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Coumarino-12-crown-4 bearing phthalocyanine photosensitizers for singlet oxygen production

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ABSTRACT

The synthesis, characterization, photophysical and photochemical properties of the new metal-free and zinc (II) phthalocyanines tetra-substituted at the peripheral (complexes **3a** and **3b**) and non-peripheral (complexes **4a** and **4b**) positions with 7,8-(12-crown-4)-3-(4-oxyphenyl)coumarin groups are reported for the first time. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H NMR, electronic spectroscopy and mass spectra. General trends are described for photodegradation, singlet oxygen and fluorescence quantum yields, and fluorescence lifetimes of these compounds in dimethylsulphoxide (DMSO). Photophysical and photochemical properties of phthalocyanine complexes are very useful for photodynamic therapy (PDT) applications. The singlet oxygen quantum yields (Φ_Δ) ranged from 0.11 to 0.80 are indicating the potential of the complexes as photosensitizers in applications of PDT.

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1. Introduction

Phthalocyanines (Pcs) are a family of an aromatic macrocycles depends on delocalized 18π- electron system [1]. There has been a growing interest in the use of Pcs in a variety of new technological fields such as semiconductor devices [2], electrochromic display devices [3], liquid crystals [4], Langmuir–Blodgett films [5,6], and as photosensitizers in photodynamic therapy of cancer (PDT) [7,8].

Crown ethers are heteromacrocycles in which the framework is typically comprised of repeating ethyleneoxy [–(CH_2CH_2O)$_n$–] units [9–11]. Crown ethers have found wide applications in molecular electronic devices due to their remarkable recognition and metal binding properties [12]. The first effort was the preparation of crown ether-substituted phthalocyaninato copper complex, Cu[Pc(15C5)$_4$], reported in 1986 [13–15]. From that time, significant efforts have been paid in introducing different species of crown-ether substituents onto the Pc ring [16].

Coumarins (2H-1-benzopyran-2-one) are a group of compounds that have important roles as food constituents; as anti-oxidants, stabilizers, and immunomodulatory substances; as fluorescent markers for use in analysis, in lasers and in clinical use [17]. The coumarin compounds exist in a variety of forms, due to the various substitutions possible in their basic structure, which modulate their biological activity [18]. A combination of these three potentially promising units (i.e. phthalocyanines, crown ethers and coumarins) for the purpose of constructing novel supramolecular structures with novel multi-functional properties has attracted research interests. Attachment of crown ether and coumarin groups to the Pc ring significantly increases the solubility of Pcs in many organic solvents, leading to significant advances in research such as biological modeling, homogeneous catalysis, alkaline or earth alkaline and lanthanide metal extractions [19,20]. The main feature of the crown ether groups is that they can hold the alkali cations within their cavity [21].

Over the last decade, a substantial number of Pc-based photosensitizers have been prepared and evaluated for their photodynamic activity, with the focus on silicon, zinc and aluminum analogues as a result of their desirable photophysical properties [22]. The first photosensitizers were hematoporphyrin derivatives and have already been described in detail in several articles [23,24]. Second generation photosensitizers such as Pcs have also been introduced for PDT in research and clinical trials [25]. Due to their high molar absorption coefficient in the red part of the spectrum, photostability and long lifetimes of the photoexcited triplet states, Pcs are known to be useful photosensitizers [26–29].

The aim of our ongoing research is to synthesize crown ether bearing coumarin substituted metal-free and zinc (II) Pcs as potential PDT agents. In this work, we report on the effects of the crown ether bearing coumarin groups as substituent and the position of the substituent on the photophysical and photochemical parameters. Aggregation behaviour, photophysical (fluorescence

