ranging from 1.4×10^{-5} to 4×10^{-6} mol dm⁻³.

Fluorescence quantum yields and lifetimes

Complexes **3a** and **6a** showed similar fluorescence behaviour in DMSO. Fig. 6 shows the absorption, fluorescence emission and excitation spectra for complexes (**3a**, **5a** and **6a**) in DMSO. Complex **5a** was aggregated in DMSO, but the fluorescence spectra shows it was only the monomer that fluoresced, as judged by the narrowing of the fluorescence peak. Fluorescence emission peaks were observed at: 702 nm for **3a**, 707 nm for **5a** and 716 nm for **6a** in DMSO (Table 3). The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra in DMSO (Fig. 6) for **3a** and **6a**. The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for all complexes suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in DMSO. The observed Stokes shifts (Table 3) were typical of MPc complexes in DMSO.

The fluorescence quantum yields (Φ_F) of all complexes were similar and typical of MPc complexes, Table 4. Although the Φ_F value of the tetrasubstituted complex (**3a**) is larger than for unsubstituted **ZnPc**, the Φ_F values of the tetra- (**5a**) and octasubstituted complexes (**6a**) are lower than unsubstituted **ZnPc** in DMSO. The tetrasubstituted complex (**3a**) shows the largest (Φ_F) value in DMSO compared to the other complexes. The tetrasubstituted complex (**5a**) shows the lowest Φ_F value in DMSO, which can be ascribed to the aggregation tendencies of the molecules in this solvent (Fig. 2). Aggregation reduces the likelihood of radiative deactivation (fluorescence) through dissipation of energy by the aggregates.

Lifetimes of fluorescence (τ_F) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been found³⁵ for the experimentally and theoretically determined fluorescence lifetimes for the unaggregated molecules, as is the case in this work for **3a** and **6a** in DMSO. Thus, we believe that the values obtained using this equation are a good measure of fluorescence lifetimes. τ_F values are longer for complexes **3a**

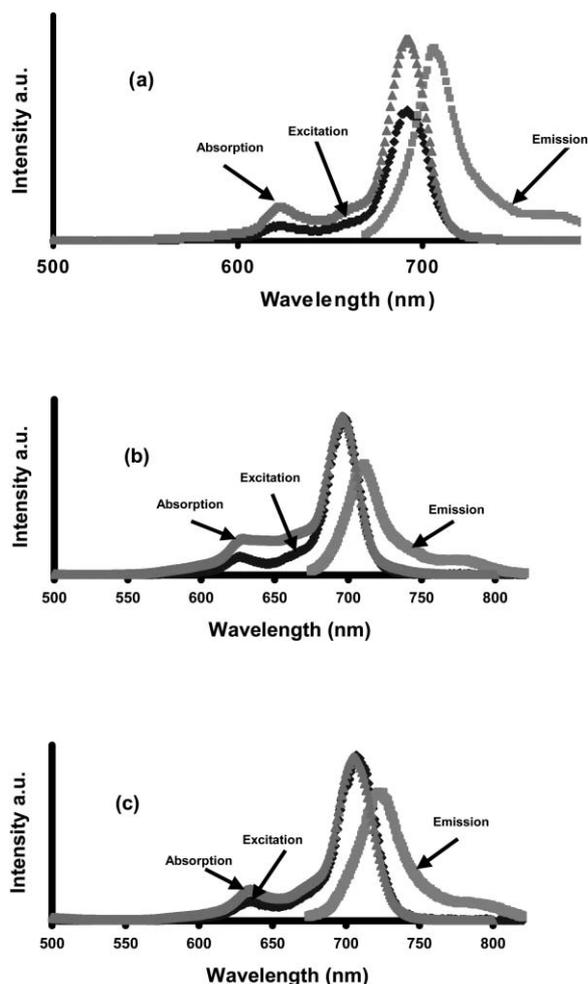


Fig. 6 Absorption, excitation and emission spectra of the compound **3a** (a), **5a** (b) and **6a** (c) in DMSO. Excitation wavelength = 665 nm.

