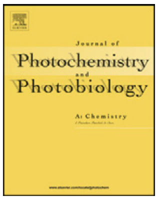
Journal of Photochemistry and Photobiology A: Chemistry 223 (2011) 37–49

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Highly soluble 7-oxy-3-(4-methoxyphenyl)coumarin bearing zinc phthalocyanines: Synthesis and investigation of photophysical and photochemical properties

Mehmet Pişkin[a], Mahmut Durmuş[b], Mustafa Bulut[a,*]

[a] Marmara University, Faculty of Art and Science, Department of Chemistry, 34722 Kadikoy-Istanbul, Turkey
[b] Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, Gebze 41400, Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 11 May 2011
Received in revised form 13 July 2011
Accepted 23 July 2011
Available online 30 July 2011

Keywords:
Phthalocyanine
Coumarin (2*H*-chromen-2-one)
Zinc
Fluorescence
Quantum yield
Singlet oxygen

ABSTRACT

The synthesis of 7-oxy-3-(4-methoxyphenyl)coumarin-substituted peripherally and non-peripherally tetrakis- and peripherally octakis-tetrachloro zinc(II) phthalocyanine complexes are described for the first time in this study. The new compounds have been characterized by elemental analysis, IR, ^{1}H NMR, UV–vis spectroscopy and mass spectra. The photophysical and photochemical properties are important for photodynamic therapy applications and these properties of studied phthalocyanine complexes are investigated in N,N-dimethyl formamide (DMF). The effects of the number of the substitution and the position (peripheral or non-peripheral) on the photophysical and photochemical parameters of the zinc(II) phthalocyanine complexes are reported. The fluorescence quenching behaviour of the studied zinc(II) phthalocyanine complexes by the addition of 1,4-benzoquinone are also described.

1. Introduction

As an important group of organic heterocyclic compounds, coumarin (2H-1-benzopyran-2-one) and its derivatives, have been extensively exploited in biological, chemical and physical fields. Coumarins have outstanding optical properties, including an extended spectral range, superior photostability and good solubility in common solvents. Many natural and synthetic coumarin derivatives are widely used as laser dyes [1]. The medical properties of the coumarins include inhibitions of platelet aggregation and steroid 5-reductase, antibacterial, anticancer and anti HIV-1 activities have been studied [2]. 7-Hydroxycoumarin derivatives have been reported to inhibit the proliferation of a number of human malignant cell lines *in vitro* [3,4] and have demonstrated activity against several types of animal tumors [5–7]. These compounds have also been reported in clinical trials to demonstrate activity against prostate cancer, malignant melanoma, and metastatic renal cell carcinoma [8,9]. For coumarins, generally the *in vitro* structure–activity relationship studies have shown that cytotoxicity is found with derivatives containing ortho-dihydroxy substituents [10]. Also, the chemical-structure/biological activity study of the coumarins showed that the addition of a cathecolic group to the basic structure induces increased cytotoxic activity in tumor cell lines [10]. The different cytotoxic values found for the coumarins could be related to the presence and the positions of the hydroxyl groups in their structures.

Phthalocyanines (Pcs) and related macrocyclic compounds have found widespread application in various areas including liquid crystals, non-linear optical devices, catalysts, electrochromic and photochromic materials, chemical sensors, data storage systems, organic photovoltaics in solar cells [11,12] and second generation photosensitizers for photodynamic therapy (PDT) [13].

Numerous studies have been carried out to modify these macrocyclic compounds with the goal of moderating their properties and optimizing their performance for advanced materials. A decisive disadvantage of metal free phthalocyanines (Pcs) and metallo phthalocyanines (MPcs) is their low solubility in organic solvents or water. While the solubility in organic solvents can be increased by introducing alkyl or alkoxy groups [14], the solubility in aqueous solutions can also be increased by introducing sulfonates, carboxylates, phosphanates or quaternized amino groups into the peripheral and non-peripheral positions of the phthalocyanine framework [15]. In contrast to octa-substituted systems, tetra-substituted phthalocyanines are obtained as a mixture of

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[*] Corresponding author. Tel.: +90 216 3479641 1370; fax: +90 216 3478783.
E-mail addresses: mbulut@marmara.edu.tr, mustafabulut50@gmail.com (M. Bulut).

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doi:10.1016/j.jphotochem.2011.07.014

constitutional isomers by statistical synthesis starting from corresponding mono-substituted phthalonitriles or corresponding diiminoisoindolines. Depending on their substituent positions two types (non-peripherally and peripherally substituted) of tetrasubstituted macrocycles which show significant differences in their chemical and physical behaviour can be obtained.

Recently, there has been considerable interest in the tetrapyrrolic photosensitizers by Dudkowiak et al. [16–20]. Pc complexes which are a class of the tetrapyrrolic photosensitizers have found applications as photosensitizers in PDT as second generation photosensitizers [21,22]. The zinc(II) Pc complexes have attracted much interest because of their appreciably long triplet lifetimes [23–25], high selectivity for tumoral targets and enhanced cytotoxic efficiency due to singlet oxygen photogeneration [23].

Addition of groups to the peripheral positions of MPc complexes is known to influence the properties of the MPc to a large degree [26–30]. For instance, the peripheral substituents increase the distance between the planar macrocycle rings carrying the π-electrons thereby making solvation easier. Solvents affect aggregation in Pc complexes. Organic solvents are known to reduce aggregation whereas aqueous medium results in highly aggregated complexes. However, many Pc complexes remain aggregated even in non-aqueous solutions [31–33]. Aromatic solvents such as benzene or toluene are known to give narrow Q-bands for Pc complexes whereas broadening is observed in non-aromatic solvents [34].

The zinc(II) Pc complexes show fascinating photophysical and photochemical properties especially high singlet oxygen quantum yields which are very important for PDT of cancer. In this study, the studied zinc(II) phthalocyanine complexes have good singlet oxygen quantum yields and show potential as Type-II photosensitizers. In this work, we report on the effects of the coumarin groups as substituent and the position of the substituent (peripheral or non-peripheral) on the photophysical and photochemical parameters. Aggregation behaviour, photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet oxygen generation and photodegradation quantum yields) properties are investigated in this study. This work also explores the effects of ring substitutions and position on the fluorescence quenching of zinc Pc by 1,4-benzoquinone (BQ) using the Stern–Volmer relationship. Since PDT activity is mainly based on singlet oxygen, its production is determined by the dye-sensitized photooxidation of 1,3-diphenylisobenzofuran (DPBF), a specific scavenger of this toxic species [35]. Studies of the photostability of zinc Pc complexes during photosensitization reactions are also of immense importance. Herein, we report the synthesis, spectroscopic, photophysical and photochemical properties of novel zinc Pcs with 7-oxy-3-(4-methoxyphenyl)coumarin (Scheme 1).

2. Experimental

2.1. 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 [36]. Zinc(II) acetate dihydrate, K_2CO_3 and unsubstituted zinc phthalocyanine were purchased from the Aldrich Chemical Company. 1,3-Diphenylisobenzofuran (DPBF) was purchased from Fluka. Silica gel was purchased from Merck. 7-Hydroxy-3-(4-methoxyphenyl)coumarin (**1**) was prepared by Perkin condensation of *p*-methoxyphenylacetic acid with 2,4-dihydroxybenzaldehyde in acetic anhydride in the presence of NaOAc as the base [37] with subsequent deacylation of the 7-acetoxy-3-(4-methoxyphenyl)coumarin. 4-Nitrophthalonitrile (**2**) [38], 3-nitrophthalonitrile (**3**) [39], and 4,5-dichlorophthalonitrile (**4**) [40] were synthesized and purified according to well-known literature procedures. Then starting materials **5**, **6** and **7** were obtained by the reaction of 7-hydroxy-3-(4-methoxyphenyl)coumarin (**1**) with **2**, **3** and **4**, respectively.