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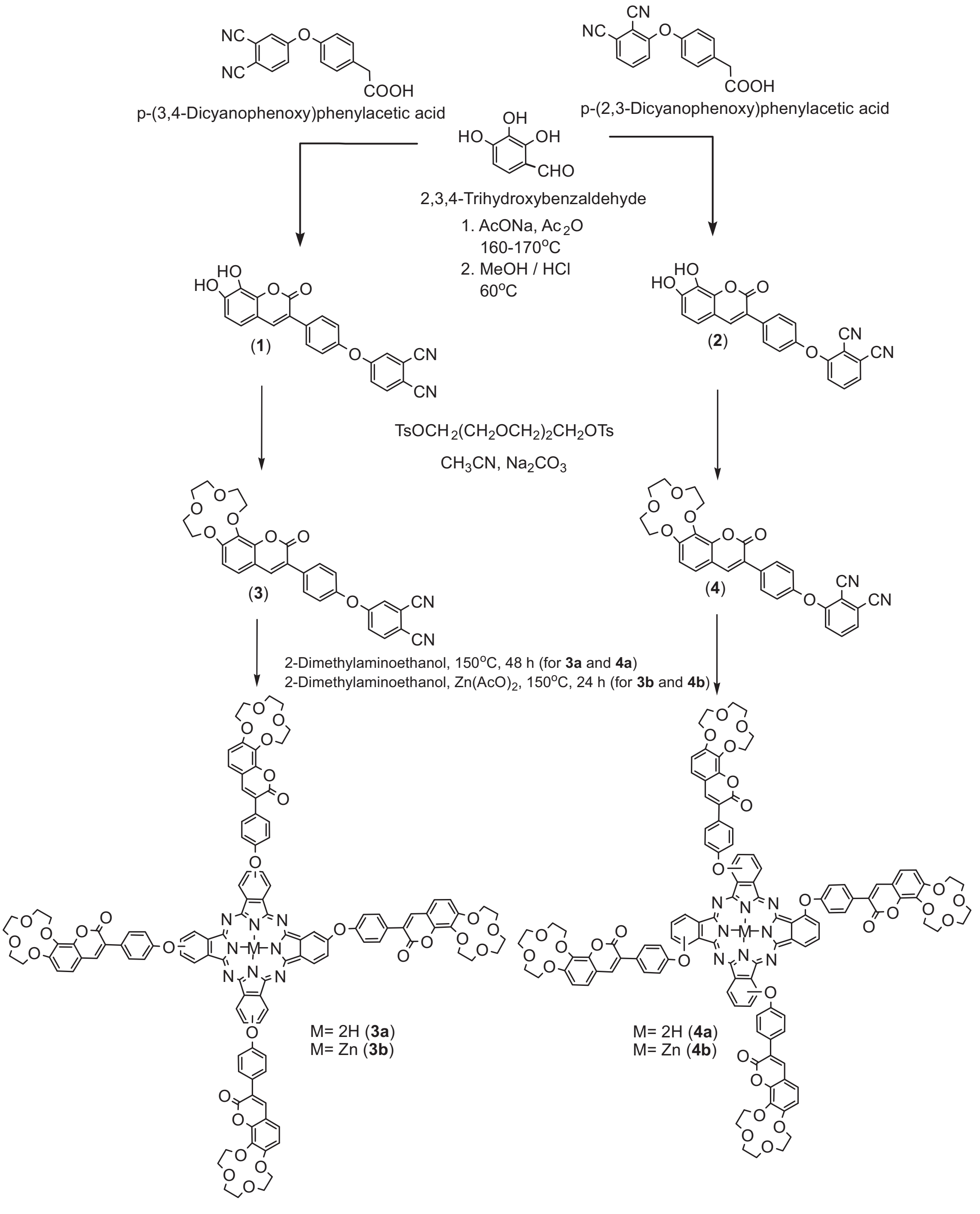
lifetime and quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties are investigated. This work also explores the effects of ring substitutions and position on the fluorescence quenching of metal-free and zinc (II) Pcs by 1,4-benzoquinone (BQ) using the Stern–Volmer 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 [30]. We report herein on the synthesis, spectroscopic, photophysical and photochemical properties of metal-free and zinc (II) Pcs tetra-substituted at the peripheral (complexes **3a** and **3b**) and non-peripheral (complexes **4a** and **4b**) positions with 7,8-(12-crown-4)-3-(4-oxyphenyl)coumarin groups (Scheme 1).

2. Experimental

2.1. Materials and equipment

Unsubstituted zinc (II) phthalocyanine (ZnPc), 1,3-diphenylisobenzofuran (DPBF), 2,3,4-trihydroxybenzaldehyde, tetrabutylammonium hydroxide (TBAOH) and trifluoroacetic acid (TFA) were purchased from Aldrich. Zinc (II) acetate, sodium carbonate (Na_2CO_3), sodium acetate (NaOAc) and triethylene glycol ditosylate were purchased from Fluka. Basic aluminum oxide (Al_2O_3) was purchased from Aldrich. All solvents were dried as described by Perrin and Armarego [31] before use. p-(2,3-Dicyanophenoxy)phenylacetic acid [32] and 7,8-



Scheme 1. Synthesis route of new phthalonitriles (**2**, **3** and **4**), metal-free (**3a** and **4a**) and zinc (II) Pcs (**3b** and **4b**).

dihydroxy-3-[p-(3′,4′-dicyanophenoxy)phenyl]coumarin (**1**) [33] were synthesized and purified according to literature procedures.

