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Synthesis and investigation on photophysical and photochemical properties of 7-oxy-3-methyl-4-phenylcoumarin bearing zinc phthalocyanines

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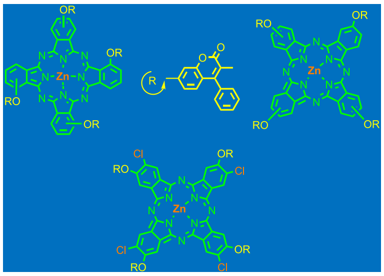
HIGHLIGHTS

- ▶ The synthesis of novel coumarin substituted zinc(II) phthalocyanines are reported.
- ▶ The studied complexes exhibited excellent solubility in general organic solvents.
- ▶ Photophysical and photochemical properties of new compounds are studied in DMF.
- ▶ Non-peripheral or peripheral position effect for tetra substitution is determined.

GRAPHICAL ABSTRACT

The synthesis of peripherally and non-peripherally tetrakis(7-oxy-3-methyl-4-phenylcoumarin) and peripherally octakis[tetrachloro-tetra(7-oxy-3- methyl-4-phenylcoumarin)] substituted zinc(II) phthalocyanine complexes are performed and characterized for the first time in this study. The photophysical and photochemical properties of phthalocyanine complexes are also investigated in dimethylformamide.



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ABSTRACT

The synthesis of peripherally and non-peripherally tetrakis-(7-oxy-3-methyl-4-phenylcoumarin) and peripherally octakis-[tetrachlorotetra-(7-oxy-3-methyl-4-phenyl coumarin)] substituted zinc(II) phthalocyanines are performed and characterized for the first time in this study. The new compounds show excellent solubility in organic solvents, which makes them candidates for use in different applications. Photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation under light irradiation) properties of these novel coumarino phthalocyanines are investigated in dimethylformamide (DMF). The effects of the positions (peripheral or nonperipheral) of the substituents on the photophysical and photochemical parameters of the coumarino zinc(II) phthalocyanines are reported. The fluorescence quenching behavior of the studied zinc(II) phthalocyanines by addition of 1,4-benzoquinone (BQ) are also described.

Introduction

Coumarins (2H-chromen-2-ones) are one of the most important compounds of natural products. They have been used largely in pharmaceuticals, perfumery and agrochemical industries as starting or intermediate material. They are also used as fluorescent brightener, efficient laser dye and as additives in food and cosmetics [1–3]. Several bioactivities of coumarins such as antibacterial, anticancer, inhibitory of platelet aggregation, steroid 5α-reductase, and HIV-1 protease, have also been reported [1,4–6]. Coumarins also belong to an important class of fluorescent compounds having interesting photophysical properties and a wide range of applications as laser dyes [7], photosensitizers [8], pesticides [9], etc. The coumarin compounds with an aryl- or heteroaryl substituent at 3-position exhibit excellent fluorescence properties but the studied coumarin in this work; the delocalization stopped at the 3-position of the coumarin moiety because of the substitution with

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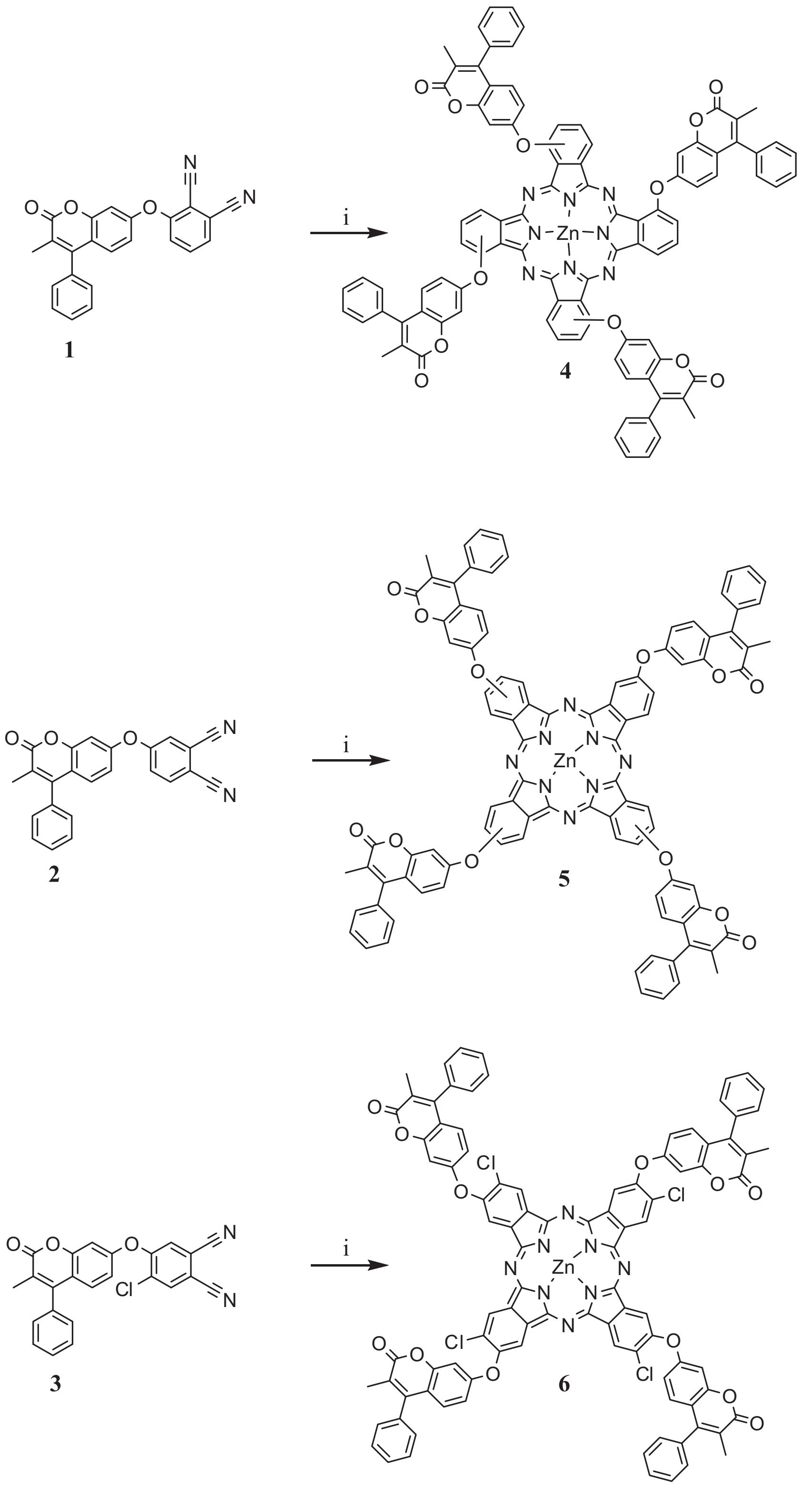
methyl groups at 3-position and with phenyl groups at 4-position, so the molecule showed very low fluorescence properties [10–12].