2.2. Measurements

Absorption spectra in the UV–visible region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluoremeter using 1 cm pathlength 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. A 2,5-dihydroxybenzoic acid (DHB, 20 mg/mL in THF) was used as matrix. MALDI samples were prepared by mixing the complex (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 $CDCl_3$ on a Varian 500 MHz spectrometer.

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],

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**8**–**10**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [42] was employed as the standard. Both the samples and standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

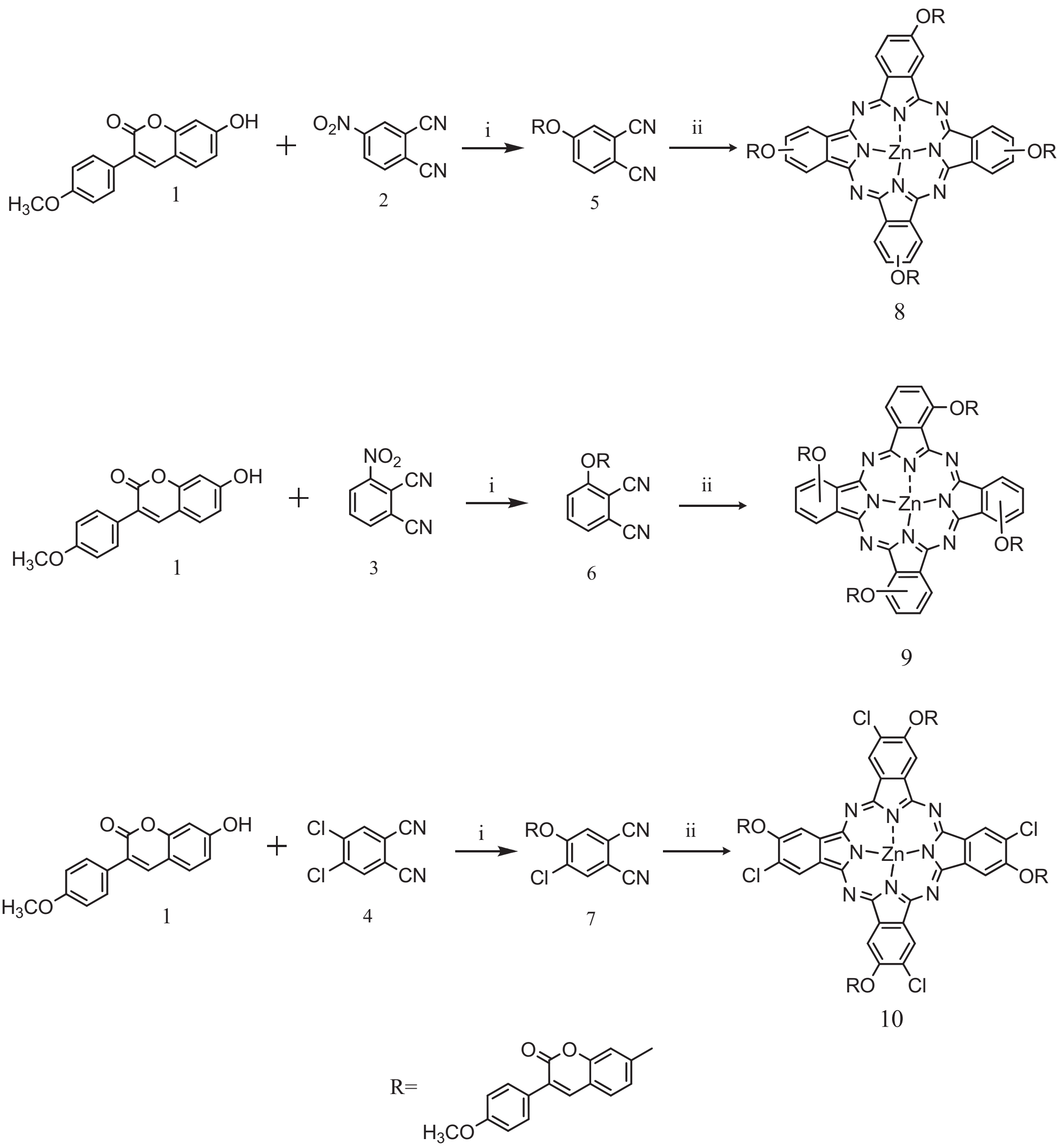
Natural radiative (τ_0) lifetimes were determined using PhotochemCAD program which uses the Strickler–Berg equation [43,44]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \qquad (2)$$

2.4. Photophysical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen (Φ_Δ) quantum yield determinations were carried out using the experimental set-up described in literature [45], in DMF. Typically, a 3 mL portion of the respective substituted zinc(II) Pc (**8**–**10**) 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 [45]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with unsubstituted ZnPc (in DMF) as reference. DPBF was



Scheme 1. Synthesis of tetra- and chloro-octa-(7-oxy-3-(4-methoxyphenyl)coumarin)-substituted zinc(II) phthalocyanine complexes (**8–10**). (i) DMF, K_2CO_3, RT; (ii) DMAE, $Zn(OAc)_2 \cdot 2H_2O$, reflux.

used as chemical quenchers for singlet oxygen in DMF. Eq. (3) was employed for the calculations:

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

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi_\Delta^{Std} = 0.56$ in DMF) [42]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**8–10**) and standards, respectively. I_{abs} and I_{abs}^{Std} are absorbed light by the samples (**8–10**) and standards, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [46], the concentration of quenchers was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer ($C = 1 \times 10^{-5}$ 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.

2.4.2. *Photodegradation quantum yields*

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [45]. Photodegradation quantum yields were determined using Eq. (4),

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

where C_0 and C_t are the samples (**8–10**) 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 (**8**–**10**). A light intensity of 2.20×10^{16} photons s^{-1} 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 complexes (**8**–**10**) 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 mol dm^{-3}. The fluorescence spectra of substituted ZnPc complexes (**8**–**10**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) equation [47] (Eq. (5)):

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

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.

2.5. Synthesis

2.5.1. 4-[3-(4-Methoxyphenyl)-2-oxo-2H-chromen-7-yloxy]phthalonitrile (**5**)

7-Hydroxy-3-(4-methoxyphenyl)coumarin (**1**) (0.5 g, 1.86 mmol) and 4-nitrophthalonitrile (**2**) (0.32 g, 1.86 mmol) were dissolved in dried DMF (9 mL) under argon atmosphere. After stirring for 15 min, finely ground anhydrous potassium carbonate (0.38 g, 2.80 mmol) was added in portion during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at room temperature for 48 h. The reaction mixture was then poured into cold water (150 mL) and the precipitate was filtered off and washed with water to the pink product. Purification of this product was accomplished by column chromatography with silica gel using dichloromethane/methanol (5/2) as eluent. The compound (**5**) is soluble in tetrahydrofurane (THF), DMF and dimethylsulfoxide (DMSO). Yield: 0.59 g (80%). M.p.: 114 °C. FT-IR [(KBr) ν_{max}/cm^{-1}]: 3084 (Ar–CH), 2964 (CH), 2230 (C≡N), 1723 (C=O lactone), 1592 (C=C), 1284 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: Aromatic protons: 7.79 (d, 8.79 Hz, 1H), 7.68 (d, 8.79 Hz, 2H), 7.62 (d, 8.54 Hz, 1H), 7.38 (d, 2.44 Hz, 1H), 7.34 (d, 8.79 Hz, 1H), 7.07 (d, 1.96 Hz, 1H), 6.98 (d, 8.79 Hz, 3H), aliphatic protons: 7.78 (s, 1H, CH), 3.86 (s, 3H, $-OCH_3$). Anal. Calc. for $C_{24}H_{14}N_2O_4$ (394.38): C, 73.09; H, 3.58; N, 7.10%; Found: C 72.93, H 3.47, N 6.93%. MS (MALDI-TOF) m/z: 394.98 $[M]^+$.

