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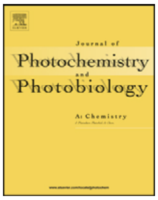

Tetra-3-[(2-diethylamino)ethyl]-7-oxo-4-methylcoumarin-substituted zinc phthalocyanines: Synthesis, characterization and aggregation effects on photophysical/photochemical properties

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ABSTRACT

A synthesis of a novel zinc phthalocyanine with four 3-[(2-diethylamino)ethyl]-7-oxo-4-methylcoumarin dye groups at the non-peripheral positions was performed and characterized. The photophysical and photochemical properties of the peripherally (**p**) and non-peripherally (**np**) tetra-3-[(2-diethylamino)ethyl]-7-oxo-4-methylcoumarin substituted zinc (II) phthalocyanines are reported. The effects of the position of the substituents and the aggregation on the photophysical/photochemical properties of these complexes are also investigated. General trends are described for photodegradation, singlet oxygen and fluorescence quantum yields, and fluorescence lifetimes in dimethylsulphoxide (DMSO) for **np-ZnPc** and in both DMSO and DMSO + Triton-X 100 solutions for **p-ZnPc**. The fluorescence of the tetra-substituted zinc phthalocyanine complexes (**np-ZnPc** and **p-ZnPc**) are effectively quenched addition of 1,4-benzoquinone (BQ).

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1. Introduction

Since their accidental synthesis in 1928, phthalocyanines (Pcs) have enjoyed considerable industrial importance as dyes, paints and color for metal surfaces, fabrics and plastics. In recent years, various Pc complexes have been synthesized, characterized and investigated in terms of their properties [1,2]. Pcs are highly stable and versatile aromatic macrocyclic compounds, capable of including more than 70 metallic and non-metallic ions in the ring cavity. The optical and electronic properties of the phthalocyanine macrocycles make them suitable for a wide range of applications [3]. Some technological applications of these macrocycles have been intensively investigated, such as dyes and pigments [4], light emitting diodes [5], in optical limiting devices [6–8], in molecular electronics [9], for non-linear optical applications [10], as liquid crystals [11,12], gas sensors [13], semiconductor materials [14], in photovoltaic cells [15,16], photodynamic therapy [17–20] and for electrochromic displays [21,22]. Numerous studies have been performed to modify these macrocyclic compounds with the goal of tuning their properties and utilizing their efficacy for the above applications [23–25].

On the other hand, coumarin (2H-1-benzopyran-2-one, 2H-chromen-2-one) and its derivatives are biologically active substances with numerous metabolites, and widespread in nature [26]. Some coumarin derivatives were used as anticoagulants, additives in food and cosmetics, reagents in the preparation of insecticides and as optical brighteners [27–32]. Coumarins are one kind of significant organic fluorescent chromophores and widely used in synthesizing laser dyes, fluorescent whiteners, organic nonlinear optical materials and so on [33].

Some of the coumarin derivatives show anti-clotting activity [34,35]. For example, carbochromen (3-diethylaminoethyl-7-ethoxycarbonylmethoxy-4-methylcoumarin) is a potent specific coronary vasodilator used for many years in the treatment of angina pectoris [27,36]. A number of coumarin metal complexes have been synthesized and their biological activities have been determined [37].

A major disadvantage of Pcs is their low solubility in common organic solvents or in water. Their insolubility causes difficulties for many applications rendering the syntheses of soluble derivatives an important task. Peripheral substitution with bulky groups or long alkyl, alkoxy or alkylthio chains leads to phthalocyanine products which are soluble in apolar solvents [1].

In view of the biological importance of both coumarins and Pcs it is worthwhile to combine these two functional molecules into a single compound and combine via synthetic methodology and

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prepare and characterize their ZnPc derivatives, which may also exhibit biological activities.

In this work, we report the synthesis and characterization of a newly synthesized non-peripherally ZnPc bearing four substituents of 3-[(2-diethylamino)ethyl]-7-oxy-4-methylcoumarin. Photodegredation, singlet oxygen and fluorescence quantum yields, and fluorescence lifetimes are investigated for **np-ZnPc** in DMSO and for **p-ZnPc** in DMSO and DMSO + Triton-X 100. The effects of the central metal atom, substitution position and aggregation on the photophysical and photochemical properties of studied compounds are investigated. The fluorescence quenching properties of these complexes are also reported. The combined structures of the coumarin and Pc can be a potential candidate for the application of PDT.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. 3-[(2-Diethylamino)ethyl]-7-hydroxy-4-methylcoumarin hydrochloride was purchased from the Aldrich Chemical Company. 1,3-Diphenylisobenzofuran (DPBF) was purchased from Fluka. 1,2-Dicyano-3-nitrobenzene [38], 1,2-dicyano-4-nitrobenzene [39], 3-[(2-diethylamino)ethyl]-7-[(2,3-dicyanophenoxy)]-4-methylcoumarin (**1**) and 2(3),9(10),16(17),23(24)-tetrakis[7-oxo-(3-[(2-diethylamino)ethyl)]-4-methylcoumarin]-phthalocyanine (**p-ZnPc**) [40] were synthesized and purified according to well known literature.

2.2. Equipment

The IR spectra were recorded on a Shimadzu Fourier Transform FTIR-8300 using KBr pellets. ^{1}H NMR spectra were recorded on a Varian 500 MHz spectrometer in $CDCl_3$ at Gebze Institute of Technology. Elemental analysis carried out using a LECO CHN 932 was performed by the Instrumental Analysis Laboratory of TUBITAK Ankara Test and Analysis Laboratory. Mass spectra were performed on a Bruker Daltonic Autoflex III MALDI-TOF spectrometer at Marmara University. Absorption spectra in the UV–vis region were recorded with a Shimadzu 2001 UV and Shimadzu UV-1601 spectrophotometers. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature.

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.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. (1) [41,42]

$$\Phi_F = \Phi_F(\mathrm{Std}) \frac{F \cdot A_{\mathrm{Std}} \cdot n^2}{F_{\mathrm{Std}} \cdot A \cdot n^2_{\mathrm{Std}}} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**np-ZnPc** and **p-ZnPc**) and the standard, respectively. A and A_{Std} are the relative absorbance of the sample and standard at the excitation wavelength, respectively. n^2 and n^2_{Std} are the refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [43] was employed as the standard. Both the sample and standard were excited at the same wavelength. The absorbance of the solutions was ranged between 0.04 and 0.05 at the excitation wavelength.