and **6a** when compared to unsubstituted **ZnPc** in DMSO. Thus, the substitution on the phthalocyanine ring increased the τ_F values. The τ_F value for **5a** is lower than unsubstituted **ZnPc** in DMSO because of the aggregation in this solvent, Table 5. The natural radiative lifetime (τ_0) values of substituted complexes (**3a**, **5a** and **6a**) also increased with the number of substituents in DMSO. The rate constants for fluorescence (k_F) decreased with the number of the substituents in DMSO. k_F values for tetra- (**5a**) and octasubstituted complexes (**6a**) are lower than unsubstituted complex (**ZnPc**), while longer for tetrasubstituted complex (**3a**) in DMSO. The substituted complexes (**3a** and **6a**) showed lower rate constant (k_{IC}) and quantum yield for internal conversion (Φ_{IC}) in DMSO when compared to unsubstituted **ZnPc**, Table 4 and Table 5. Complex **5a** showed higher k_{IC} and Φ_{IC} values when compared to unsubstituted **ZnPc** in DMSO, again due to the aggregation. In addition, complexes **3a** and **6a**, and **ZnPc** showed almost the same rate constants for intersystem crossing (k_{ISC}) values, while complex **5a** showed larger k_{ISC} in DMSO when compared to unsubstituted **ZnPc**.

Triplet lifetimes and quantum yields

Transient spectrum for complex **3a** in DMSO is shown in Fig. 7, and shows a maximum at 540 nm, hence the triplet lifetimes and

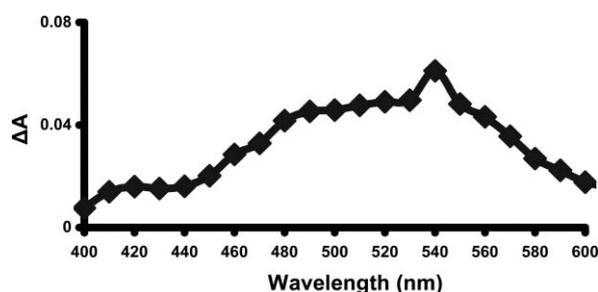
Table 4 Photophysical and photochemical parameters of unsubstituted, tetra- and octasubstituted zinc phthalocyanines in DMSO. Triplet absorption wavelength used = 510 nm for **ZnPc** and 540 nm for **3a**, **5a** and **6a**^a

Compound	Φ_F	$\tau_T/\mu s$	Φ_T	Φ_{IC}	$\Phi_d(x10^{-5})$	Φ_Δ	S_Δ
ZnPc	0.18 [36]	350	0.65 [39]	0.17	2.61	0.67 [42]	1.03
3a	0.22	220	0.73	0.05	0.26	0.72	0.98
5a	0.10	210	0.71	0.19	0.19	0.62	0.87
6a	0.15	300	0.75	0.10	1.94	0.60	0.80

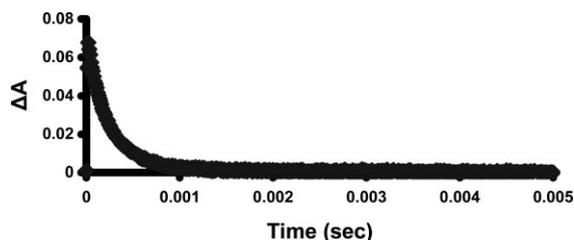
^a References in brackets**Table 5** Rate and quenching constants for various excited state deactivation processes of unsubstituted, tetra- and octasubstituted zinc phthalocyanines in DMSO

Compound	τ_F (ns)	τ_0 (ns)	$k_F/s^{-1}(x10^8)^a$	$k_{ISC}/s^{-1}(x10^8)^b$	$k_{IC}/s^{-1}(x10^7)^c$	$k_d/s^{-1}(x10^{-2})^d$	K_{SV}/M^{-1}	$k_q/dm^3 mol^{-1} s^{-1}(x10^{10})$
ZnPc	1.22	6.80	1.47	5.32	13.9	7.4	31.90	2.61
3a	1.34	5.95	1.68	5.44	3.73	1.2	21.07	1.57
5a	0.83	8.29	1.20	8.55	22.89	0.9	14.76	1.78
6a	1.57	10.47	0.95	4.77	6.37	6.4	11.77	0.75

^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 $k_d = \Phi_d/\tau_T$.