2.5.2. 3-[3-(4-Methoxyphenyl)-2-oxo-2H-chromen-7-yloxy]phthalonitrile (6)

7-Hydroxy-3-(4-methoxyphenyl)coumarin (**1**) (0.55 g, 2.05 mmol) was dissolved in dried DMF (10 mL) under argon atmosphere and 3-nitrophthalonitrile (**3**) (0.35 g, 2.05 mmol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (0.56 g, 4.10 mmol) was added in portion during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at room temperature for 54 h. The reaction mixture was then poured into cold water (170 mL) and the precipitate was filtered off and washed with water. Purification of this product was accomplished by column chromatography with silica gel using dichloromethane/methanol (20/1) as eluent. The compound (**6**) is soluble in chloroform ($CHCl_3$), dichloromethane, THF, DMF and DMSO. Yield: 0.61 g (76%). M.p.: 123 °C. FT-IR [(KBr) ν_{max}/cm^{-1}]: 3096 (Ar–CH), 2955–2840 (CH), 2239 (C≡N), 1718 (C=O lactone), 1608 and 1470 (C=C), 1281 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: Aromatic protons: 7.95 (d, 6.83 Hz, 1H), 7.94 (d, 8,30 Hz, 1H), 7.88 (t, 1H), 7.86 (d, 7.56 Hz, 1H), 7.7 (d, 7.57 Hz, 2H), 7.55 (d, 8.30 Hz, 1H), 7.36 (s, 1H), 7.02 (d, 7.57 Hz, 2H), aliphatic protons: 8.24 (s, 1H, CH), 3.81 (s, 3H, $-OCH_3$). Anal. Calc. for $C_{24}H_{14}N_2O_4$ (394.38): C, 73.09; H, 3.58; N, 7.10%; Found: C, 72.88; H, 3.48; N, 6.96%. MS (MALDI-TOF) m/z: 394.89 $[M]^+$.

2.5.3. 4-Chloro-5-[3-(4-methoxyphenyl)-2H-chromen-7-yloxy] phthalonitrile (**7**)

7-Hydroxy-3-(4-methoxyphenyl)coumarin (**1**) (0.40 g, 1.50 mmol) was dissolved in dried DMF (8 mL) under argon atmosphere and 4,5-dichlorophthalonitrile (**4**) (0.29 g, 1.50 mmol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (0.41 g, 3.00 mmol) was added in portion during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at room temperature for 48 h. The reaction mixture was then poured into cold water (150 mL) and the precipitate was filtered off and washed with water to the yellow product. Purification of this product was accomplished by column chromatography with silica gel using dichloromethane/methanol (20/1) as eluent. The compound **7** is soluble in $CHCl_3$, dichloromethane, THF, DMF and DMSO. Yield: 0.51 g (79%). M.p.: 105 °C. FT-IR [(KBr) ν_{max}/cm^{-1}]: 3090 (Ar–CH), 2924 (CH), 2234 (C≡N), 1732 (C=O lactone), 1606 (C=C), 1277 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: Aromatic protons: 7.90 (d, 2 Hz 1H), 7.65 (dd, 9.0 Hz, 2 Hz, 2H), 7.60 (dd, 8.5 Hz, 2 Hz, 1H), 7.23 (d, 2 Hz, 1H), 7.02 (d, 2 Hz, 1H), 6.96 (dd, 9.0 Hz, 2 Hz, 3H), aliphatic protons: 7.75 (s, 1H), 3.83 (s, 3H, $-OCH_3$). Anal. Calc. for $C_{24}H_{13}ClN_2O_4$ (428,82): C, 67.22; H, 3.06; N, 6.53%; Found: C 67.04; H 2.92; N 6.50%. MS (MALDI-TOF) m/z: 428.97 $[M]^+$.

2.5.4. 2(3),9(10),16(17),23(24)-Tetrakis[3-(4-methoxyphenyl)-2-oxo-2H-chromen-7-yloxy]phthalocyaninato zinc(II) (**8**)

A mixture of **5** (0.3 g, 0.76 mmol), zinc(II) acetate dihydrate (0.17 g, 0.76 mmol) and N,N-dimethylaminoethanol (DMAE) (2 mL) was heated to reflux temperature for 16 h under argon atmosphere in a round-bottomed flask. The resulting green suspension was cooled to room temperature and the crude product was precipitated by addition of acetic acid. The green solid product was precipitated and collected by filtration and washed several times with hot acetic acid, water, methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether. The crude green product was purified by column chromatography with silica gel using $CHCl_3$ as eluent. The compound **8** is soluble in $CHCl_3$, dichloromethane, toluene, THF, DMF and DMSO. Yield: 0.09 g (30%). M.p. > 300 °C. UV–vis (DMF): λ_{max}/nm ($\log \varepsilon$): 353 (5.04), 609 (4.50), 678 (5.22, FWHM = 23 nm). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3066 (Ar–CH), 2954 (CH), 1724 (C=O, lactone), 1604 (C=C), 1253 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: Aromatic protons: 7.92–6.40 (m, 44H), aliphatic protons: 3.73 (s, 12H). Anal. Calc. for $C_{96}H_{56}N_8O_{16}Zn$ (1642,93): C, 70.18; H, 3.44; N, 6.82%; Found: C 69.92, H 3.17, N 6.59%. MS (MALDI-TOF) m/z: 1642,44 $[M]^+$, 1664,40 $[M+Na]^+$.

2.5.5. 1(4),8(11),15(18),22(25)-Tetrakis[3-(4-methoxyphenyl)-2-oxo-2H-chromen-7-yloxy]phthalocyaninato zinc(II) (**9**)

A mixture of **6** (0.3 g, 0.76 mmol), zinc(II) acetate dihydrate (0.17 g, 0.76 mmol) and DMAE (2 mL) was heated to reflux for 16 h under argon atmosphere in a round-bottomed flask. The resulting green suspension was cooled to room temperature and the crude product was precipitated by addition of acetic acid. The green solid product was precipitated and collected by filtration and washed several times with hot acetic acid, water, methanol, ethanol, ethyl acetate, acetonitrile, acetone and diethyl ether. The crude green product was purified by column chromatography with silica gel using $CHCl_3$ as eluent. The compound **9** is soluble in $CHCl_3$, dichloromethane, toluene, THF, DMF and DMSO. Yield: 0.10 g (32%). M.p. > 300 °C. UV–vis (DMF): λ_{max}/nm (log ε): 340 (4.31), 619 (4.83), 690 (5.10, FWHM = 22 nm). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3040 (Ar–H), 2920 (CH), 1722 (C=O, lactone), 1609 (C=C), 1251 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: Aromatic protons: 7.88–6.84 (m, 44H), aliphatic protons: 3.74 (s, 12H). Anal. Calc. for $C_{96}H_{56}N_8O_{16}Zn$ (1642,93): C, 70.18; H, 3.44; N, 6.82%; Found: C 69.95, H 3.20, N 6.68%. MS (MALDI-TOF) *m/z*: 1642.57 [M]$^+$.

*2.5.6. Octakis{[2,9,16,23-(3-(4-methoxyphenyl)-2-oxo-2H-chromen-7-yloxy)-3,10,17,24-chloro]}phthalocyaninato zinc(II) (**10**)*

A mixture of **7** (0.3 g, 0.70 mmol), zinc(II) acetate dihydrate (0.15 g, 0.7 mmol) and DMAE (2 mL) was heated to reflux temperature for 16 h under argon atmosphere in a round-bottomed flask. The resulting green suspension was cooled to room temperature and the crude product was precipitated by addition of acetic acid. The green solid product was precipitated and collected by filtration and washed several times with hot acetic acid, water, methanol, ethanol, ethyl acetate, acetonitrile, acetone and diethyl ether. The crude green product was purified by column chromatography with silica gel using $CHCl_3$ as eluent. The compound **10** is soluble in $CHCl_3$, dichloromethane, toluene, THF, DMF and DMSO. Yield: 0.09 g (29%). M.p. > 300 °C. UV–vis (DMF): λ_{max}/nm (log ε): 349 (4.32), 612 (4.91), 679 (4.99, FWHM = 23 nm). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3043 (Ar–CH), 2845 (CH), 1719 (C=O, lactone), 1608 (C=C), 1245 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: Aromatic protons: 6.50–8.00 (m, 40H), aliphatic protons: 3.74 (s, 12H). Anal. Calc. for $C_{96}H_{52}Cl_4N_8O_{16}Zn$ (1780.71): C, 64.75; H, 2.94; N, 6.29; Zn, 3.67%; Found: C 64.58, H 2.80, N 7.78%. MS (MALDI-TOF) *m/z*: 1780.95 [M]$^+$.