Natural radiative lifetimes (τ_0) were determined using Photochem CAD program which uses the Strickler–Berg equation [44]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out by using the experimental set-up described in literature [45–47]. Typically, 3 mL portion of the respective unsubstituted, peripherally and non-peripherally tetra- substituted zinc (II) phthalocyanine (**ZnPc**, **np-ZnPc** and **p-ZnPc**) solutions (concentration = 1×10^{-5} M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references [45–47]. Φ_Δ was determined in air using the relative method using ZnPc (in DMSO) as a reference. DPBF was used as chemical quenchers for singlet oxygen in DMSO. Eq. (3) was employed for the calculations of Φ_Δ:

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}} \frac{R \cdot I_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}} \cdot I_{\mathrm{abs}}} \tag{3}$$

where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yields for the standard ZnPc ($\Phi_\Delta^{\mathrm{Std}} = 0.67$ in DMSO) [48]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**np-ZnPc** and **p-ZnPc**) and standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by the samples (**np-ZnPc** and **p-ZnPc**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [49], the concentration of quencher was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer containing DPBF was prepared in the dark and irradiated in the Q band region using the above set-up. DPBF degradation at 417 nm was monitored. The light intensity was 6.66×10^{15} photons/s cm^2 for Φ_Δ determinations.

2.4.2. Photodegredation quantum yields

Determinations of photodegredation quantum yield (Φ_d) were carried out as previously described in the literature [45–47]. Φ_d was determined using Eq. (4),

$$\Phi_d = \frac{(C_0 - C_t) V N_A}{I_{\mathrm{abs}} S t} \tag{4}$$

where C_0 and C_t are the samples (**np-ZnPc** and **p-ZnPc**) concentrations before and after irradiation, respectively, V, N_A, S, t and I_{abs} are reaction volume, the Avogadro's constant, irradiated cell area, irradiation time and the overlap integral of the radiation light source intensity, respectively. A light intensity of 2.22×10^{16} photons/s cm^2 was employed for Φ_d determinations.

2.4.3. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the substituted ZnPc derivatives (**np-ZnPc** and **p-ZnPc**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complexes, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence spectra of substituted ZnPc derivatives (**np-ZnPc** and **p-ZnPc**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer

(S–V) equation [50] as shown in Eq. (5):

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

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and K_{SV} is the Stern–Volmer constant which is the product of the bimolecular quenching constant (k_q) and the τ_F and is expressed in Eq. (6).

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

The ratios of I_0/I were calculated and plotted against [BQ] according to Eq. (5), and K_{SV} is determined from the slope.

2.5. Synthesis

2.5.1. 3-[(2-Diethylamino)ethyl]-7-[(2,3-dicyanophenoxy)]-4-methylcoumarin (*1*)

3-[(2-Diethylamino)ethyl]-7-hydroxy-4-methylcoumarin hydrochloride (0.500 g, 1.60 mmol) and 1,2-dicyano-3-nitrobenzene (0.277 g, 1.60 mmol) were added successively with stirring to dry dimethylformamide (DMF) (10 mL) and DMSO (5 mL). After stirring for 15 min, finely ground anhydrous K_2CO_3 (0.332 g, 2.40 mmol) was added portionwise over 2 h. After heating (50 °C) and stirring for 5 days under nitrogen the reaction mixture was poured into iced water and acidified with aqueous HCl solution. The precipitate formed was filtered, washed with water until neutral and the crude product was dried. The yellow product (**1**) obtained as pure. The compound is soluble in ethanol, methanol, tetrahydrofuran, chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide.

Compound **1**: Yield: 0.562 g (87%); m.p.: 150–153 °C. IR (KBr pellet) γ_{max} (cm^{-1}): 3075 (aryl CH), 2810–2919 (alkyl CH), 2230 (C≡N), 1709 (C=O lactone), 1614 and 1572 (C=C), 1278 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$) δ_H: 7.87 (t, 1H, Ar–H), 7.80 (d, 8 Hz, 1H, Ar–H), 7.60 (dd, 8 Hz, 3 Hz, 1H, Ar–H), 7.54 (dd, 8 Hz, 2 Hz, 1H, Ar–H), 7.12 (d, 8 Hz, 1H, Ar–H), 7.10 (dd, 8 Hz, 2 Hz, 1H, Ar–H), 3.41 (t, 2H, $ArCH_2CH_2$), 3.01 (q, 4H, NCH_2), 2.06 (t, 2H, $ArCH_2$), 2.42 (s, 3H, CH_3), 1.02 (t, 6H, NCH_2CH_3). UV–vis λ_{max} (nm) (log ε) (THF) (1.061 × 10^{-5} M): 316 (4.18). Anal. Calcd. for $C_{24}H_{23}N_3O_3$: C 71.82; H 5.73; N 10.47%. Found: C 70.94; H 5.02; N 10.41%. MS (MALDI-TOF) *m*/*z*: 401 [M]$^+$, 402 [M+1]$^+$.

2.5.2. 1(4)-Tetrakis-[7-oxo-(3-[(2-diethylamino)ethyl)]-4-methylcoumarin]-phthalocyaninato zinc (II) (*np-ZnPc*)

The mixture of compound **1** (0.1 g, 0.25 mmol) and anhydrous $Zn(CH_3COO)_2$ (0.014 g, 0.06 mmol) was heated at 145 °C with 2 mL of dry 2-N,N-dimethylaminoethanol in a sealed tube, and stirred for 24 h. After cooling to room temperature, the reaction mixture was treated with acetone, the precipitate then filtered off and washed with water to remove unreacted $Zn(CH_3COO)_2$. The green product was purified on silica gel column chromatography with chloroform as eluent. The compound is soluble in chloroform, dimethylformamide and dimethylsulfoxide.