Infrared (IR) spectra were recorded on a Shimadzu FTIR-8300 Fourier Transform Infrared Spectrophotometer using KBr pellets, electronic spectra were recorded on a Shimadzu UV-2450 and Shimadzu UV-2001 UV–vis spectrophotometers. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ^{1}H NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer using TMS as an internal standard. Mass spectra were performed on a Bruker Autoflex III MALDI-TOF spectrometer using 2,5-dihydroxybenzoic acid (DHB, 0.02 g cm^{-3} in THF) as matrix. MALDI samples were prepared by mixing the complex (0.02 g cm^{-3} in DMF) with the matrix solution (1:10 v/v) in a 0.5 cm^3 Eppendorf micro tube. Finally, 1×10^{-3} cm^3 of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. 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.

2.2. Synthesis

2.2.1. 7,8-Dihydroxy-3-[p-(2′,3′-dicyanophenoxy)phenyl] coumarin (2)

A mixture of p-(2,3-dicyanophenoxy)phenylacetic acid (2.71 g, 9.74 mmol), 2,3,4-trihydroxybenzaldehyde (1.50 g, 9.74 mmol), anhydrous NaOAc (3.99 g, 48.70 mmol) and anhydrous acetic anhydride (15 ml) was heated with stirring at 160–170 °C in a sealed glass tube for 8 h under nitrogen. After cooling to room temperature, water was added and the mixture stirred overnight. The resulting solid was filtered, washed with water and dried. The crude product 7,8-diacetoxy-3-[p-(2′,3′-dicyanophenoxy)phenyl]coumarin was suspended in methanol. A 10% aqueous HCl solution was added to adjust the pH to 3 and the ensuing mixture was heated and stirred at 60 °C for 18 h under nitrogen. The resulting solid (7,8-dihydroxy-3-[p-(2′,3′-dicyanophenoxy)phenyl]coumarin) was filtered, washed with water and dried. The crude product was purified by recrystallisation from ethanol. Yield: 3.180 g (82%). M.p. > 300 °C. FT-IR (KBr), υ_{max}/(cm^{-1}): 3320 (OH), 3092–3054 (Ar–CH), 2229 (C≡N), 1686 (C=O, lactone), 1606 (C=C), 1586–1463 (Ar C=C), 1298 (Ar–O–Ar). ^{1}H NMR (DMSO-d$_6$, 500 MHz): 10.15 (bs, 1H, –OH), 9.45 (bs, 1H, –OH), 8.22 (s, 1H, coumarin 4-H), 7.92–7.89 (m, 4H, Ar-H), 7.41 (d, *J* = 8 Hz, 1H, Ar-H), 7.35 (d, *J* = 8 Hz, 2H, Ar-H), 7.16 (d, *J* = 8 Hz, 1H, Ar-H), 6.89 (d, *J* = 8 Hz, 1H, Ar-H). UV–vis (THF) λ_{max} (nm) (log ε): 346 (4.13). MS (MALDI-TOF): *m*/*z* 396 [M]$^+$, 419 [M+Na]$^+$. Anal. Calc. for $C_{23}H_{12}N_2O_5$: C, 69.70; H, 3.05; N, 7.07. Found: C, 69.75; H, 3.65; N, 7.01%.

2.2.2. 7,8-(12-Crown-4)-3-[p-(3′,4′-dicyanophenoxy)phenyl] coumarin (3)