3. Results and discussion

3.1. Synthesis and characterization

The preparation of 7-oxy-3-(4-methoxyphenyl)coumarin substituted phthalonitriles from 7-hydroxy-3-(4-methoxyphenyl)coumarin (**1**) and 4-nitrophthalonitrile (**2**), 3-nitrophthalonitrile (**3**) or 4,5-dichlorophthalonitrile (**4**) (Scheme 1) through base catalysed nucleophilic aromatic displacement reaction [48,49]. The reactions were carried out in DMF at room temperature and gave yields of about 76–80%. The 7-oxy-3-(4-methoxyphenyl)coumarin substituted phthalonitriles (**5**–**7**) were purified by column chromatography in each case using a mixed solvent system of dichloromethane/methanol as eluent.

The preparation of phthalocyanine derivatives from the aromatic 1,2-dinitriles occurs under different reaction conditions. The syntheses of zinc(II) Pc complexes (**8**–**10**) were achieved by treatment of 7-oxy-3-(4-methoxyphenyl)coumarin substituted phthalonitriles (**5**–**7**) with zinc(II) acetate in DMAE (Scheme 1). The 7-oxy-3-(4-methoxyphenyl) coumarin substituted phthalocyanines (**8**–**10**) were washed several times with different solvents and then were purified by column chromatography with silica gel using $CHCl_3$ as eluent. Tetra- and octa-substituted zinc(II) phthalocyanine complexes (**8-10**) were prepared by cyclotetramerization of 7-oxy-3-(4-methoxyphenyl)coumarin substituted phthalonitriles (**5**–**7**). 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, synthesized tetrakis-(7-oxy-3-(4-methoxyphenyl)coumarin substituted zinc(II) Pc complexes are obtained as isomer mixtures as expected. No attempt was made to separate the isomers of complexes **8** and **9**.

Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. All studied zinc(II) Pc complexes (**8**–**10**) exhibited excellent solubility in organic solvents such as dichloromethane, $CHCl_3$, THF, DMF and DMSO. 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 Section 2.

Comparison of the IR spectra at each step gave some insights on the nature of the products. The –OH stretching band of 7-hydroxy-3-(4-methoxyphenyl)coumarin group at 3173 cm^{-1} disappeared for all dinitrile compounds in the IR spectra. The IR spectra of the all dinitrile compounds showed a sharp peak at around 2230-2239 cm^{-1} for C≡N stretching. These peaks disappeared and the color changed to green after conversion, indicative of phthalocyanines formation.

The ^{1}H NMR spectra of substituted dinitrile compounds (**5**–**7**) were recorded in $CDCl_3$. Aromatic and aliphatic protons signals were obtained in their respective regions in the ^{1}H NMR spectra. In the ^{1}H NMR spectra of substituted dinitrile compounds (**5**–**7**), the aromatic protons were observed at between 7.79 and 6.98 ppm for compound **5**, 7.95 and 7.36 ppm for compound **6** and 7.90 and 6.96 ppm for compound **7** integrating totally 10 protons for compounds **5** and **6**, and 9 protons for compounds **7**. The aliphatic methyl protons were observed at 3.86 ppm for compound **5**, 3.81 ppm for compound **6**, 3.83 ppm for compound **7** integrating 3 protons for each compound. The protons for coumarin lactone ring were observed at 7.78 ppm for compound **5**, 8.24 ppm for compound **6**, 7.75 ppm for compound **7** integrating 1 proton for each compound.

In the mass spectra of phthalonitrile compounds obtained by the MALDI-TOF technique, the molecular ion peaks were observed at *m/z*: 394.98 [M]$^+$ for **5**, 394.89 [M]$^+$ for **6** and 428.97 [M]$^+$ for **7**.

The C≡N stretching peaks of the dinitrile compounds at around 2230–2240 cm^{-1} disappeared after formation of the phthalocyanine complexes. In the IR spectra for Pc complexes (**8**–**10**), vibrations bands were observed at: 3040–3066 cm^{-1} for aromatic C–H stretching, 2845–2954 cm^{-1} for aliphatic C–H stretching, 1719–1724 cm^{-1} for C=O vibration of the ester groups, 1604–1609 cm^{-1} for aromatic C=C stretching and 1246–1253 cm^{-1} for Ar–O–Ar stretching.

The ^{1}H NMR spectra of Pcs (**8**–**10**) were recorded in $CDCl_3$. The ^{1}H NMR spectra of substituted phthalocyanine complexes (**8**–**10**) have broad absorptions when compared with that of corresponding phthalonitrile derivatives (**5**–**7**). 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 complexes) which are expected to show chemical shifts which slightly differ from each other. The 7-oxy-3-(4-methoxyphenyl)coumarin substituted zinc(II) Pc complexes 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 (**8**–**10**), the aromatic protons were observed at between 7.92 and 6.40 ppm for compound (**8**), 7.88 and 6.84 ppm for compound (**9**) and 8.00 and 6.50 ppm for compound (**10**) integrating totally 44, 44, 40 protons for each Pcs respectively. The aliphatic

Table 1
Absorption, excitation and emission spectral data for unsubstituted (ZnPc), peripherally tetrakis (**8**), non-peripherally tetrakis (**9**) and peripherally octakis-tetra-chloro substituted (**10**) zinc(II) phthalocyanine complexes in DMF.

Compound	Q band λ_{max}, (nm)	$\log \varepsilon$	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift Δ_{Stokes}, $\times 10^4$ (kJ/mol)
8	678	5.22	679	689	1.08
9	690	5.15	691	702	0.99
10	679	4.99	679	687	1.49
ZnPc[a]	670	5.37	670	676	1.99

[a] Data from Ref. [61].

methyl protons were observed at 3.73, 3.74, 3.74 ppm for all Pcs respectively integrating totally 12 protons for each Pcs (**8**, **9** and **10**).

In the mass spectra of phthalocyanines obtained by the MALDI-TOF technique, the molecular ion peaks were observed at *m*/*z*: 1642.44 $[M]^+$ for **8**, 1642.57 $[M]^+$ for **9**, 1780.95 $[M]^+$ for **10** (Fig. 1).

3.2. Ground state electronic absorption spectra

The electronic spectra of the 7-oxy-3-(4-methoxyphenyl)coumarin substituted zinc(II) Pc complexes (**8**–**10**) showed characteristic absorption in the Q band region at around 678–690 nm in DMF, Table 1. The B bands were observed at around 340–353 nm (Fig. 2). The spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes [50]. In DMF, the Q bands were observed at: 670 nm for unsubstituted (ZnPc), 678 nm for peripherally tetrakis (**8**), 690 nm for non-peripherally tetrakis (**9**) and 679 nm for peripherally octakis-tetra-chloro substituted (**10**) zinc(II) phthalocyanine complexes, Table 1. The red-shifts were observed for zinc(II) Pc complexes following substitution with coumarin groups. The observed Q band absorptions of the studied complexes (**8**–**10**) are similar with those of ZnPcs bearing similar substituents like alkoxyl- and phenoxyl-groups [51,52]. The Q band of the non-peripheral substituted complex (**9**) is red-shifted when compared to the corresponding peripheral tetra-(**8**) and octa-(**10**) substituted complexes in DMF (Fig. 2). The red-shifts are 12 nm (0.99×10^4 kJ/mol) between **8** and **9**, 11 nm (1.08×10^4 kJ/mol) between **9** and **10**. The observed red spectral shifts are typical of Pcs with substituents at the non-peripheral positions and have been explained in the literature [53].