Compound **np-ZnPc**: Yield: 0.045 g (43%); m.p.: >300 °C. IR (KBr pellet) γ_{max} (cm^{-1}): 3058 (aryl CH), 2916-2974 (alkyl CH), 1706 (C=O lactone), 1616, 1581 (C=C), 1244 (Ar–O–Ar). UV–vis λ_{max} (log ε) (nm) (DMF) (1.271 × 10^{-5} M): 687 (4.87), 312 (4.56). Anal. Calcd. for $C_{96}H_{92}N_{12}O_{12}Zn$: C 69.02; H 5.51; N 10.06%. Found: C 68.76; H 5.59; N 9.84%. MS (MALDI-TOF) *m*/*z*: 1669 [M]$^+$, 1670 [M+1]$^+$.

2.5.3. 2(3),9(10),16(17),23(24)-Tetrakis[7-oxo-(3-[(2-diethylamino)ethyl)]-4-methylcoumarin]-phthalocyanine (*p-ZnPc*)

This phthalocyanine complex was synthesized according to literature procedure [40].

Compound **p-ZnPc**: Yield: 0.040 g (77%); m.p.: >300 °C. IR γ_{max} (cm^{-1}): 3051 (aryl CH), 2916-2947 (alkyl CH), 1701 (C=O lactone), 1604, 1465 (C=C), 1238 (Ar–O–Ar). UV–vis (DMF) λ_{max} (log ε) (nm): 679 (4.08), 617 (4.38), 337 (4.56). Anal. Calcd. for $C_{96}H_{92}N_{12}O_{12}Zn$: C 69.02; H 5.51; N 10.06%. Found: C 68.16; H 5.59; N 9.84%. MS (MALDI-TOF) *m*/*z*: 1669 [M]$^+$, 1670 [M+1]$^+$

3. Result and discussion

3.1. Syntheses and characterization

3-[(2-Diethylamino)ethyl]-7-[(2,3-dicyanophenoxy)]-4-methylcoumarin (**1**) was prepared by K_2CO_3 catalyzed nucleophilic aromatic nitro displacement of 1,2-dicyano-3-nitrobenzene with 3-[(2-diethylamino)ethyl]-7-hydroxy-4-methylcoumarin hydrochloride in DMF/DMSO (2/1) under N_2 atmosphere at room temperature and the yield was 87%.

Cyclotetramerization of the phthalonitrile derivative (**1)** was accomplished in anhydrous 2-N,N-dimethylaminoethanol (DMAE) in the presence of anhydrous $Zn(CH_3COO)_2$ salt at 145 °C affording **np-ZnPc** (Fig. 1). The **p-ZnPc** was prepared according to the literature [40] (Fig. 2). The tetraoxycoumarin substituted **np-ZnPc** was purified on silica gel column chromatography with chloroform as an eluent. Characterization of the products involved a combination of methods including elemental analysis, ^{1}H NMR, IR, UV–vis, fluorescence and MALDI-TOF spectroscopy.

Spectral data of the newly synthesized compounds are consistent with the proposed structures. The IR spectrum of compound **1** clearly indicates the appearance of the new absorption bands at 2230 cm^{-1} (C≡N) and 1278 cm^{-1} (Ar–O–Ar). After reaction of the dinitrile derivative (**1**), the sharp peak for the C≡N vibration around 2230 cm^{-1} disappeared and the color of the reaction was converted to green. The C=O and C=C bands for **np-ZnPc** in IR spectra was broader and shorter than those of **1** because of the H-type aggregation of coumarin moiety.

The ^{1}H NMR spectrum of **1** exhibited aromatic protons at 7.87, 7.80, 7.60, 7.54, 7.12, 7.10 ppm and aliphatic protons at 3.41 ppm $ArCH_2CH_2$, 3.01 ppm NCH_2, 2.06 ppm $ArCH_2$, 2.42 ppm CH_3, 1.02 ppm NCH_2CH_3.

The mass spectra of **np-ZnPc** confirmed the proposed structure. The [M$^+$] peak was identified easily. The MALDI-TOF MS spectra provided definitive characterization of the structure of newly synthesized compounds. Linear mode positive ion MALDI mass spectra were obtained in 7-hydroxycoumarin (umbelliferone) MALDI matrix. The protonated molecular ion peak of the complex **np-ZnPc** was observed at 1669 Da.

3.2. Electronic absorption spectroscopic properties

The electronic spectra of the non-peripherally tetra-substituted phthalocyanine complex (**np-ZnPc**) showed intense Q absorption band at 693 nm (Fig. 3) in DMSO. The spectrum showed monomeric behaviour evidenced by a single (narrow) Q band, typical for metallated phthalocyanine complexes [51]. In DMSO, the absorption spectra of peripherally tetra-substituted compound (**p-ZnPc**) indicate its co-facial aggregation, as evidenced by the presence of two peaks in the Q band region (Fig. 3, Table 1). The lower energy (red-shifted) band at 678 nm is due to the monomeric species, while the higher energy (blue-shifted) band at 639 nm is due to the aggregated species. The addition of surfactants such as Triton-X