A mixture of 7,8-dihydroxy-3-[p-(3′,4′-dicyanophenoxy) phenyl]coumarin (**1**) (1.00 g, 2.52 mmol), triethylene glycol ditosylate (1.158 g, 2.52 mmol) and anhydrous Na_2CO_3 (0.535 g, 5.05 mmol) in acetonitrile (CH_3CN) (100 ml) was heated to reflux for 3 days under nitrogen atmosphere. After the removal of solution by distillation, the precipitate was dissolved in chloroform ($CHCl_3$), washed with water and dried on Na_2SO_4. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as eluent. Yield: 0.228 g (18%). M.p.: 208 °C. FT-IR (KBr), υ_{max}/(cm^{-1}): 3070–3055 (Ar–CH), 2955–2870 (Aliphatic –CH), 2227 (C≡N), 1728 (C=O, lactone), 1600 (C=C), 1576–1454 (Ar C=C), 1298–1246 (Ar–O–Ar), 1176–1109 (Ar–O–C). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.85 (s, 1H, coumarin 4-H), 7.83 (bd, 2H, Ar-H), 7.78 (d, *J* = 8 Hz, 1H, Ar-H), 7.38 (bd, 1H, Ar-H), 7.35 (dd, *J* = 8 and 2 Hz, 1H, Ar-H), 7.30 (d, *J* = 2 Hz, 1H, Ar-H), 7.18 (dd, *J* = 8 and 2 Hz, 2H, Ar-H), 6.94 (d, *J* = 8 Hz, 1H, Ar-H), 4.46 (t, *J* = 6 Hz, 2H, –OCH_2), 4.29 (t, *J* = 6 Hz, 2H, –OCH_2), 4.03 (t, *J* = 6 Hz, 2H, –$OCCH_2$), 3.90 (t, *J* = 6 Hz, 2H, –$OCCH_2$), 3.87–3.70 (m, 4H, –$OCCO(CH_2)_2$). UV–vis ($CHCl_3$) λ_{max} (nm) (log ε): 341 (4.82). MS (MALDI-TOF): *m*/*z* 533 [M+Na]$^+$. Anal. Calc. for $C_{29}H_{22}N_2O_7$: C, 68.23; H, 4.34; N, 5.49. Found: C, 68.25; H, 4.31; N, 5.45%.

2.2.3. 2(3),9(10),16(17),23(24)-Tetra[7,8-(12-crown-4)-3-(4-oxyphenyl)coumarin]-phthalocyanine (3a)

A solution of **3** (0.100 g, 0.196 mmol) in dry 2-dimethylaminoethanol (DMAE) (1.5 ml) was refluxed with stirring for 48 h under nitrogen atmosphere. After cooling to room temperature, methanol (5 ml) was added to precipitate the product. The green product was filtered and washed with water, methanol, ethanol, acetonitrile, ethyl acetate, aceton, acetic acid and diethyl ether. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as eluent. Yield: 0.038 g (38%). M.p. > 300 °C. FT-IR (KBr), υ_{max}/(cm^{-1}): 3292 (NH), 3082–3046 (Ar–CH), 2928–2864 (aliphatic CH), 1719 (C=O, lactone), 1604 (C=C), 1510–1464 (Ar C=C), 1296–1238 (Ar–O–Ar), 1124–1080 (Ar–O–C). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.66–7.32 (m, 40H, Ar-H), 4.37–3.62 (m, 48H, –OCH_2). UV–vis λ_{max} ($CHCl_3$) (nm) (log ε): 341 (4.89), 599 (shoulder, 4.15), 633 (shoulder, 4.33), 665 (4.63), 700 (4.65). MS (MALDI-TOF, DHB as matrix): *m*/*z* 2042 [M]$^+$, 2043 [M+H]$^+$, 2044 [M+2H]$^+$, 2045 [M+3H]$^+$, 2065 [M+Na]$^+$. Anal. Calc. for $C_{116}H_{90}N_8O_{28}$: C, 68.17; H, 4.41; N, 5.49. Found: C, 68.20; H, 4.45; N, 5.45%.

2.2.4. 2(3),9(10),16(17),23(24)-Tetra[7,8-(12-crown-4)-3-(4-oxyphenyl)coumarin]-phthalocyaninato zinc (II) (3b)

Compound **3** (0.050 g, 0.098 mmol), $Zn(AcO)_2$ (0.0045 g, 0.0245 mmol) and dried DMAE (1.5 ml) were refluxed with stirring under nitrogen atmosphere for 24 h. After cooling to room temperature the solution was treated with methanol (5 ml) and the product was filtered off and washed with water, methanol, ethanol, acetonitrile, ethyl acetate, aceton, acetic acid and diethyl ether. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as eluent. Yield: 0.035 g (68%). M.p. > 300 °C. FT-IR (KBr), υ_{max}/(cm^{-1}): 3059–3042 (Ar–CH), 2914–2860 (aliphatic CH), 1717 (C=O, lactone), 1602 (C=C), 1508–1464 (Ar C=C), 1294–1234 (Ar–O–Ar), 1122–1080 (Ar–O–C). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.60–7.43 (m, 40H, Ar-H), 4.42–3.71 (m, 48H, –OCH_2). UV–vis λ_{max} ($CHCl_3$) (nm) (log ε): 342 (5.05), 599 (shoulder, 4.15), 607 (shoulder, 4.17), 675 (4.79). MS (MALDI-TOF, DHB as matrix): *m*/*z* 2105 [M]$^+$, 2106 [M+H]$^+$, 2107 [M+2H]$^+$, 2108 [M+3H]$^+$, 2128 [M+Na]$^+$. Anal. Calc. for $C_{116}H_{88}N_8O_{28}Zn$: C, 66.13; H, 4.18; N, 5.32. Found: C, 66.18; H, 4.14; N, 5.36%.