Phthalocyanines (Pcs) are multi faceted grade of synthetic organic dyes, electron-rich planar aromatic macrocycles. Pcs exhibit a wide variety of applications in materials science, industries, and science of medicine [13,14]. The chemical and physical characteristics of these compounds have been affected by the central metal ion, peripheral substituents and organic molecule attached to the central metal atom as axial ligand [13]. The wide planar organic surface of the Pc molecule causes aggregation of the complexes both in solution and in solid state [15,16]. The aggregation of the Pc molecules affects solubility of Pcs. A major



Scheme 1. Synthesis of (7-oxy-3-methyl-4-phenylcoumarin)-substituted zinc(II) phthalocyanine compounds (**4–6**) (i) DMAE, $Zn(OAc)_2 \cdot 2H_2O$, reflux.

disadvantage of Pcs and MPcs is their low solubility in organic solvents or in water. Substituted Pcs have become more soluble in common solvents. Depending on the polarity of the substituents, Pcs become more soluble in apolar or polar solvents [17,18]. Water-soluble Pcs are among the most promising photosensitizers to date, a number of Pcs bearing hydrophilic moieties, such as carboxylates, sulfonates, glucose, phosphonates, amino, and carboranyl groups have been reported. The introduction of either long chains or bulky substituents onto the periphery of the macrocycle hinders the aggregation in organic solvents, but has almost no contribution to enhance solubility in aqueous medium; similarly, an ionic substituent such as sulfonate, carboxylate or ammonium leads to products extensively soluble in aqueous media [19].

In recent years, metallophthalocyanines (MPcs) have been extensively studied in non-linear optic applications, chemical sensors, catalysis, liquid crystals, photovoltaic cells, semiconductive materials and photodynamic therapy (PDT) [20–23]. PDT is the novel treatment in cancer therapy and this technique based on a photochemical reaction, which is initiated by light activation of a photosensitizing drug causing tumor cell death. Pcs are useful photosensitizers due to their intense absorption in red region of the visible light [24]. Especially zinc Pc complexes are often used due to their long triplet lifetimes [25]. Such long lifetimes constitute a great advantage since the number of diffusional encounters between the triplets excited state and the ground state molecular oxygen increases with the lifetime of the excited state [26].

The aim of our ongoing research is to synthesize 7-oxy-3-methyl-4-phenylcoumarin substituted zinc Pcs as potential PDT agents. In view of the biological importance of both coumarins and Pcs it is worthwhile to combine these two functional molecules into a single compound. In this work, the synthesis, characterization and spectroscopic behavior as well as photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation quantum yields) properties of non-peripherally (**4**) and peripherally tetrakis(7-oxy-3-methyl-4-phenylcoumarin) (**5**) and peripherally octakis[tetrachloro-tetra(7-oxy-3-methyl-4-phenylcoumarin)] substituted zinc(II) Pcs (**6**) (Scheme 1) are presented. These compounds show good solubility in common organic solvents. The effects of the number of the substituents, substitution positions and aggregation on the photophysical and photochemical properties of novel compounds were investigated. The effects of the number of substituents and their position on the fluorescence quenching of coumarino zinc Pcs were also explored by using 1,4-benzoquinone (BQ). The compounds **4**, **5** and **6** might be a potential candidate for the application of PDT.

Experimental

Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were purified as described in Perrin and Armarego before use [27]. Zinc(II) acetate dihydrate, K_2CO_3 and unsubstituted zinc Pc were purchased from the Aldrich Chemical Company. 1,3-Diphenylisobenzofuran (DPBF) and silica gel (70–230 mesh) were purchased from Merck. 3-(3-methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalonitrile (**1**) [28], 4-(3-methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalonitrile (**2**) [28], 4-chloro-5-(3-methyl-4-phenyl-2H-chromen-7-yloxy)phthalonitrile (**3**) [28], 4-nitrophthalonitrile [29], 3-nitrophthalonitrile [30] and 4,5-dichlorophthalonitrile [31] were synthesized and purified according to well known literature.

Equipment

Absorption spectra in the UV–*vis* region were recorded with a Shimadzu 2001 UV–*vis* spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. IR spectra (KBr pellets) were recorded on a Bio-Rad FTS 175C FTIR spectrometer. Elemental analyses 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 Autoflex III MALDI–TOF spectrometer using 2,5-dihydroxybenzoic acid (DHB, 20 mg/mL in THF) as matrix. MALDI samples were prepared by mixing the compound (2 mg/mL in THF) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf micro tube. Finally, 1 μL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. ^{1}H-NMR spectra were recorded in $CDCl_3$ for Pc compounds (**4–6**) on a Varian 500 MHz spectrometer.

General Electric quartz line lamp (300 W) was used for photo-irradiations studies. 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 (Into, 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.