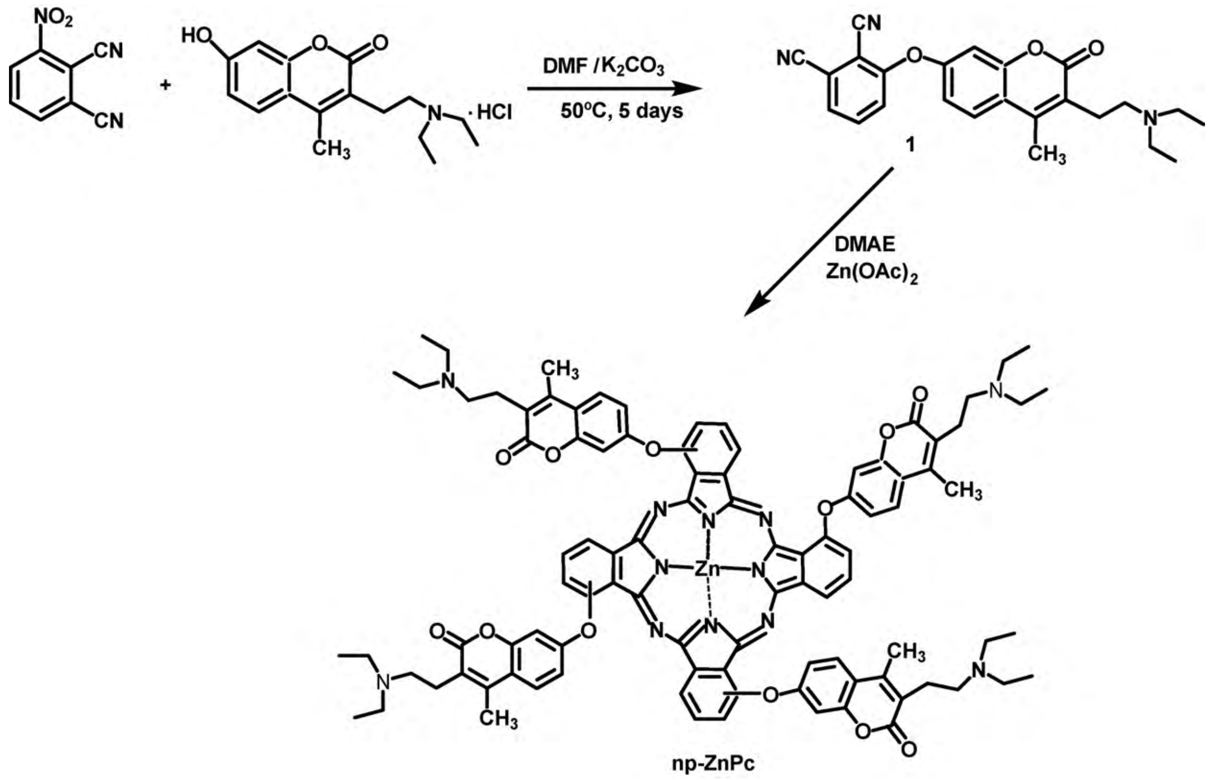

Fig. 1. Synthesis route of the non-peripherally tetra-3-[(2-diethylamino)ethyl]-7-oxo-4-methylcoumarin-substituted zinc (II) phthalocyanines complex (**np-ZnPc**).

100 can reduce aggregation. The aggregated molecules are dissociated thanks to the intercalation of the surfactant. Addition of Triton-X 100 (0.1 mL) to DMSO solution of the peripherally tetra-substituted zinc phthalocyanine complex (**p-ZnPc**) (concentration = 1.0×10^{-5} M) brings about considerable increase in intensity of the low energy side of the Q band (Fig. 4), suggesting that the molecules are aggregated and that addition of Triton-X 100 enhances monomerization. The electronic spectra of the peripherally tetra-substituted phthalocyanine complex (**p-ZnPc**) showed intense Q absorption band at 677 nm (Fig. 4) in DMSO + Triton-X 100 solution.

In DMSO, the Q bands were observed at 672 nm (**ZnPc**), 693 nm (**np-ZnPc**), 678 nm (**p-ZnPc**) (Table 1). The Q band was observed at 677 nm for complex **p-ZnPc** in DMSO + Triton-X 100 solution (Table 1). Thus substitution of the ZnPc with coumarin substituents increased the wavelength of the Q band. The Q band of the non-peripherally tetra-substituted compound (**np-ZnPc**) was red-shifted 15 nm compared to the peripherally tetra-substituted complex (**p-ZnPc**) in DMSO (Table 1). The observed red spectral shift is typical of phthalocyanines with substituents at the non-peripheral positions and has been explained [52,53] due to linear combination of the atomic orbitals (LCAO) coefficients at the non-peripheral positions of the highest occupied molecular orbital (HOMO) being greater than those at the peripheral positions. As a result, the HOMO level is more destabilized upon non-peripherally substitution than peripherally substitution. Essentially, the energy gap (ΔE) between the HOMO and lowest unoccupied molecular orbital (LUMO) becomes smaller, resulting in a ~20 nm bathochromic shift. The B-bands were broad due to the superimposition of the B_1 and B_2 bands in the 300–350 nm regions. The shoulder between 400 and 420 nm may be due to charge transfer from the electron-rich ring to the electron-poor metal (Fig. 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, center metal ions and temperature [54,55]. 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 [56].

The aggregation behaviour of the coumarin substituted phthalocyanine complexes (**np-ZnPc** and **p-ZnPc**) were investigated at different concentrations in DMSO for complex **np-ZnPc** and in DMSO + Triton-X 100 for complex **p-ZnPc** (Fig. 5 as an example for complex **np-ZnPc** in DMSO). In DMSO or DMSO + Triton-X 100 solutions, as the concentration was increased, the intensity of the Q band absorption also increased and there were no new bands (normally blue-shifted) due to the aggregated species for complex **np-ZnPc** in DMSO and for complex **p-ZnPc** in DMSO + Triton-X 100

Table 1
Absorption, excitation and emission spectral data for unsubstituted (**ZnPc**) and non-peripherally tetra-substituted zinc phthalocyanine (**np-ZnPc**) in DMSO and for peripherally tetra-substituted zinc phthalocyanine (**p-ZnPc**) in DMSO or DMSO + Triton-X 100 (TX).

Compound	Solvent	Q band λ_{max} (nm)	($\log \varepsilon$)	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift Δ_{Stokes} (nm)
ZnPc[a]	DMSO	672	5.14	672	682	10
np-ZnPc	DMSO	693	5.11	693	703	10
p-ZnPc	DMSO	678, 639	4.56, 4.48	681	687	9
p-ZnPc	DMSO + TX	677	4.70	678	687	10

[a] Ref: [62].