2.2.5. 7,8-(12-Crown-4)-3-[p-(2′,3′-dicyanophenoxy)phenyl] coumarin (4)

A mixture of 7,8-dihydroxy-3-[p-(2′,3′-dicyanophenoxy) phenyl]coumarin (**2**) (1.00 g, 2.52 mmol), triethylene glycol ditosylate (1.158 g, 2.52 mmol) and anhydrous Na_2CO_3 (0.535 g, 5.05 mmol) in acetonitrile (100 ml) was heated to reflux for 3 days under nitrogen atmosphere. After the removal of solution by distillation, the precipitate was dissolved in $CHCl_3$, washed with water and dried on Na_2SO_4. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as eluent. Yield: 0.140 g (11%). M.p.: 202–204 °C. FT-IR (KBr), υ_{max}/(cm^{-1}): 3076–3052 (Ar–CH), 2913–2861 (aliphatic –CH), 2232 (C≡N), 1716 (C=O, lactone), 1606 (C=C), 1509–1458 (Ar C=C), 1281 (Ar–O–Ar), 1118–1074 (Ar–O–C). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.83 (s, 1H, coumarin 4-H), 7.81 (bd, 2H, Ar-H), 7.64 (t, *J* = 6 Hz, 1H, Ar-H), 7.53 (d, *J* = 8 Hz, 1H, Ar-H), 7.30 (bd, 1H, Ar-H), 7.23 (d, *J* = 8 Hz, 1H, Ar-H), 7.19 (dd, *J* = 8 and 2 Hz, 2H, Ar-H), 6.94 (d, *J* = 8 Hz, 1H, Ar-H), 4.46 (t, *J* = 6 Hz, 2H, $-OCH_2$), 4.29 (t, *J* = 6 Hz, 2H, $-OCH_2$), 4.03 (t, *J* = 6 Hz, 2H, $-OCCH_2$), 3.90 (t, *J* = 6 Hz, 2H, $-OCCH_2$), 3.87–3.75 (m, 4H, $-OCCO(CH_2)_2$). UV–vis ($CHCl_3$) λ_{max} (nm) (log ε): 339 (4.09). MS (MALDI-TOF): *m/z* 533 $[M+Na]^+$. Anal. Calc. for $C_{29}H_{22}N_2O_7$: C, 68.23; H, 4.34; N, 5.49. Found: C, 68.27; H, 4.36; N, 5.52%.

2.2.6. 1(4),8(11),15(18),22(25)-Tetra[7,8-(12-crown-4)-3-(4-oxyphenyl)coumarin]-phthalocyanine (4a)

Compound **4a** was prepared and purified according to the procedure described for **3a**, starting from 0.100 g (0.196 mmol) **4** and DMAE (1.5 ml). Yield: 0.023 g (23%). M.p. > 300 °C. FT-IR (KBr), $\upsilon_{max}/(cm^{-1})$: 3288 (NH), 3053–3046 (Ar–CH), 2924–2861 (aliphatic CH), 1715 (C=O, lactone), 1603 (C=C), 1507–1452 (Ar C=C), 1294–1246 (Ar–O–Ar), 1122–1074 (Ar–O–C). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.63–7.38 (m, 40H, Ar-H), 4.34–3.65 (m, 48H, $-OCH_2$). UV–vis λ_{max} ($CHCl_3$) (nm) (log ε): 339 (4.99), 614 (shoulder, 3.83), 648 (shoulder, 4.10), 684 (4.65), 717 (4.72). MS (MALDI-TOF, DHB as matrix): *m/z* 2042 $[M]^+$, 2043 $[M+H]^+$, 2044 $[M+2H]^+$, 2045 $[M+3H]^+$, 2065 $[M+Na]^+$. Anal. Calc. for $C_{116}H_{90}N_8O_{28}$: C, 68.17; H, 4.41; N, 5.49. Found: C, 68.13; H, 4.38; N, 5.46%.