Photophysical parameters

Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. (1) [32],

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4–6**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n and n_{std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc ($\Phi_F = 0.20$) [33] was employed as the standard in DMSO. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program [34] which uses the Strickler–Berg equation. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

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

Photochemical parameters

Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature [35–37], in DMF. Typically, a 3 mL portion of the respective substituted zinc(II) Pc (**4–6**) solutions ($C = 1 \times 10^{-5}$ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references [35–37]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with unsubstituted ZnPc (in DMF) as reference. DPBF was used as chemical quenchers for singlet oxygen in DMF. Eq. (3) was employed for the calculations:

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

where Φ_{Δ}^{Std} is the singlet oxygen quantum yield for the standard unsubstituted ZnPc (Φ_{Δ}^{Std} = 0.56 in DMF) [38]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**4**–**6**) and standards, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples (**4**–**6**) and standards, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [39], the concentration of quenchers was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (1×10^{-5} M) containing DPBF was 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 6.60×10^{15} photons s^{-1} cm^{-2} was used for Φ_{Δ} determinations.

Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [35–37]. Photodegradation quantum yields were determined using Eq. (4),

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

where C_0 and C_t are the samples (**4–6**) concentrations before and after irradiation respectively, V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area, t is the irradiation time and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**4–6**). A light intensity of 2.20×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

Fluorescence quenching studies by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the substituted zinc(II) Pc compounds (4–6) were carried out by the addition of different concentrations of BQ to a fixed concentration of the compounds, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024 and 0.032 M. The fluorescence spectra of substituted zinc(II) Pc compounds (**4**–**6**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) equation [40] (Eq. (5)):

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

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 this is the product of the bimolecular quenching constant (k_q) and the fluorescence lifetime τ_F (Eq. (6)):

$$K_{SV} = k_q \tau_F \tag{6}$$

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

Synthesis

*1(4),8(11),15(18),22(25)-Tetrakis(7-oxy-3-methyl-4-phenylcoumarin) phthalocyaninato zinc(II) (**4**)*

The compound **1** (0.5 g, 1.32 mmol), zinc(II)acetate dihydrate (0.29 g, 0.65 mmol) and dried *N*,*N*-dimethylamino ethanol (2 mL) were refluxed with stirring under argon atmosphere for 24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid product was precipitated and collected by filtration and washed with several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and dried. The green product was purified by passing through a silica gel column using chloroform as the eluting solvent. The compound (**4**) is soluble in chloroform, dichloromethane, tetrahydrofuran, dimethylformamide and dimethylsulfoxide.

Yield: 0.17 g (32%). UV–*vis* λ_{max} (nm) (logε) (DMF): 319 (4.51), 645 (4.57), 690 (4.75). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3061 (Ar–CH), 2957–2926 (aliphatic CH), 1721 (C=O, lactone), 1609–1582 (Ar–C=C), 1276 (Ar–O–Ar). ^{1}H NMR (CDCl$_3$): δ, ppm: Aromatic protons, at 7.75–7.20 (m, 44H) and alkyl protons at 1.57 (s, 12H). MS (MALDI–TOF) m/z: Calculated, 1578.93; Found: 1578.85 [M]$^+$ and 1601.45 [M + Na]$^+$. Anal. Calc. for $C_{96}H_{56}N_8O_{12}Zn$ (1578.93): C, 73.03; H, 3.57; N, 7.10; Found: C 72.88, H 3.41, and N 7.28%.

*2(3),9(10),16(17),23(24)-Tetrakis(7-oxy-3-methyl-4-phenylcoumarin) phthalocyaninato zinc(II) (**5**)*

The compound **2** (0.5 g, 1.32 mmol), zinc(II)acetate dihydrate (0.29 g, 0.65 mmol) and dried *N*,*N*-dimethylaminoethanol (2 mL) were refluxed with stirring under argon atmosphere for 24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid product was precipitated and collected by filtration and washed with several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and dried. The green product was purified by passing through a silica gel column using chloroform as the eluting solvent. The compound (**5**) is soluble in chloroform, dichloromethane, tetrahydrofuran, dimethylformamide and dimethylsulfoxide.

Yield: 0.16 g (30%). UV–*vis* λ_{max} (nm) (logε) (DMF): 324 (4.74), 653 (4.66), 677 (5.04). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3045 (Ar–H), 2922–2852 (aliphatic CH), 1714 cm^{-1} (C=O, lactone) 1656 cm^{-1} (Ar–C=C), 1237 (Ar–O–Ar). ^{1}H NMR (CDCl$_3$): δ, ppm: Aromatic protons, at 8.04–7.02 (m, 44H) and alkyl protons at 1.52 (s, 12H). MS (MALDI–TOF) m/z: Calculated, 1578.93; Found 1578.152 [M]$^+$. Anal. Calc. for $C_{96}H_{56}N_8O_{12}Zn$ (1578.93) C, 73.03; H, 3.57; N, 7.10; Found: C 72.76, H 3.43, and N 7.24%.

*Octakis[2,9,16,23-(7-oxy-3-methyl-4-phenylcoumarin)-3,10,17,24-chloro] phthalocyaninato zinc(II) (**6**)*

The compound **3** (0.5 g, 1.21 mmol), zinc(II)acetate dihydrate (0.27 g, 1.21 mmol) and dried *N*,*N*-dimethylamino ethanol (2 mL) were refluxed with stirring under argon atmosphere for 24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid product was precipitated and collected by filtration and washed with several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and dried. The green product was purified by passing through a silica gel column using chloroform as the eluting solvent. The compound (**6**) is soluble in chloroform, dichloromethane, tetrahydrofuran, dimethylformamide and dimethylsulfoxide.

Yield: 0.18 g (34%). UV–*vis* λ_{max} (nm) (logε) (DMF): 328 (4.47), 629 (4.48), 679 (4.80). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3060 (Ar–H), 2919–2850 (aliphatic CH), 1715 (C=O, lactone), 1600 (Ar–C=C), 1272–1242 (Ar–O–Ar). ^{1}H NMR (CDCl$_3$): δ, ppm: Aromatic protons, at 7.70–7.35 (m, 40H) and alkyl protons at 1.54 (s, 12H). MS (MALDI–TOF) m/z: Calculated, 1715.5; Found: 1715.26 [M]$^+$, 1755.33 [M + K]$^+$. Anal. Calc. for $C_{96}H_{52}Cl_4N_8O_{12}Zn$ (1715.5): C, 67.17; H, 3.05; N, 6.53; Found: C 66.94, H 2.93, and N 6.84%.