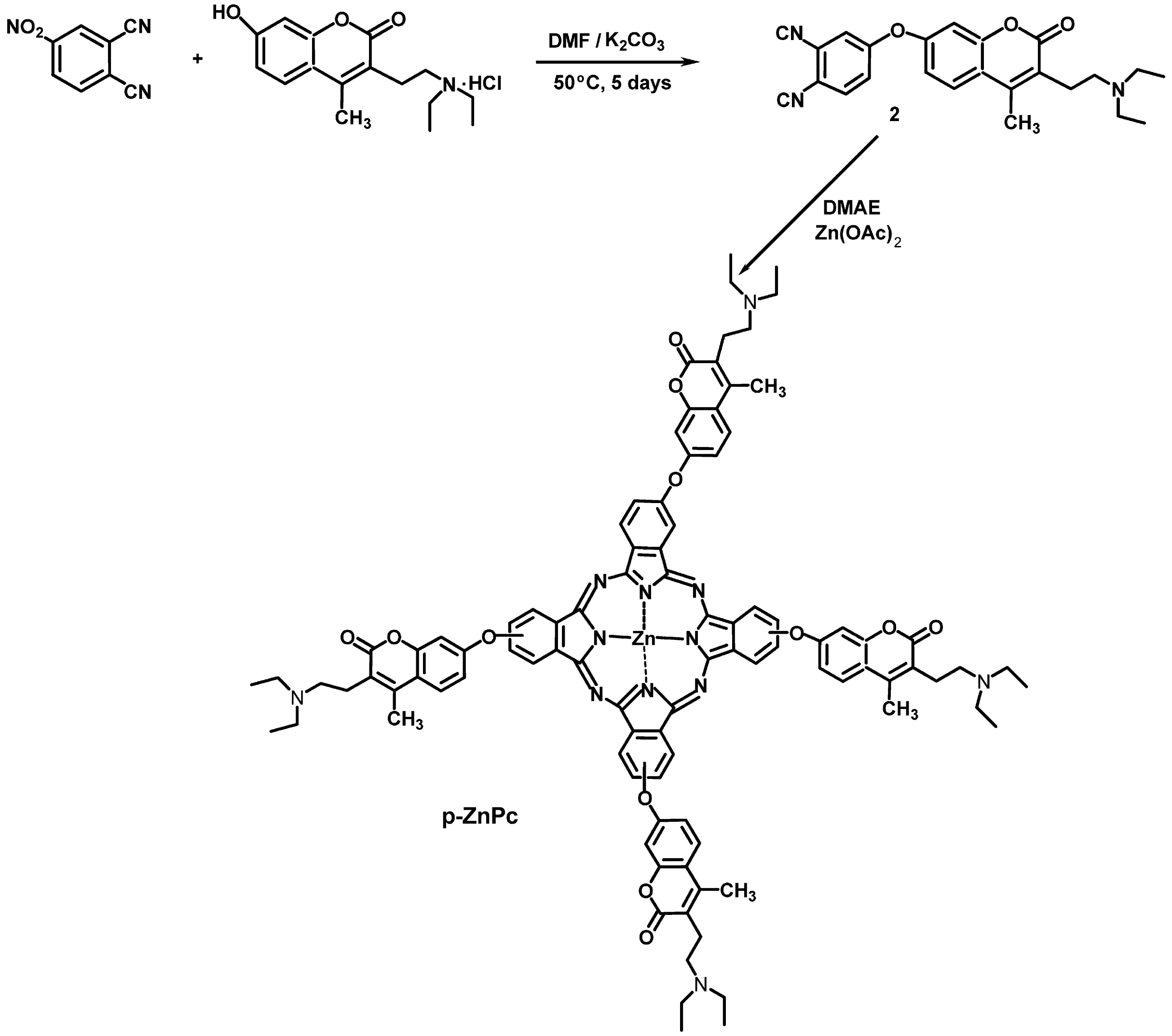

Fig. 2. Synthesis route of the peripherally tetra-3-[(2-diethylamino)ethyl]-7-oxo-4-methylcoumarin-substituted zinc (II) phthalocyanines complex (**p-ZnPc**).

solution (Fig. 5 as an example for complex **np-ZnPc** in DMSO). Thus, the non-peripherally tetra-substituted phthalocyanine complex (**np-ZnPc**) did not show aggregation in DMSO at different concentrations. The peripherally tetra-substituted compound (**p-ZnPc**) showed a little aggregation in DMSO + Triton-X 100 solution. Lambert-Beer low was obeyed for all of these compounds in the concentrations ranging from 1.4×10^{-5} to 4×10^{-6} M.

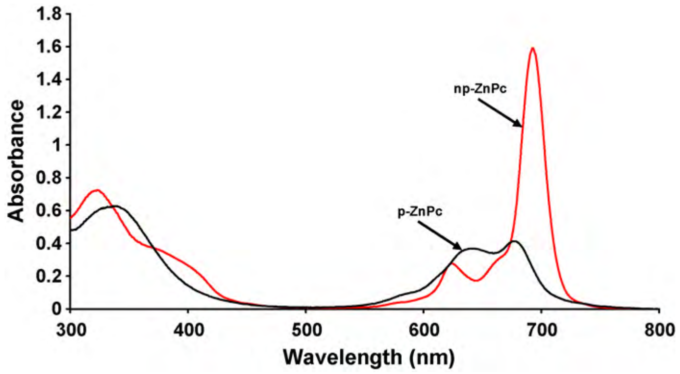

Fig. 3. Absorption spectrum of tetra-substituted zinc phthalocyanine complexes (**np-ZnPc** and **p-ZnPc**) in DMSO. Concentration = 1×10^{-5} M.

3.3. Fluorescence quantum yields and lifetimes

Fig. 6 shows the absorption, fluorescence emission and excitation spectra for the compounds (**np-ZnPc** and **p-ZnPc**) in DMSO. **p-ZnPc** was aggregated in DMSO, but the fluorescence spectra show

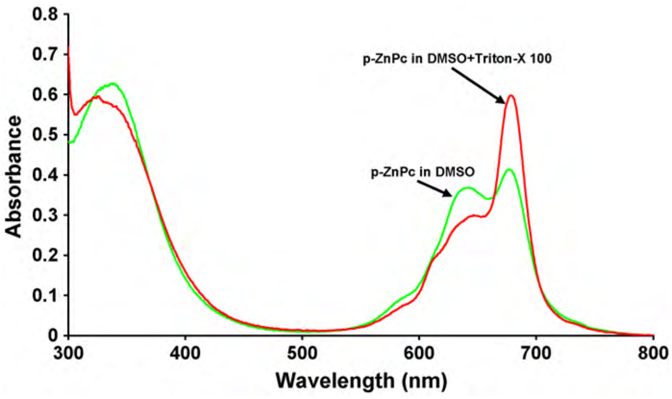

Fig. 4. Absortion spectral changes for peripherally tetra-substituted phthalocyanine complex (**p-ZnPc**) observed on addition of Triton-X 100 in DMSO. Concentration = 1×10^{-5} M.