2.2.7. 1(4),8(11),15(18),22(25)-Tetra[7,8-(12-crown-4)-3-(4-oxyphenyl)coumarin]-phthalocyaninato zinc (II) (4b)

Compound **4b** was prepared and purified according to the procedure described for **3b**, starting from 0.104 g (0.204 mmol) **4**, $Zn(AcO)_2$ (0.0093 g, 0.051 mmol) and DMAE (1.5 ml). Yield: 0.064 g (60%). M.p. > 300 °C. FT-IR (KBr), $\upsilon_{max}/(cm^{-1})$: 3048–3016 (Ar–CH), 2913–2859 (aliphatic CH), 1717 (C=O, lactone), 1603 (C=C), 1505–1479 (Ar C=C), 1294–1242 (Ar–O–Ar), 1120–1077 (Ar–O–C). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.68–7.45 (m, 40H, Ar-H), 4.45–3.78 (m, 48H, $-OCH_2$). UV–vis λ_{max} ($CHCl_3$) (nm) (log ε): 337 (4.90), 620 (shoulder, 4.11), 658 (shoulder, 4.26), 692 (4.79), 736 (*J* band, 4.45). MS (MALDI-TOF, DHB as matrix): *m/z* 2105 $[M]^+$, 2106 $[M+H]^+$, 2107 $[M+2H]^+$, 2108 $[M+3H]^+$, 2128 $[M+Na]^+$. Anal. Calc. for $C_{116}H_{88}N_8O_{28}Zn$: C, 66.13; H, 4.18; N, 5.32. Found: C, 66.09; H, 4.22; N, 5.26%.

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) [34,35]:

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{FA_{\mathrm{Std}}n^2}{F_{\mathrm{Std}}An^2_{\mathrm{Std}}} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**3a**, **3b**, **4a** and **4b**) and the standard, respectively. A and A_{Std} are the relative absorbance of the samples and standard at the excitation wavelength, respectively. n and n_{Std} are the refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc ($\Phi_F = 0.20$ in DMSO) [36] 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 [37]. 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 yields (Φ_Δ) of the samples (**3a**, **3b**, **4a** and **4b**) were determined as previously explained in detail [38–40]. Typically, 2 cm^3 portion of the samples (**3a**, **3b**, **4a** and **4b**) 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 [38–40]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with unsubstituted ZnPc (in DMSO) as reference; and DPBF as chemical quencher for singlet oxygen, using Eq. (3):

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

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard ($\Phi_\Delta^{Std} = 0.67$ for unsubstituted ZnPc in DMSO) [41]; R and R^{Std} are the DPBF photobleaching rates in the presence of the samples (**3a**, **3b**, **4a** and **4b**) and standard, respectively; I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples (**3a**, **3b**, **4a** and **4b**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [42], the concentration of quencher (DPBF) was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer containing the quencher (DPBF) were prepared in the dark and irradiated in the Q band region using the photoirradiation setup. DPBF degradation at 417 nm was monitored. The light intensity 7.33×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations. The error in the determination of Φ_Δ was ~10% (determined from several Φ_Δ values).

2.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [38–40]. For determination of photodegradation quantum yields (Φ_d), the usual Eq. (4) was employed:

$$\Phi_d = \frac{(C_0 - C_t)VN_{\mathrm{A}}}{I_{abc}\,St} \tag{4}$$

where C_0 and C_t are the samples (**3a**, **3b**, **4a** and **4b**) concentrations before and after irradiation, respectively. V is the reaction volume; S is the irradiated cell area (2.0 cm^2); t is the irradiation time; N_A is Avogadro's number and I_{abs} is the overlap integral of the radiation source intensity and the absorption of the Pc (the action spectrum) in the region of the interference filter transmittance. 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 of Pc complexes (**3a**, **3b**, **4a** and **4b**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the Pc 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 Pc complexes (**3a**, **3b**, **4a** and **4b**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) Eq. (5) [43]:

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

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)):