3.3. Aggregation studies

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [54]. It has been established that Pcs can form H- and J-aggregates depending on the orientation of the induced transition dipoles of their constituent monomers [55]. In H-aggregates, the component monomers are arranged into a face-to-face conformation, and transition dipoles are perpendicular to the line connecting their centers [56,57]. In the aggregated state the electronic structure of the complexed phthalocyanine rings are perturbed resulting in alternation of the ground and excited state electronic structures [58]. In this study, the aggregation behaviour of 7-oxy-3-(4-methoxyphenyl)coumarin substituted zinc(II) Pc complexes (**8-10**) were investigated at different concentrations in DMF (Fig. 3, for complex **9** as an example). The Beer–Lambert law was obeyed for all of these compounds at concentrations ranging from 1.4×10^{-5} to 4×10^{-6} M. The 7-oxy-3-(4-methoxyphenyl)coumarin substituted zinc(II) Pc complexes did not show aggregation at these concentration ranging in DMF. The full width at half maximum (FWHM) values are another main evidence about the aggregation properties of the molecules. While the aggregated molecules exhibit high FWHM values, the non-aggregated molecules show low FWHM values. The FWHM values of the substituted zinc(II) Pc complexes (**8**–**10**) are approximately 20 nm in DMF and similar to non-aggregated phthalocyanine complexes studied in the literature [59,60].

3.4. Fluorescence spectra

Fig. 4 shows fluorescence emission, absorption and excitation spectra of 7-oxy-3-(4-methoxyphenyl)coumarin substituted zinc(II) Pc complexes **8** (Fig. 4A), **9** (Fig. 4B) and **10** (Fig. 4C) in DMF. Fluorescence emission peaks were listed in Table 1. The observed Stokes shifts were within the region observed for zinc(II) Pc complexes. All zinc(II) Pc complexes (**8**–**10**) showed similar fluorescence behaviour in DMF (Fig. 4). The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for all zinc(II) Pc complexes 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 all zinc(II) Pc complexes suggest that the nuclear configurations of the ground and excited states are similar and not affected by excitation.

3.5. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of the studied zinc Pc complexes (**8**, **9** and **10**) are given in Table 2. The Φ_F values of the zinc Pc complexes are similar and typical of other studied zinc Pc complexes in DMF [51,61–64]. For comparison among the studied zinc(II) Pc complexes, the Φ_F values of the peripherally chloro octa-substituted zinc(II) Pc (**10**) is the lowest among the studied zinc(II) Pc complexes, it could be attributed to a little aggregation of this complex in DMF.

The fluorescence lifetime (τ_F) values (Table 2) were calculated by Eq. (2) using natural radiative lifetime (τ_0) values. The τ_F values of the substituted zinc(II) Pc complexes are higher compared to unsubstituted zinc(II) Pc complexes in DMF, suggesting less quenching by substitution. τ_F values are higher for non-peripherally tetra-substituted zinc(II) Pc complex (**9**) when compared to peripherally tetra-substituted (**8**) and peripherally octa-substituted (**10**) zinc(II) Pc complex, 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 complexes [51,61–64].

Table 2
Photophysical and photochemical parameters of unsubstituted (ZnPc), peripherally tetrakis (**8**), non-peripherally tetrakis (**9**) and peripherally octakis-tetra-chloro substituted (**10**) zinc(II) phthalocyanine complexes 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
8	0.16	1.44	9.00	11.11	3.69	0.72
9	0.19	2.50	13.17	7.60	12.72	0.76
10	0.13	1.87	14.43	6.95	8.99	0.70
ZnPc[b]	0.17	1.03	6.05	16.53	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. [61].

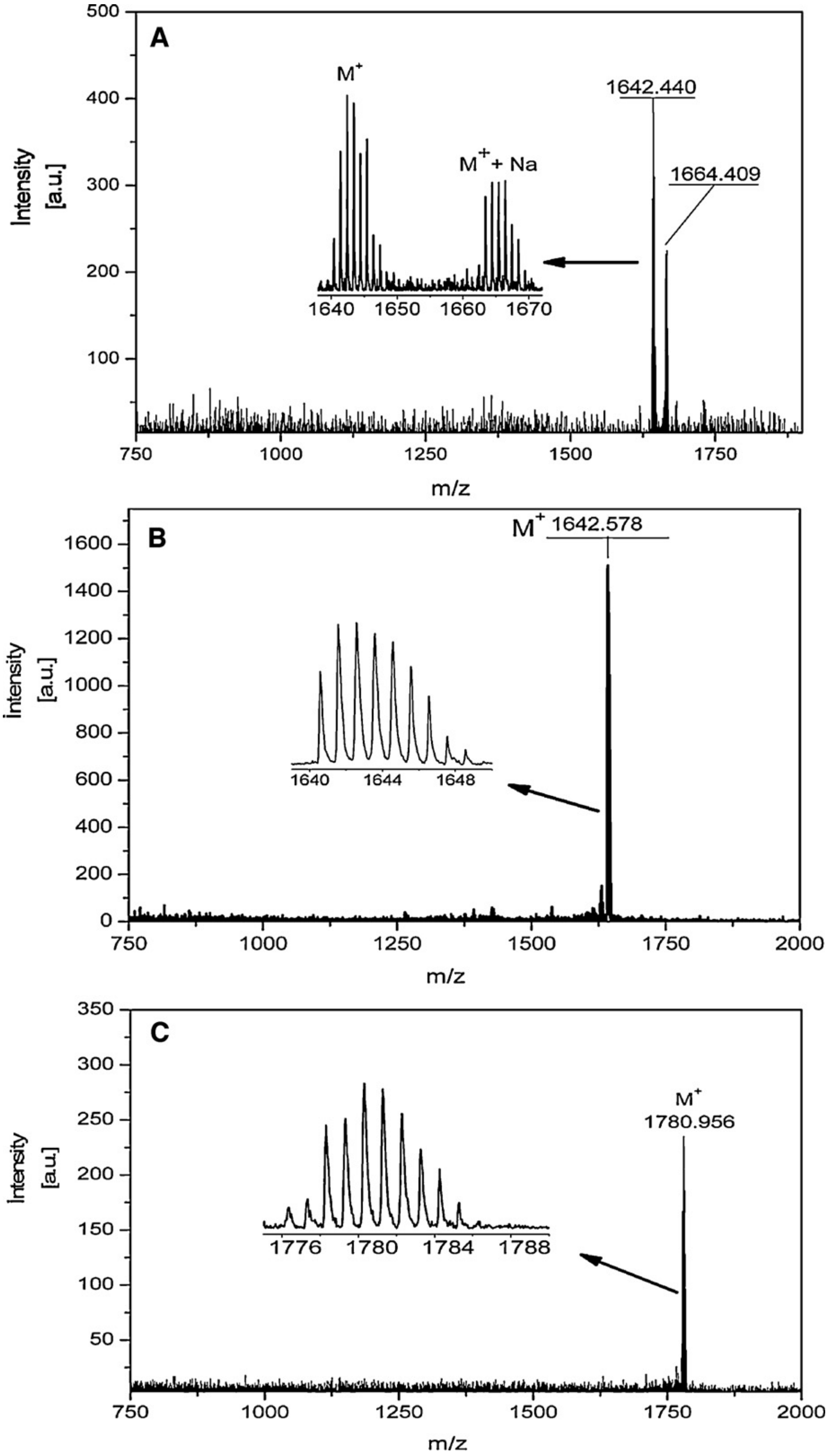


Fig. 1. Mass spectra of the phthalocyanine complexes: (A) for complex **8**, (B) for complex **9** and (C) for complex **10**.