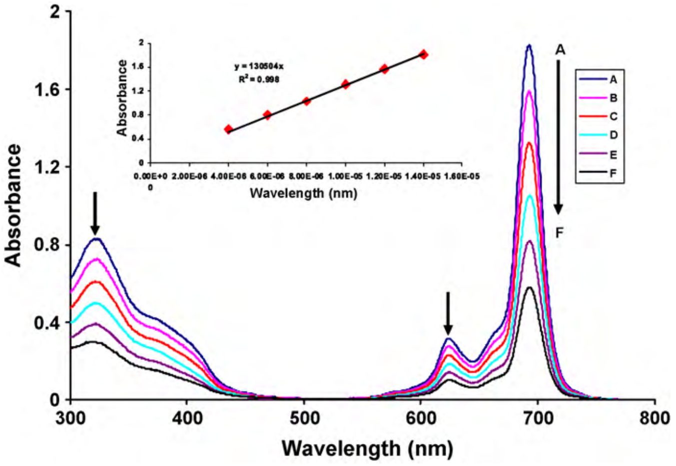

Fig. 5. Aggregation behaviour of **np-ZnPc** in DMSO at different concentrations: 14×10^{-6} (A), 12×10^{-6} (B), 10×10^{-6} (C), 8×10^{-6} (D), 6×10^{-6} (E), 4×10^{-6} (F) M (inset: plot of absorbance versus concentration).

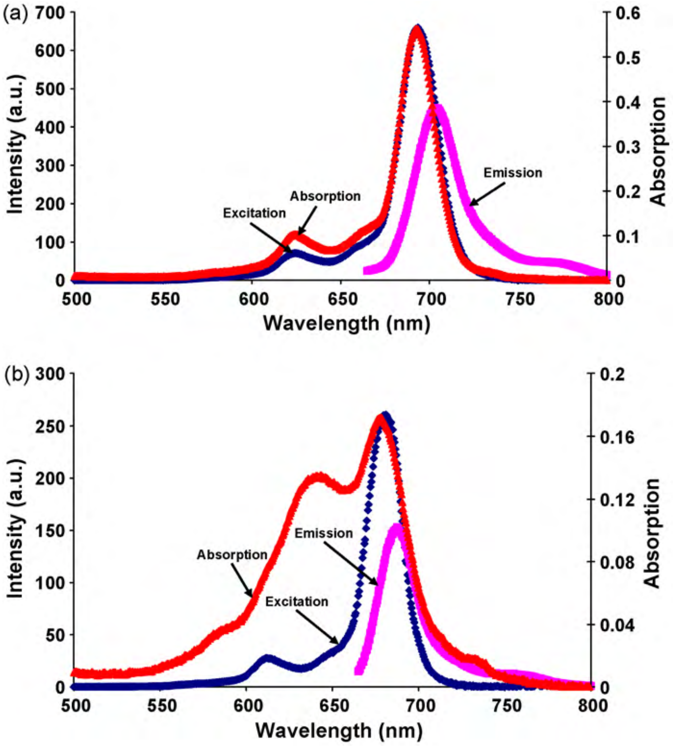

Fig. 6. Absorption, excitation and emission spectra of the compound **np-ZnPc** (a) and **p-ZnPc** (b) in DMSO. Excitation wavelength = 655 nm.

only the monomer species which fluoresced as judged by the narrowing of the fluorescence peak. Fluorescence emission peaks were observed at 703 nm for **np-ZnPc** and 687 nm for **p-ZnPc** in DMSO (Table 1). The excitation spectrum was similar to absorption spectrum and both were mirror images of the fluorescent spectrum for complex **np-ZnPc** in DMSO (Fig. 6a). The excitation spectrum was different from absorption spectrum for complex **p-ZnPc** in DMSO due to the aggregation of this complex in DMSO (Fig. 6b). This observation is typical of aggregated species. Aggregated MPc complexes are not known [57] to fluoresce since aggregation lowers the photoactivity of molecules through dissipation of energy by aggregates. The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for **np-ZnPc** suggests that the nuclear configurations of the ground and excited states were similar and not affected by excitation in DMSO. The observed Stokes shifts (Table 1) were typical of MPc complexes in DMSO or DMSO + Triton-X 100 solutions. The fluorescence emission peak of **p-ZnPc** is lower than **np-ZnPc** in DMSO (Fig. 6a and 6b) and the addition of the Triton-X 100 increased the intensity of the emission peak of **p-ZnPc**.

The fluorescence quantum yields (Φ_F) of the studied zinc phthalocyanine complexes are given in Table 2. The Φ_F value of non-peripherally complex was similar and typical of MPc complexes in DMSO (Table 2). But the Φ_F value of the peripherally complex was lower than MPc complexes due to the aggregation of this complex in DMSO. The Φ_F values of the substituted zinc phthalocyanine complexes are lower compared to unsubstituted zinc phthalocyanine complex in DMSO, which implies that the presence of the coumarin substituents certainly results in fluorescence quenching. The Φ_F value of **p-ZnPc** was lower than that of **np-ZnPc** due to the aggregation. The addition of the Triton-X 100 in the DMSO solutions of the **p-ZnPc** increased the Φ_F values of this complex due to the decrease in aggregation in the presence of the Triton-X 100 (Table 2).

Fluorescence lifetime (τ_F) refers to the average time a molecule stays in its excited state before fluorescing, and its value is directly related to that of Φ_F; i.e. the longer lifetime, the higher the quantum yield of fluorescence. Any factor that shortens the fluorescence lifetime of a fluorophore indirectly reduces the value of Φ_F. Such factors include internal conversion and intersystem crossing.