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

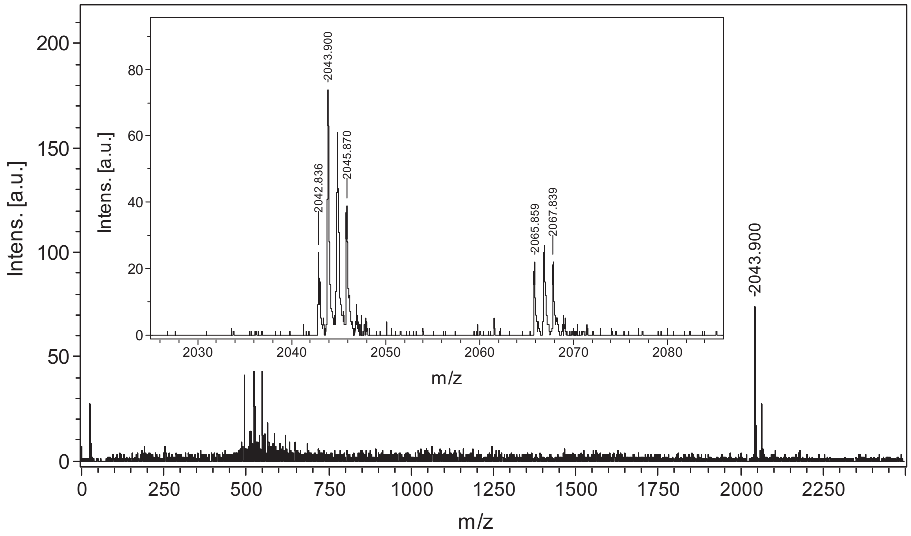


Fig. 1. MALDI-TOFF mass spectra of complex **3a**.

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

3. Results and discussion

3.1. Synthesis and characterization

The general synthetic routes for the synthesis of new phthalonitriles (**2**, **3** and **4**), metal-free (**3a** and **4a**) and zinc (II) Pcs (**3b** and **4b**) are given in Scheme 1. 7,8-Dihydroxy-3-[p-(3′,4′-dicyanophenoxy)phenyl]coumarin (**1**) and 7,8-dihydroxy-3-[p-(2′,3′-dicyanophenoxy)phenyl]coumarin (**2**) were prepared by the condensation of 2,3,4-trihydroxybenzaldehyde with p-(3,4-dicyanophenoxy)phenylacetic acid (for **1**) or p-(2,3-dicyanophenoxy)phenylacetic acid (for **2**) in the presence of sodium acetate and acetic anhydride at 160 °C. The crude products (**1** and **2**) purified by crystallization from ethanol. Compounds **1** and **2** reacted with triethylene glycol ditosylate to give the crown ethers (**3** and **4**) in the presence of Na_2CO_3 in CH_3CN. The crude products (**3** and **4**) were purified by column chromatography on silica gel with $CHCl_3$ as eluent. Cyclotetramerization of the **3** and **4** to the metal-free Pcs (**3a** and **4a**) was accomplished in DMAE at 150 °C under nitrogen atmosphere. The zinc (II) Pcs (**3b** and **4b**) were obtained from the dicyano derivatives (**3** and **4**) and anhydrous $Zn(AcO)_2$ in DMAE at 150 °C under nitrogen atmosphere. The novel compounds have been characterized by elemental analysis, FT-IR, ^1H NMR and MALDI-TOFF mass spectroscopy. The results were in accord with the proposed structures.

The FT-IR spectrum of **2** exhibits the intense absorption band at 2229 cm^{-1} corresponding to the C≡N stretching, and characteristic frequencies at 3320 (–OH), 3092–3054 (Ar–CH) and 1686 (C=O, lactone) cm^{-1}. The ^1H NMR spectrum of **2**, the –OH protons appeared at 10.15 and 9.45 ppm as broad singlets, the aromatic protons appeared at 7.92–6.89 ppm as doublets and the proton of coumarin at 4 position appeared at 8.22 ppm as a singlet. The mass spectra of **2** which showed peaks at $m/z = 396\ [M]^+$ and 419 $[M+Na]^+$ support the proposed formula for this compound.