The τ_0 and the rate constants for fluorescence (k_F) values are also given in Table 2. The τ_0 values of the substituted zinc(II) Pc complexes (**8**–**10**) are higher than unsubstituted zinc(II) Pc complex in DMF. The chloro octa-substituted zinc(II) Pc complex showed the highest τ_0 value than peripherally and non-peripherally tetra-substituted zinc(II) Pc complexes (**8** and **9**) in DMF (Table 2). This is due to the heavy atom effect of chlorine atom. The non-peripheral substituted zinc(II) Pc complex (**9**) showed higher τ_0 value than peripheral substituted zinc(II) Pc complex (**8**) complexes in DMF (Table 2) due to the position effect. The heavy chlorine atoms reduce the rate constants for fluorescence (k_F) increase the natural radiative lifetime (τ_0). The rate constants for fluorescence (k_F) of substituted zinc(II) Pc complex (**8**) is the highest among the studied zinc Pc complexes. The fluorescence quantum yields (Φ_F) of

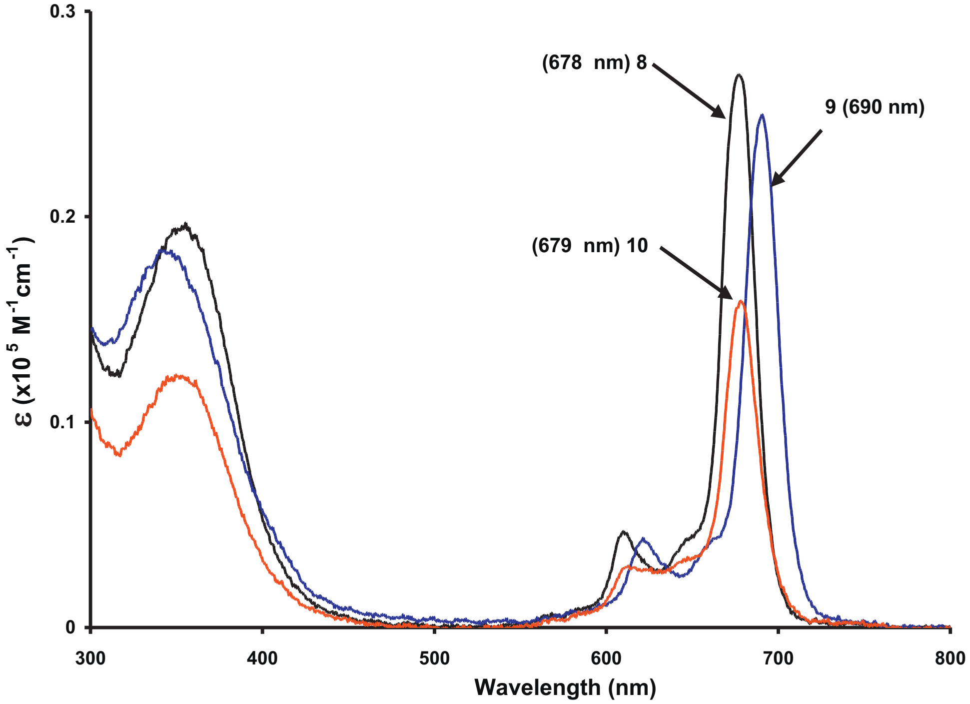


Fig. 2. Absorption spectra of substituted zinc(II) phthalocyanine complexes (**8**, **9** and **10**) in DMF. Concentration = 1×10^{-5} M.

the studied complexes (**8**–**10**) higher than those of ZnPcs bearing similar substituents like phenoxyl-groups of (Φ_F) [51,52].

3.6. Singlet oxygen quantum yields

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 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, $O_2(3\Sigma g)$, 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. 5 as an example for complex **8**). The singlet oxygen generation was measured in air. The Φ_Δ values of the substituted zinc(II) Pc complexes (**8**–**10**) are higher when

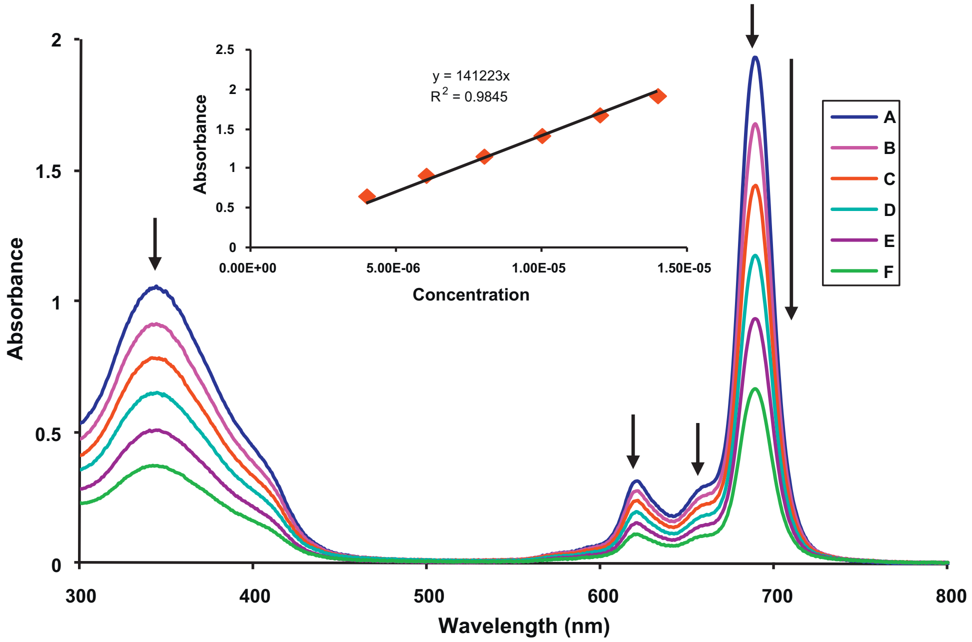


Fig. 3. Absorption spectral changes of **9** in DMF at different concentrations: 14×10^{-6} (A), 12×10^{-6} (B), 10×10^{-6} (C), 8×10^{-6} (D), 6×10^{-6} (E), 4×10^{-6} (F) M (Inset: plot of absorbance versus concentration).