Fluorescence lifetimes (τ_F) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been [42] found for the experimentally and theoretically determined fluorescence lifetimes for the phthalocyanine molecules as is the case in this work for **np-ZnPc** in DMSO and **p-ZnPc** in both DMSO and DMSO + Triton-X 100 solutions. While τ_F value of non-peripherally complex (**np-ZnPc**) was higher the τ_F value of peripherally complex (**p-ZnPc**) was lower than unsubstituted ZnPc complex in DMSO because of the aggregation of **p-ZnPc** complex in this solvent (Table 2). The addition of Triton-X 100 increased the τ_F value of non-peripherally complex (**np-ZnPc**). The natural radiative lifetime (τ_0) values of tetra-substituted zinc phthalocyanine complexes (**np-ZnPc** and **p-ZnPc**) were also longer when compared to unsubstituted ZnPc in DMSO. The rate constants for fluorescence (k_F) of tetra-substituted zinc phthalocyanine

Table 2
Photophysical and photochemical parameters for unsubstituted (**ZnPc**) and non-peripherally tetra-substituted zinc phthalocyanine (**np-ZnPc**) in DMSO and for peripherally tetra-substituted zinc phthalocyanine (**p-ZnPc**) in DMSO or DMSO + Triton-X 100 (TX).

Compound	Solvent	Φ_F	τ_F (ns)	τ_0 (ns)	k_F (s^{-1})[a] ($\times 10^8$)	Φ_d ($\times 10^{-4}$)	Φ_Δ
ZnPc[b]	DMSO	0.18	1.22	6.80	1.47	2.61	0.67
np-ZnPc	DMSO	0.13	1.39	10.73	0.93	5.70	0.90
p-ZnPc	DMSO	0.03	0.88	29.46	0.34	0.40	0.33
p-ZnPc	DMSO + TX	0.10	2.65	26.53	0.38	4.72	0.55

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] [62].

complexes (**np-ZnPc** and **p-ZnPc**) were lower when compared to unsubstituted ZnPc in DMSO. k_F value for **p-ZnPc** was lower than **np-ZnPc** in DMSO. The addition of the Triton-X 100 also increased the k_F value of the peripherally substituted complex.

3.4. Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO and DMSO + Triton-X 100 solutions using a chemical method using 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. It is believed that during photosensitization, the phthalocyanine molecule is first excited to the singlet state and through intersystem crossing forms the triplet state, and then transfers the energy to ground state oxygen, $O_2(^3\sum_g)$, generating excited singlet state oxygen, $O_2(^1\Delta_g)$, the chief cytotoxic species, which subsequently oxidizes the substrate by Type II mechanism.

There was no change in the Q band intensity during the Φ_Δ determinations, confirming that complexes were not degraded during singlet oxygen studies (Fig. 7 as an example for complex **np-ZnPc** in DMSO). The Φ_Δ value of **np-ZnPc** was higher when compared to unsubstituted ZnPc in DMSO. The Φ_Δ value of **p-ZnPc** was lower when compared to unsubstituted ZnPc in DMSO and DMSO + Triton-X 100 solutions due to the aggregation of this complex. **np-ZnPc** showed highest Φ_Δ value in DMSO (Table 2). The addition of the Triton-X 100 reduced the aggregation of **p-ZnPc** and increased the Φ_Δ value of this complex from 0.33 to 0.55.

3.5. 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 into different forms of MPc absorbing in the visible region.

Fig. 8 shows that for zinc phthalocyanine complexes, there was a change in spectra following photodegradation. The spectral changes involved a decrease in the Q band and an increase in the absorption near 570 nm, suggesting that this band is due to reduction products of the complexes. The first ring reduction in MPc complexes is characterized by a decrease in the Q band and the formation of weak bands between 500 and 600 nm [58]. Thus, we propose that during photodegradation, the zinc phthalocyanine complexes were partly transformed to an anion (Pc^{-3}) species. This type of transformation has been observed before during the photodegradation of phthalocyanine complexes [59].

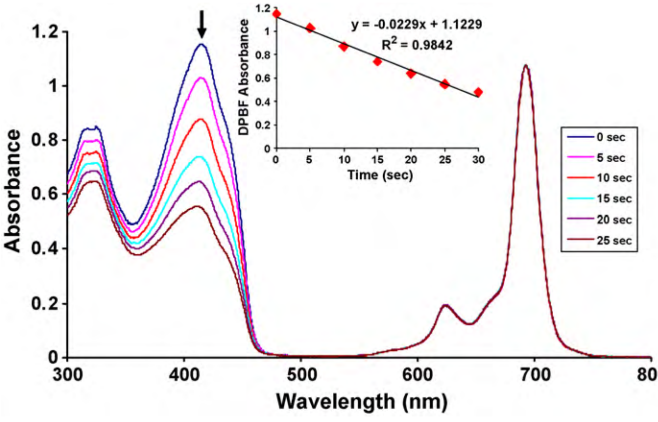

Fig. 7. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **np-ZnPc** in DMSO at a concentration of 1×10^{-5} M (inset: plot of DPBF absorbance versus time).

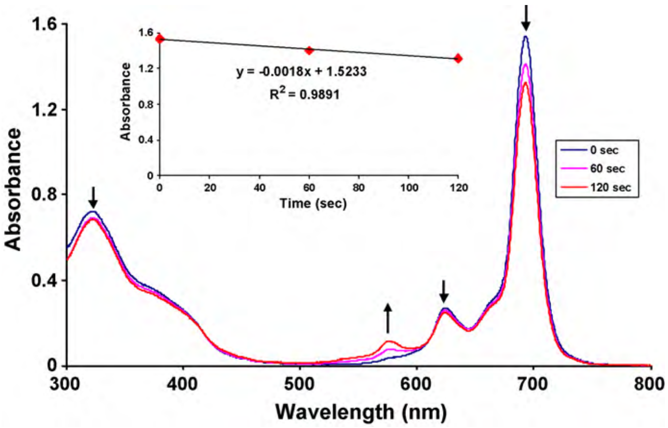

Fig. 8. The photodegredation of compound **np-ZnPc** in DMSO showing the disappearance of the Q-band at one minutes intervals (inset: plot of absorbance versus time).

All the studied zinc phthalocyanine complexes showed about the same stability with Φ_d of the order of 10^{-4} (Table 2). The Φ_d values, found in this study, are similar to zinc phthalocyanine complexes having different substituents on the phthalocyanine ring in literature [57,60,61].

Stable zinc phthalocyanine complexes show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [57]. It seems that zinc phthalocyanine complexes in this study also show similar Φ_d values and stability to the known zinc phthalocyanine complexes.