Results and discussion

Synthesis and characterization

Tetra- and octa-substituted zinc(II) Pc compounds (**4–6**) were prepared by cyclotetramerization of 7-oxy-3-methyl-4-phenylcoumarin substituted phthalonitrile derivatives (**1–3**). In both cases, a mixture of four possible structural isomers is obtained for tetra-substituted zinc(II) Pcs. The four probable isomers can be designed by their molecular symmetry as C_{4h}, C_{2v}, C_s and D_{2h}. In this study, compounds **4** and **5** are obtained as isomer mixtures as expected. No attempt was made to separate the isomers mixture.

The preparation of substituted phthalonitriles from 3-nitrophthalonitrile, 4-nitrophthalonitrile, and 4,5-dichlorophthalonitrile were used to prepare compounds **1**, **2** and **3** respectively, through base catalyzed nucleophilic aromatic displacement [28].

The syntheses of zinc(II) Pc compounds (**4**–**6**) were achieved by treatment of 7-oxy-3-methyl-4-phenyl-2H-chromen-2-one substituted phthalonitriles (**1**–**3**) with zinc(II) acetate in *N*,*N*-dimethylaminoethanol (DMAE) (Scheme 1). The compounds **4**, **5** and **6** were washed several times with different organic solvents and dried then purified by column chromatography with silica gel using chloroform as eluenting solvent. Generally, Pc compounds are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. All studied zinc(II) Pc compounds (**4**–**6**) exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, DMF and DMSO.

The combination of phthalocyanine and coumarin compounds into a single molecule was studied in our earlier work [41]. In this work, 7-oxy-3-methyl-4-phenylcoumarin group was connected as substituent on the phthalocyanine framework. We have been also investigated the position effect of coumarin groups. Moreover, the effect of chlorine atom on the phthalocyanine framework on photochemical and photophysical properties of coumarin substituted phthalocyanine complexes was also investigated in this study. The synthesis, photophysical and photochemical properties of indium(III) acetate counterparts of 7-oxy-3-methyl-4-phenylcoumarin substituted zinc(II) phthalocyanine complexes were reported by our earlier work [28]. When compared to 7-oxy-3-methyl-4-phenylcoumarin substituted zinc(II) and indium(II) phthalocyanine complexes, while the singlet oxygen generation of 7-oxy-3-methyl-4-phenylcoumarin substituted indium(III) acetate phthalocyanines are higher than zinc(II) phthalocyanine derivatives containing same substituents, the stability of indium (III) acetate complexes are lower than zinc(II) phthalocyanine complexes which investigated in this study approximately 10 times. The photostability of compounds during photosensitized reactions are immense importance. The fluorescence quenching properties of 7-oxy-3-methyl-4-phenylcoumarin substituted zinc(II) phthalocyanine complexes by 1,4-benzoquinone were also examined in this work. The effective fluorescence quenching of the complexes by BQ suggests that systems that are composite of complexes and quinones could well serve as good light harvesters and energy transducers.

The new compounds were characterized by UV–*vis*, FT–IR and NMR spectroscopies, MALDI–TOF mass spectra and elemental analysis. The analyses are consistent with the predicted structures as shown in the experimental section. In the IR spectra of Pc compounds (**4**–**6**), vibration bands were observed at: 3061–3045 cm^{-1} for aromatic C–H stretching, 2957–2850 cm^{-1} for aliphatic C–H stretching, 1721–1714 cm^{-1} for C=O vibration of the ester groups, 1600–1582 cm^{-1} for C=C stretching and 1276–1237 cm^{-1} for Ar–O–Ar stretching. The C=O and C=C bands for zinc(II) Pc compounds (**4**–**6**) in IR spectra were broader and shorter than those of dinitrile compounds (**1**–**3**) because of the H-type aggregation of coumarin moiety.

The ^{1}H NMR spectra of Pcs (**4**–**6**) were recorded in $CDCl_3$. The ^{1}H NMR spectra of substituted Pc compounds (**4**–**6**) have broad absorptions when compared with that of corresponding phthalonitrile derivatives (**1**–**3**). It is likely that broadness is due to both chemical exchange caused by aggregation–disaggregation equilibrium in $CDCl_3$ and the fact that the product obtained in this reaction is a mixture of four positional isomers (for tetra-substituted compounds) which are expected to show chemical shifts which slightly differ from each other. The compounds **4**, **5** and **6** were found to be pure by ^{1}H NMR with all the substituents and ring protons observed in their respective regions. In the ^{1}H NMR spectra of Pcs (**4**–**6**), the aromatic protons were observed at between 7.75–7.20 ppm for compound **4**, 8.04–7.02 ppm for compound **5** and 7.70–7.35 ppm for compound **6** integrating totally 44, 44, 40, protons for each Pcs respectively. The aliphatic methyl protons were observed at 1.57, 1.52, 1.54 ppm for all Pcs respectively integrating 12 protons for each Pcs (**4**, **5** and **6**).

In the mass spectra of Pcs obtained by the MALDI–TOF technique, the molecular ion peaks were observed at m/z: 1578.85 for **4**, 1578.15 for **5**, 1715.26 for **6** as M^+ ion peaks (Fig. 1). The melting points of the new synthesized compounds (**4**, **5** and **6**) are higher than 300 °C.