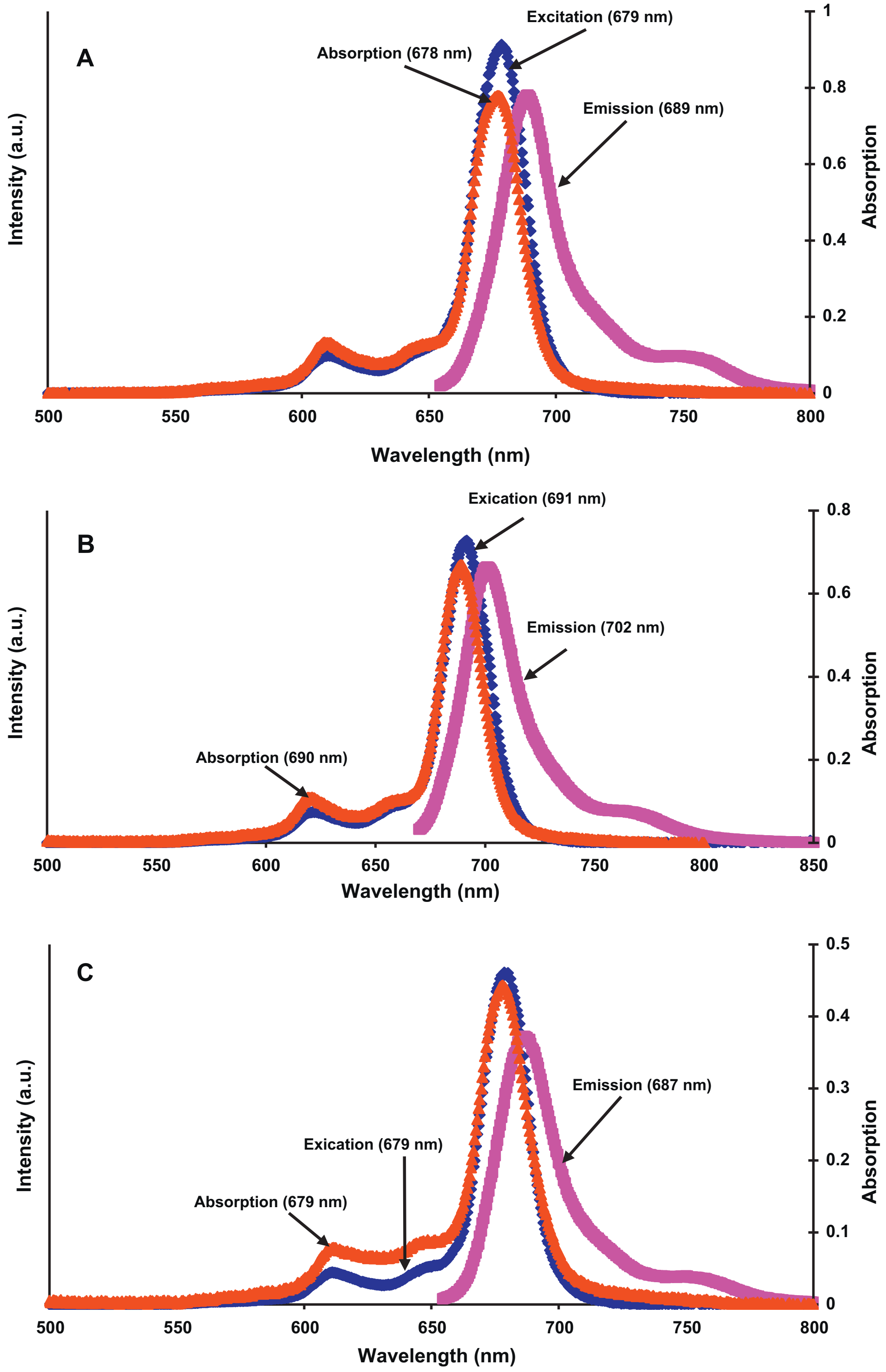


Fig. 4. Absorption, excitation and emission spectra of the compounds: (A) for complex **8**, (B) for complex **9** and (C) for complex **10** in DMF. Excitation wavelength = 645 nm for **8** and **10**, 660 nm for **9**.

compared to unsubstituted zinc(II) Pc complex in DMF (Table 2). The Φ_Δ value of chloro octa substituted complex (**10**) slightly lower than other substituted zinc(II) Pc complexes in DMF, it could be attributed to a little aggregation of this complex in DMF. The non-peripherally tetra-substituted zinc(II) Pc complex (**9**) showed the highest Φ_Δ value among the studied zinc(II) Pc complexes (Table 2) may be due to absorption of light at longer wavelength than peripherally substitution. The Φ_Δ values of the studied complexes (**8**–**10**) were also measured under nitrogen atmosphere. Nitrogen was purged in the solutions of the samples for 15 min before singlet oxygen determination. The Φ_Δ values of complexes **8** and **9** increased from 0.72 to 0.83 and from 0.76 to 0.94, respectively. The Φ_Δ value of complex **10** reduced from 0.70 to 0.63 under nitrogen atmosphere. The Φ_Δ values of the studied complexes (**8**–**10**) higher than those of ZnPcs bearing similar substituents like phenoxyl-groups of Φ_Δ values [51,52].

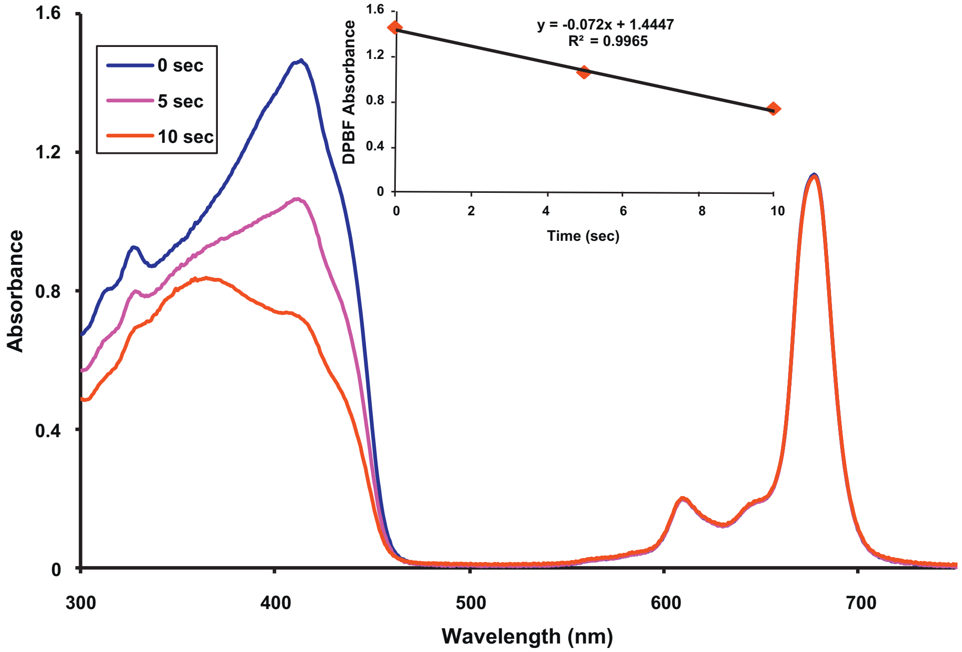


Fig. 5. The absorption spectral changes during the determination of singlet oxygen quantum yields. This determination was for compound **8** in DMF at a concentration of 1 × 10^{-5} M (Inset: plot of DPBF absorbance versus time).

3.7. 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 photodegradation not associated with phototransformation into different forms of MPc absorbing in the visible region (Fig. 6 as an example for complex **9** in DMF) The Φ_d values, found in this study, are higher than phthalocyanine derivatives having different metals and substituents on the phthalocyanine ring in literature [51,52]. Stable zinc phthalocyanine molecules show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [52]. Table 2 shows that all substituted complexes (**8**–**10**) were less stable to degradation compared to unsubstituted ZnPc in DMF. Thus, the substitution of ZnPc with 7-oxy-3-(4-methoxyphenyl)coumarin groups seem to decrease the stability of the complexes in DMF. The non-peripherally substituted zinc(II) Pc complex (**9**) was less stable when compared to the other substituted complexes (**8** and **10**). The peripherally substituted complex (**8**) is the most stable than the other complexes. It seems zinc(II) metal and 7-oxy-3-(4-methoxyphenyl)coumarin

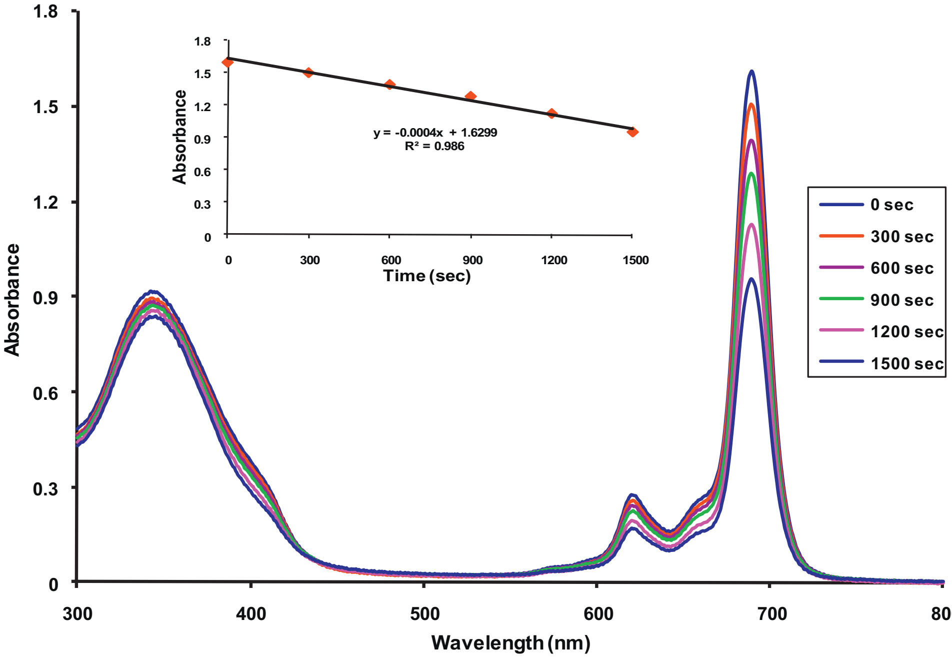


Fig. 6. The absorption spectral changes of compound **9** in DMF under light irradiation showing the disappearance of the Q-band at five minutes intervals (Inset: plot of absorbance versus time).