3.6. Fluorescence quenching studies by 1,4-benzoquinone [BQ]

The fluorescence quenching of zinc phthalocyanine complexes by 1,4-benzoquinone (BQ) in DMSO and DMSO + Triton-X 100 solutions was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 9 shows the quenching of complex **p-ZnPc** by BQ in DMSO + Triton-X 100 solution as an example. The slope of the plots shown in Fig. 10 gave K_{SV} values, listed in Table 3. The K_{SV} values of the tetra-substituted zinc

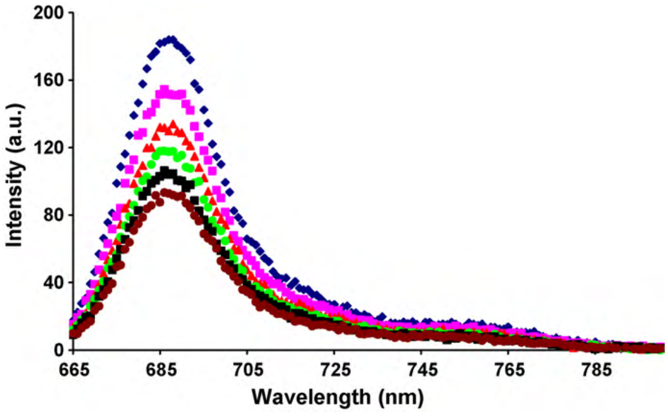

Fig. 9. Fluorescence emission spectral changes of **p-ZnPc** (1.00×10^{-5} M) on addition of different concentrations of BQ in DMSO + Triton-X 100. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

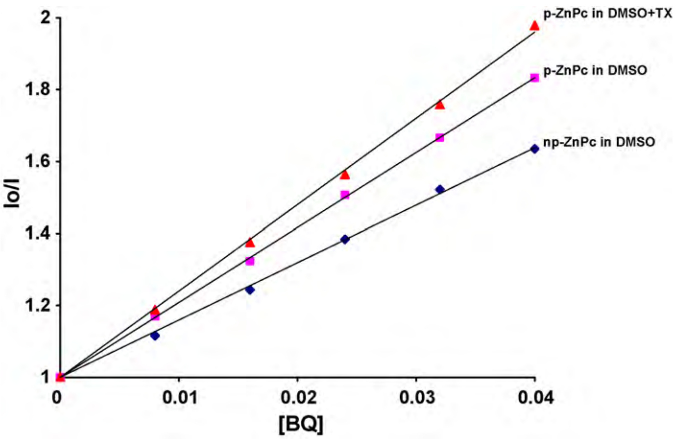

Fig. 10. Stern–Volmer plots for 1,4-benzoquinone (BQ) quenching of **np-ZnPc** in DMSO and **p-ZnPc** in DMSO and DMSO + Triton-X 100. [MPc] ~1.00 × 10^{-5} M. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

Table 3
Fluorescence quenching data for unsubstituted (**ZnPc**) and non-peripherally tetra-substituted zinc phthalocyanine (**np-ZnPc**) in DMSO and for peripherally tetra-substituted zinc phthalocyanine (**p-ZnPc**) in DMSO or DMSO + Triton-X 100 (TX).

Compound	Solvent	K_{SV} (M^{-1})	$k_q/10^{10}$ ($dm^3 mol^{-1} s^{-1}$)
ZnPc[a]	DMSO	31.90	2.61
np-ZnPc	DMSO	15.95	1.15
p-ZnPc	DMSO	20.83	2.36
p-ZnPc	DMSO + TX	24.00	0.90

[a] Ref: [62].

phthalocyanine complexes (**np-ZnPc** and **p-ZnPc**) were lower than unsubstituted ZnPc. When compared, the substituted complexes, **p-ZnPc** showed higher K_{SV} value than **np-ZnPc** in DMSO which can be due to the steric effect of the non-peripheral complex. The addition of Triton-X 100 to DMSO solution of **p-ZnPc** increased the K_{SV} value of this complex. The substitution with coumarin 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 (**np-ZnPc** and **ZnPc**) were also lower than for unsubstituted ZnPc, thus substitution with coumarin group seems to decrease the k_q values of the complexes. The k_q value of **np-ZnPc** was also lower than **p-ZnPc** in DMSO.

4. Conclusion

In the presented work, the syntheses of new non-peripherally tetra-3-[(2-diethylamino)ethyl]-7-oxo-4-methylcoumarin substituted Zn(II) phthalocyanine (**np-ZnPc**) was described and characterized by standard methods (elemental analysis, ^{1}H NMR, MALDI-TOF, IR and UV–vis and fluorescence spectral data). The photophysical and photochemical properties of the non-peripherally and peripherally tetra-substituted Zn(II) phthalocyanines (**np-ZnPc** and **p-ZnPc**) were also described for comparison. All the peripherally and non-peripherally ZnPc compounds are soluble in DMF and DMSO. In solution, the absorption spectrum showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complex for **np-ZnPc** in DMSO. The peripherally tetra-substituted compound (**p-ZnPc**) showed broad band around 640 nm due to the aggregation in DMSO. The coumarin groups as substituents on the phthalocyanine ring increased the wavelength of the Q band. Although, the fluorescence quantum yield of non-peripherally tetra-substituted compound (**np-ZnPc**) was typical for MPcs, the fluorescence quantum yield of the peripherally substituted complex was lower than MPc complexes due to the aggregation of this complex in DMSO. The aggregation decreased the fluorescence quantum yield and lifetime values of the compound **p-ZnPc** and addition of the Triton-X 100 increased these values. The coumarin substituted compounds (**np-ZnPc** and **p-ZnPc**) have good singlet oxygen quantum yields (Φ_Δ), especially compound **np-ZnPc** result in the highest value. Aggregation decreased the Φ_Δ value for **p-ZnPc**. The addition of the Triton-X 100 reduced the aggregation of the compound **p-ZnPc** and increased the Φ_Δ value of this compound. The value of Φ_Δ ranged from 0.33 to 0.90 gives an indication of the potential of the compounds as photosensitizers in applications where singlet oxygen is required (Type II mechanism). The coumarin substituted compounds showed lower K_{sv} and k_q values when compared to the unsubstituted ZnPc in DMSO and DMSO + Triton-X 100 solutions. The tetra-substituted zinc phthalocyanine compounds in this study show similar Φ_d values and stabilities to the zinc phthalocyanine compounds applicable in PDT.

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