Ground state electronic absorption spectra

The electronic spectra of the compounds **4**, **5** and **6** showed characteristic absorption in the Q band region at around 677–690 nm in DMF, Table 1. The B bands were observed at around 318–338 nm (Fig. 2). The spectra showed monomeric behavior for tetra-substituted zinc Pc compounds (**4** and **5**) evidenced by a single (narrow) Q band, typical of metallated Pc compounds [42]. The peripherally tetra-substituted zinc Pc compound (**5**) exhibited unusual absorption band at 660 nm in the absorption spectrum. This unusual band did not observed at low concentration ($C = 8.4 \times 10^{-7}$ M) in DMF suggesting that this band could be due to the dimer formation of this compound at higher concentration in DMF. The octa-substituted zinc Pc compound (**6**) showed minimal aggregation in DMF (Fig. 2). It could be due to the effect of chlorine atoms on the Pc framework suggesting that the chlorine atom is an electronegative atom; it attracts electrons in the phthalocyanine ring. Therefore, chlorine atom provides aggregation due to the weak intermolecular interactions. In DMF, the Q bands were observed at: 690 nm for **4**, 677 nm for **5** and 679 nm for **6**, Table 1. The red-shifts were observed for zinc(II) Pc compounds following substitution. The Q band of the non-peripheral substituted compound (**4**) is red-shifted when compared to the corresponding peripheral tetra-(**5**) and octa-(**6**) substituted compounds in DMF (Fig. 2). The red-shifts are 13 nm between compounds **4** and **5**, 11 nm between compounds **4** and **6**. The observed red spectral shifts are typical of Pcs with substituents at the non-peripheral positions and have been explained in the literature [43] 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 are broad due to the superimposition of the B1 and B2 bands in the ~320–330 nm regions.

Fluorescence spectra

Fig. 3 shows fluorescence emission, absorption and excitation spectra of compound **4** in DMF as an example for studied zinc(II) Pc compounds. Fluorescence emission peaks were listed in Table 1. The observed Stokes shifts were within the region observed for zinc(II) Pc compounds. All zinc(II) Pc compounds (**4**–**6**) showed similar fluorescence behavior in DMF (Fig. 3 as an example for compound **4**). The excitation spectra were similar to absorption spectra and both were mirror images of the emission spectra for tetra-substituted zinc(II) Pc compounds (**4** and **5**) in DMF. The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for tetra-substituted zinc(II) Pc compounds (**4** and **5**) suggest that the nuclear configurations of the ground and excited states are

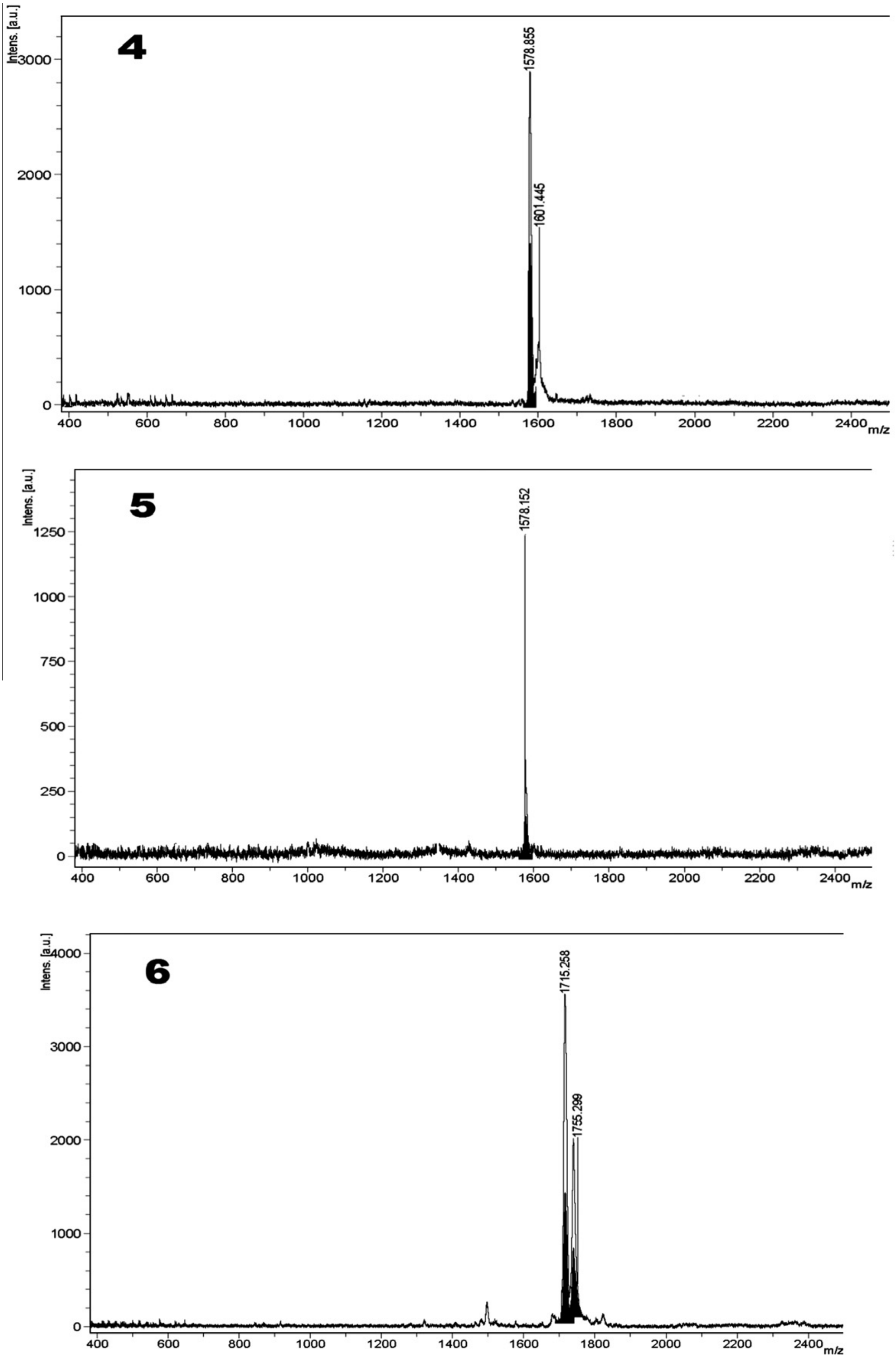


Fig. 1. Mass spectra of the studied phthalocyanine compounds (**4–6**).

similar and not affected by excitation. The chloro-octa substituted compound (**6**) showed broad absorption at Q band region in its electronic spectrum due to aggregation of this complex in DMF. However, the fluorescence spectrum of this complex showed sharp

Table 1
Absorption, excitation and emission spectral data for unsubstituted and substituted zinc(II) phthalocyanine compounds in DMF.