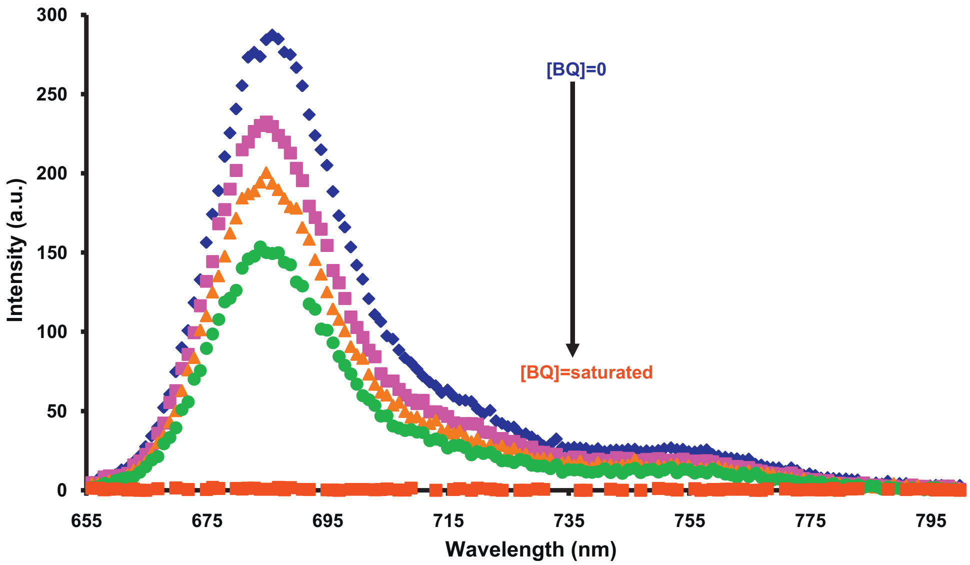


Fig. 7. Fluorescence emission spectral changes of **10** (1.00 × 10^{-5} M) on addition of different concentrations of BQ in DMF. [BQ] = 0, 0.008, 0.016, 0.024 M.

Table 3
Fluorescence quenching data for unsubstituted (ZnPc), peripherally tetrakis (**8**), non-peripherally tetrakis (**9**) and peripherally octakis-tetra-chloro substituted (**10**) zinc(II) phthalocyanine complexes in DMF.

Compound	K_{SV} (M^{-1})	$k_q/10^{10}$ (M^{-1} s^{-1})
8	32.42	2.25
9	20.70	0.83
10	28.86	1.54
ZnPc[a]	57.60	5.59

[a] Data from Ref. [61].

substituted zinc(II) Pc groups increases the Φ_d values and decreases the stability of complexes.

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

The fluorescence quenching of zinc phthalocyanine complexes by BQ in DMF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 7 shows the quenching of complex (**10**) by BQ in DMF as an example. The slope of the plots shown at Fig. 8 gave Stern–Volmer constants (K_{SV}) values, listed in Table 3. The linearity of these plots indicates that fluorescence quenching is reasonably described by a collisional quenching mechanism. The K_{SV} values of the substituted zinc phthalocyanine complexes (**8**, **9** and **10**) are lower than unsubstituted ZnPc in DMF. The peripherally substituted zinc(II) Pc complex (**8**) has highest K_{SV} value, while non-peripherally substituted zinc(II) Pc complex (**9**) has the lowest K_{SV} in DMF. The substitution with 7-oxy-3-(4-methoxyphenyl)coumarin groups seems to decrease the K_{SV} values of the complexes in DMF. The bimolecular quenching rate constant (k_q) values of the substituted zinc phthalocyanine complexes (**8**, **9** and **10**) are also lower than unsubstituted ZnPc in DMF, thus substitution with 7-oxy-3-(4-methoxyphenyl)coumarin group seems to decrease the k_q values of the complexes. Values of k_q near 10^{10} M^{-1} s^{-1} are in agreement with the theoretical Smoluchowski–Stokes–Einstein approximation at 298 K [65]. The order in k_q values among the substituted complexes was also as follows: **8** > **10** > **9** in DMF.

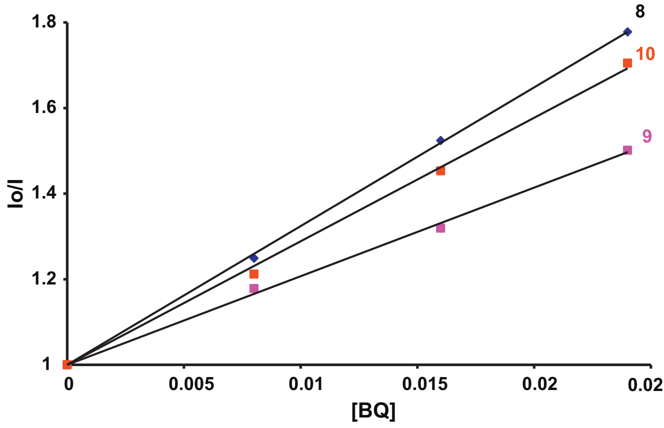


Fig. 8. Stern–Volmer plots for BQ quenching of coumarin substituted zinc(II) phthalocyanines (**8**, **9** and **10**). [MPc] = ~1.00 × 10^{-5} M in DMF. [BQ] = 0, 0.008, 0.016, 0.024 M.

4. Conclusions

In the presented work, the syntheses of new 7-oxy-3-(4-methoxyphenyl)coumarin substituted peripherally tetra-(**8**), non-peripherally tetra-(**9**) and chloro octa-(**10**) zinc(II) phthalocyanine complexes were described and new compounds were characterized by elemental analysis, ^{1}H NMR, MALDI-TOF, IR, UV–vis and fluorescence spectral data. The photophysical and photochemical properties of these zinc(II) Pc complexes were also described in DMF for comparison of the effects of the number of the substituents and their position on the phthalocyanine framework. All the studied zinc(II) Pc complexes show excellent solubity in general organic solvents. The studied zinc(II) complexes are monomeric and showed similar fluorescence behaviour in DMF. The Φ_F values of the studied zinc(II) Pc complexes are similar and typical for zinc(II) Pc complexes bearing different substitution. The Φ_Δ values of zinc(II) Pc complexes ranged from 0.70 to 0.76 gives an indication of the potential of these compounds as photosensitizers in PDT applications. The substitution of ZnPc with 7-oxy-3-(4-methoxyphenyl)coumarin groups seem to decrease the photostability of the complexes in DMF. The 7-oxy-3-(4-methoxyphenyl)coumarin substituted zinc(II) Pc complexes (**8**, **9** and **10**) showed lower K_{sv} and bimolecular quenching rate constant (k_q) values when compared to the unsubstituted ZnPc in DMF. The (k_q) values were found to be close to the diffusion-controlled limits, approximately 10^{10} M^{-1} s^{-1}.

Acknowledgement

We are thankful to the Research Foundation of Marmara University, Commission of Scientific Research Project (BAPKO) [FEN-C-DRP-110908-0232 and FEN-A-090909-0302].

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