**Fig. 7** Transient differential spectrum of complex **3a** in DMSO.

yields were determined at this wavelength for complexes **3a**, **5a** and **6a**. Fig. 8 shows the triplet decay curves of the complexes (using complex **3a** in DMSO as an example). Complex **6a** showed longer triplet lifetime when compared to the other substituted complexes (**3a** and **5a**), suggesting that it is not the plurality of the substituents that results in more quenching. The triplet lifetime (τ_T) values were lower for substituted zinc complexes (**3a**, **5a** and **6a**) when compared to unsubstituted **ZnPc**, Table 4.

**Fig. 8** Triplet decay curve of **3a** in DMSO. Excitation wavelength = 540 nm.

The triplet quantum yields (Φ_T) for substituted complexes (**3a**, **5a** and **6a**) in DMSO are higher when compared to unsubstituted **ZnPc** in DMSO. The higher values of Φ_T in DMSO suggest efficient intersystem crossing (ISC) in the presence of the substituents

for substituted complexes (**3a**, **5a** and **6a**), resulting in high Φ_T values. Complex **6a** showed larger Φ_T value when compared to the other substituted complexes (**3a** and **5a**) in DMSO.

Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using a chemical method with DPBF as a quencher. The disappearance of DPBF spectra was monitored using UV-vis spectrophotometer. Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen, including triplet excited state energy, ability of substituents and solvents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen.

There was no change in the Q band intensity during the Φ_Δ determinations, confirming that complexes are not degraded during singlet oxygen studies. The Φ_Δ values of tetrasubstituted complex **3a** were higher when compared to unsubstituted **ZnPc** in DMSO. The Φ_Δ values of tetrasubstituted (**5a**) and octasubstituted (**6a**) complexes were lower when compared to unsubstituted **ZnPc** in DMSO (Table 4). The magnitude of the S_Δ ($= \Phi_\Delta/\Phi_T$) represents the efficiency of quenching of the triplet excited state by singlet oxygen. All the complexes **3a**, **5a** and **6a** showed values of S_Δ of near unity (Table 4), suggesting efficient quenching of the triplet state by singlet oxygen. Complex **6a** showed lower S_Δ when compared to the other substituted complexes (**3a** and **5a**) in DMSO, suggesting a less efficient quenching of oxygen compared to the rest of the complexes.

Photodegradation studies

Degradation of the molecules under irradiation can be used to study their stability, and this is especially important for those molecules intended for use as photocatalysts. The collapse of the absorption spectra without any distortion of the shape confirms

clean photodegradation not associated with phototransformation. The spectral changes observed for all the complexes **3a**, **5a** and **6a** during photodegradation occurred without phototransformation.

Table 4 shows that all substituted complexes (**3a**, **5a** and **6a**) were more stable to degradation compared to unsubstituted **ZnPc** in DMSO. Thus, the substitution of **ZnPc** with a branched polyoxy group seem to increase the stability of the complexes in DMSO. The octasubstituted complex **6a** was less stable when compared to the other substituted complexes (**3a** and **5a**). The stability order among the substituted complexes was **5a** > **3a** > **6a** > **ZnPc** in DMSO, which does not follow the trend in Φ_{Δ} , suggesting that the degradation of the ring is not caused only by singlet oxygen. The rate constants for photodegradation (k_d) of substituted complexes (**3a**, **5a** and **6a**) were lower than unsubstituted **ZnPc** in DMSO.