Compound	Q band λ_{max}, (nm)	log ε	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift Δ_{Stokes}, (nm)
4	690	4.81	687	695	8
5	677	5.03	676	685	9
6	679	4.79	677	686	9
ZnPc[a]	670	5.37	670	676	6

[a] Data from Ref. [44].

band at Q band region. It is suggesting that only the monomer species are fluorescent for this complex in DMF. The fluorescence emission of the non-peripherally substituted zinc(II) Pc compound (**4**) is more intense than other studied zinc(II) Pc compounds (**5** and **6**) in DMF suggesting that less quenching of the 7-oxy-3-methyl-4-phenylcoumarin groups on the non-peripheral position.

Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of the studied zinc Pc compounds (**4**, **5** and **6**) are given in Table 2. The Φ_F values of studied zinc Pc compounds are lower than unsubstituted zinc Pc in DMF. For comparison among the studied zinc(II) Pc compounds, the Φ_F value of the compound **6** is the lowest among the studied zinc(II) Pc compounds because only the monomer species (not aggregated species) are fluorescent for this complex in DMF. The electronegative chlorine atoms on the phthalocyanine framework could be enhanced aggregation behavior of this complex due to increasing of intermolecular interactions.

Fluorescence lifetime (τ_F) values of the tetra-substituted zinc(II) Pc compounds (**4** and **5**) are higher compared to unsubstituted zinc(II) Pc compound in DMF, suggesting less quenching by substitution. The τ_F value of the compound **6** is lower than unsubstituted zinc(II) Pc compound due to the aggregation behavior of this compound in DMF again. τ_F value is higher for non-peripherally tetra-substituted zinc(II) Pc compound (**4**) when compared to peripherally tetra-substituted (**5**) and peripherally octa-substituted (**6**) zinc(II) Pc compounds, Table 2, suggesting more quenching by peripherally-tetra and octa-substitution compared to non-peripherally substitution. However, the τ_F values are typical for zinc(II) Pc compounds [44–47].

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also given in Table 2. The τ_0 values of

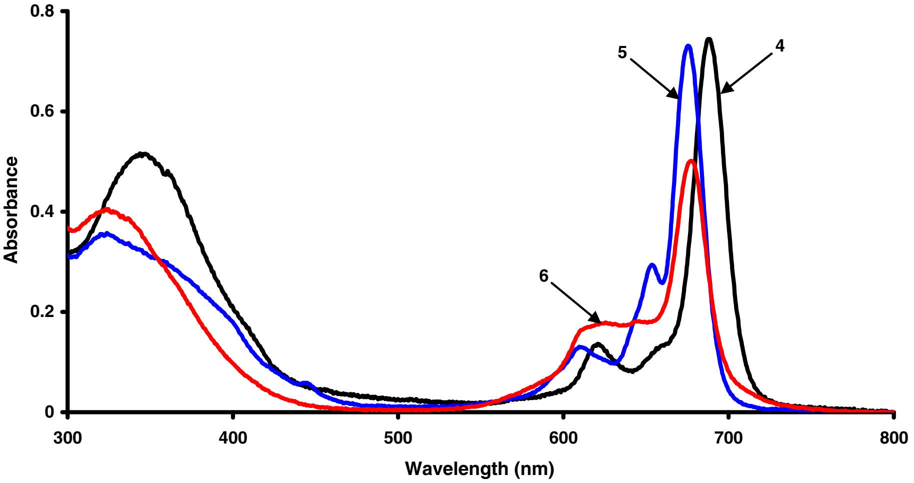


Fig. 2. Absorption spectra of substituted zinc(II) phthalocyanine compounds (**4–6**) in DMF. Concentration = 1×10^{-5} M.

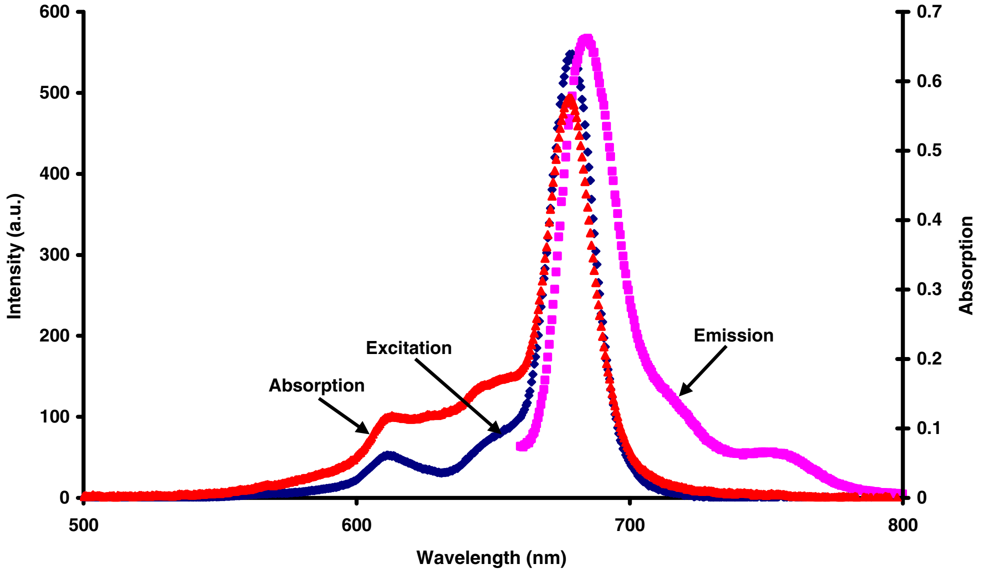


Fig. 3. Absorption, excitation and emission spectra of the compound **4** in DMF. (Excitation wavelength = 630 nm).

Table 2
Photophysical and photochemical data of unsubstituted and substituted zinc(II) phthalocyanine compounds in DMF.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	$^a k_F$ (s^{-1}) ($\times 10^7$)	Φ_d ($\times 10^{-5}$)	Φ_Δ
4	0.084	2.35	27.99	3.57	15.61	0.37
5	0.15	1.78	11.87	8.42	8.89	0.42
6	0.038	0.75	19.75	5.06	5.71	0.24
ZnPc[b]	0.17	1.03	6.05	1.65	2.3	0.56

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Data from Ref. [44].

the substituted zinc(II) Pc compounds (**4–6**) are higher than unsubstituted zinc(II) Pc compound in DMF. The non-peripherally tetra-substituted zinc(II) Pc compound (**4**) showed the highest τ_0 value among the studied zinc(II) Pc compounds in DMF (Table 2). This could be due to the position effect. The rate constants for fluorescence (k_F) of substituted zinc(II) Pc compounds (**4–6**) are higher than unsubstituted zinc(II) Pc compound in DMF. The k_F value of compound **5** is the highest among the studied zinc Pc compounds.

Singlet oxygen quantum yields

The quantity of the singlet oxygen quantum yield (Φ_Δ) is a sign of the capability of the compounds as photosensitizers in photocatalytic applications for instance PDT. The Φ_Δ values were determined in DMF using a chemical method and DPBF used as a scavenger. A reducing of DPBF absorbance at 417 nm was monitored using UV–*vis* spectrophotometer.

Many factors can be responsible for the magnitude of the determined singlet oxygen quantum yield 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 photosensitizer 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, $O_2(^1\Delta_g)$, by Type II mechanism. Singlet oxygen is the chief cytotoxic species and subsequently degradate the substrate.

There was no change in the Q band intensity during the Φ_Δ determinations, confirming that compounds were not degraded during singlet oxygen studies for the studied zinc(II) Pc compounds. The Φ_Δ values of the substituted zinc(II) Pc compounds (**4**, **5** and **6**) are given in Table 2. All substituted zinc(II) Pc compounds showed lower Φ_Δ values than unsubstituted zinc(II) Pc compound in DMF. The peripherally tetra-substituted zinc(II) Pc compound (**5**) showed the highest Φ_Δ value among the studied zinc(II) Pc compounds (Table 2). The Φ_Δ value of chloro-octa substituted compound (**6**) is lower than other substituted zinc(II) Pc compounds (**4** and **5**) in DMF due to the minimal aggregation behavior of this compound in DMF.

Photodegradation studies

Degradation of the molecules under light irradiation can be used to study their stability and this is especially important for those molecules intended for use in photocatalytic reactions. The collapse of the absorption spectra without any distortion of the shape confirms photodegradation not associated with phototransformation into different forms of MPc absorbing in the visible region.

The spectral changes observed for all the compounds (**4–6**) during light irradiation are as shown in Fig. 4 (using compound **5** as an example in DMF) and hence confirm photodegradation occurred without phototransformation. The Φ_d values, found in this study, are similar Pc derivatives having different metals and substituents on the Pc ring in literature [48]. Stable zinc Pc molecules show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [48].

Table 2 shows that all substituted compounds (**4**, **5** and **6**) were less stable to degradation under light irradiation compared to unsubstituted ZnPc in DMF. Thus, the substitution of ZnPc with 7-oxy-3-methyl-4-phenylcoumarin groups seems to decrease the stability of the compounds in DMF. The non-peripherally substituted zinc(II) Pc compound (**4**) was less stable when compared to the other substituted compounds (**5** and **6**). The chloro-octa substituted compound (**6**) is the most stable than the other compounds could be related to the aggregated nature of this compound in DMF. It seems zinc(II) metal and 7-oxy-3-methyl-4-phenylcouma-

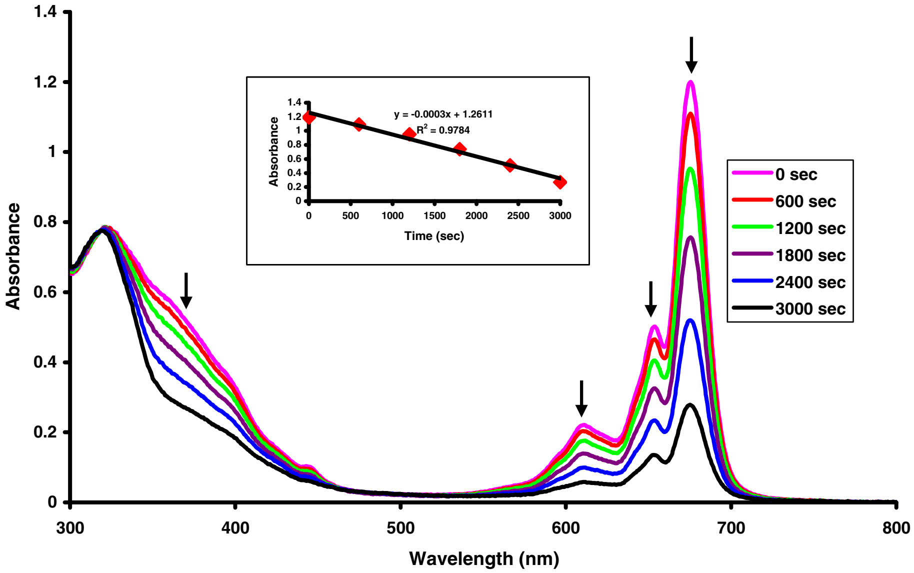


Fig. 4. Absorption changes during the photodegradation studies of compound **5** in DMF showing the disappearance of the Q-band at ten minutes intervals. (Inset: Plot of absorbance *vs* time).