Fluorescence quenching studies by benzoquinone [BQ]

The fluorescence quenching of zinc phthalocyanine complexes by BQ in DMSO was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 9 shows the quenching of complex **5a** by BQ in DMSO as an example. The slope of the plots shown at Fig. 10 gave K_{SV} values, listed in Table 5. The K_{SV} values of the substituted zinc phthalocyanine complexes (**3a**, **5a** and **6a**) are lower than unsubstituted **ZnPc** in DMSO. Of the substituted complexes, **3a** has highest K_{SV} value, while complex **6a** has the lowest K_{SV} in DMSO. The substitution with a branched polyoxy group seems to decrease the K_{SV} values of the complexes in DMSO. The bimolecular quenching constant (k_q) values of the substituted zinc phthalocyanine complexes (**3a**, **5a** and **6a**) are also lower than for

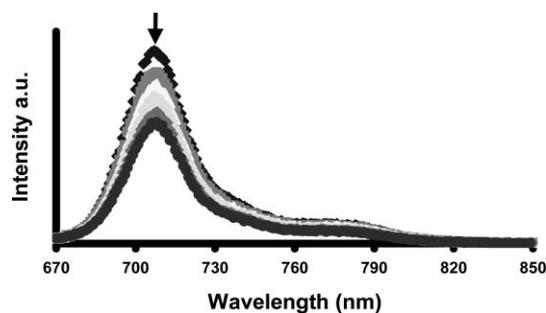


Fig. 9 Fluorescence emission spectral changes of **5a** (1.10×10^{-5} mol dm $^{-3}$) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm $^{-3}$.

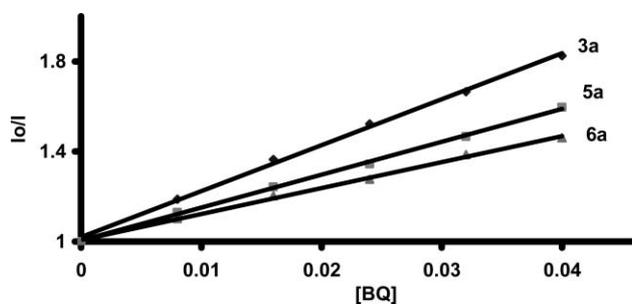


Fig. 10 Stern–Volmer plots for BQ quenching of **3a**, **5a** and **6a**. [MPc] $\sim 1.00 \times 10^{-5}$ mol dm $^{-3}$ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm $^{-3}$.

unsubstituted **ZnPc** in DMSO, thus substitution with branched polyoxy group seems to decrease the k_q values of the complexes. The order in k_q values among the substituted complexes was also as follows: **5a** > **3a** > **6a** in DMSO.

Conclusions

In the present work, the syntheses of new tetra- and octa thia(polyoxyethylene) substituted Zn(II) phthalocyanines are described and the compounds are characterized by standard methods (^1H - and ^{13}C -NMR, elemental analysis, IR, UV/Vis and mass spectrometry). In solution, the spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metalated phthalocyanine complexes for **3a** and **6a** in DMSO. Complex **5a** showed a broad band around 650 nm due to the aggregation in DMSO. The substitution of the branched polyoxy substituents on the phthalocyanine ring increased the wavelength of the Q band. The fluorescence quantum yields of substituted complexes were typical for MPcs. The substituted complexes (**3a**, **5a** and **6a**) have good singlet oxygen quantum yields (Φ_{Δ}), especially complex **3a**, which has the highest value. The singlet oxygen quantum yields, which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism), ranged from 0.60 to 0.72. Thus, these complexes show potential as Type II photosensitizers. Substitution of **ZnPc** with a branched polyoxy group seem to increase the stability of the complexes in DMSO. The stability order among the substituted complexes was **5a** > **3a** > **6a** in DMSO. The substituted complexes showed lower K_{SV} and k_q values when compared to the unsubstituted **ZnPc** in DMSO.

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