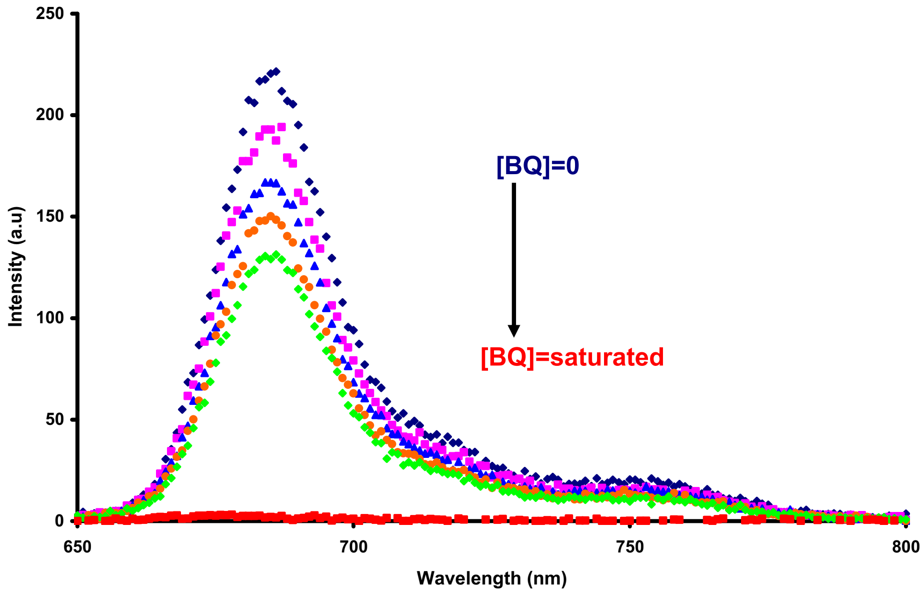


Fig. 5. Fluorescence emission spectral changes of **6** (1.00×10^{-5} M) on addition of different concentrations of BQ in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 M.

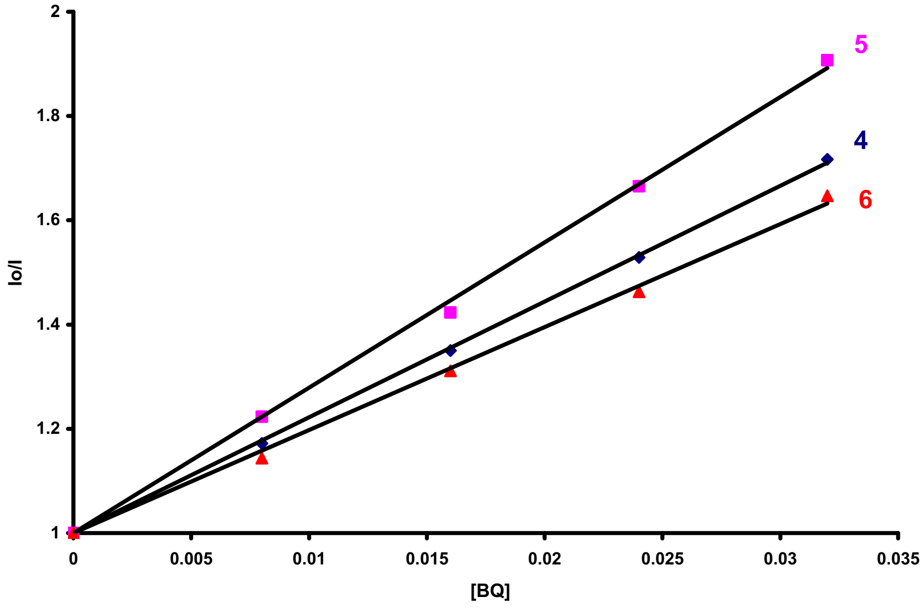


Fig. 6. Stern–Volmer plots for BQ quenching of coumarin substituted zinc(II) phthalocyanines (**4**–**6**). [MPc] ~1.00×10^{-5} M in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 M.

rin groups increases the Φ_d values and decreases the stability of compounds due to electron-donating ability of these groups [49].

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

The fluorescence quenching of zinc Pc compounds by BQ in DMF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 5 shows the quenching of compound **6** by BQ in DMF as an example. The slope of the plots shown at Fig. 6 gave K_{SV} values and listed in Table 3. The K_{SV} values of the substituted zinc Pc compounds (**4**, **5** and **6**) are lower than unsubstituted ZnPc in DMF. The peripherally substituted zinc(II) Pc compound (**5**) has highest K_{SV} value, while chloro-octa substituted compound (**6**) has the lowest K_{SV} in DMF could be related to the aggregated nature of this compound in DMF. The substitution with 7-oxy-3-methyl-4-phenylcoumarin groups seems to decrease the K_{SV} values of the compounds in DMF. The bimolecular quenching constant (k_q) values of the substituted zinc Pc compounds (**4**, **5** and **6**) are also lower than unsubstituted ZnPc in DMF, thus substitution with 7-oxy-3-methyl-4-phenylcoumarin group seems to decrease the k_q values of the compounds. The order

Table 3
Fluorescence quenching data for unsubstituted and substituted zinc(II) phthalocyanine compounds in DMF.

Compound	K_{SV} (M^{-1})	$k_q/10^{10}$ ($dm^3\ mol^{-1}\ s^{-1}$)
4	22.19	0.94
5	27.88	1.56
6	19.76	2.63
ZnPc[a]	57.60	5.59

[a] Data from Ref. [44].

in k_q values among the substituted compounds was also as follows: **6** > **5** > **4** in DMF.

Conclusions

In the presented work, the syntheses of novel zinc(II) Pc compounds (**4**–**6**) were described and they were characterized by elemental analysis, ^{1}H-NMR, MALDI–TOF, IR, UV–*vis* and fluorescence spectral data. All the studied zinc(II) Pc compounds show excellent solubility in general organic solvents (such as chloroform, dichloromethane, THF, DMF and DMSO). The photophysical and photo-chemical properties of these zinc(II) Pc compounds were also described in DMF for comparison of the effects of the position of substituents on the Pc framework and aggregation behavior as well. The tetra-substituted compounds (**4** and **5**) did not show aggregation, but the octa substituted compound (**6**) showed aggregation in DMF. The photophysical and photochemical results were for the mixture monomer and aggregates in case of octa-substituted zinc(II) Pc (**6**).

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