The FT-IR spectra of **3** and **4** showed vibration peaks for their aliphatic CH stretching frequency at 2870–2955 and 2861–2913 cm^{-1}, respectively. The characteristic vibration peaks of the nitrile (C≡N) and carbonyl groups (C=O, lactone) appeared at 2227, 2232 cm^{-1} and 1728, 1716 cm^{-1}, respectively. The ^1H NMR spectra of **3** and **4** in $CDCl_3$ showed characteristic signals

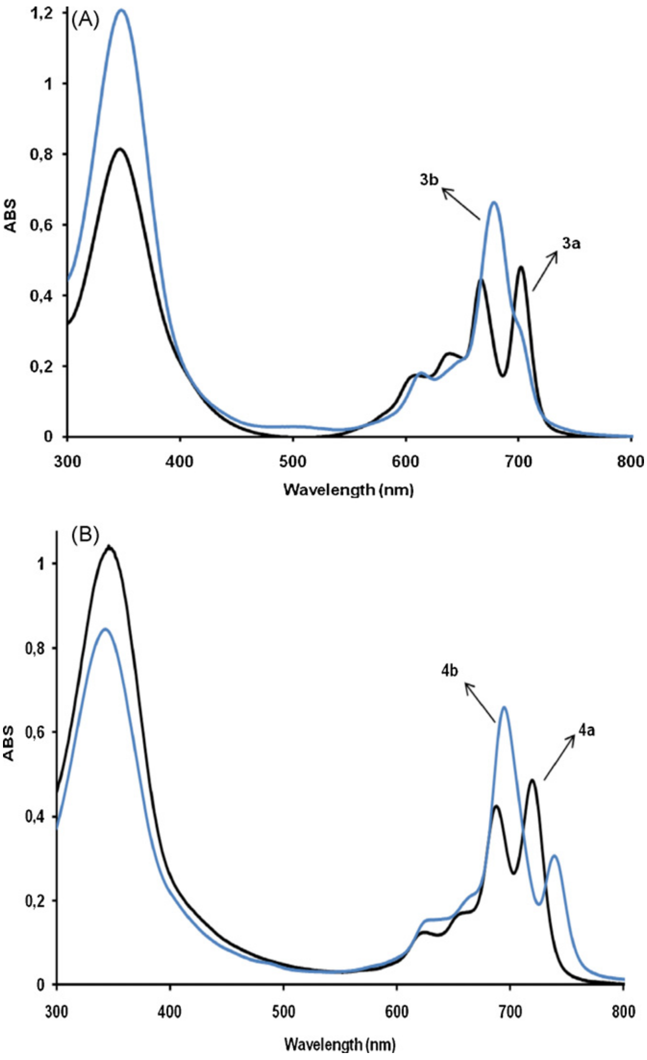


Fig. 2. Absorption spectra of substituted metal-free and zinc (II) Pc complexes: (A) **3a** and **3b**, (B) **4a** and **4b** in $CHCl_3$ (concentrations: 1×10^{-5} M).

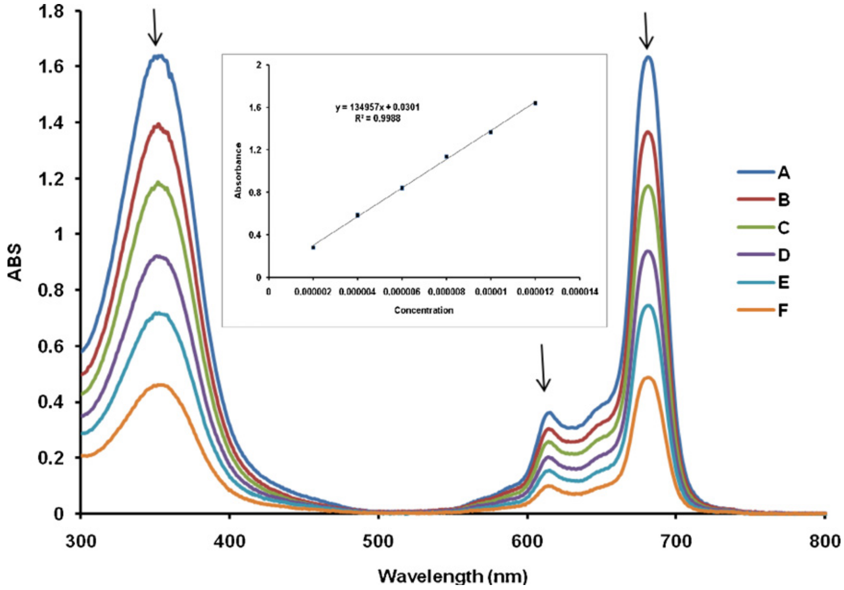


Fig. 3. Aggregation behaviour of **3b** in DMSO at different concentrations: 12×10^{-6} (A), 10×10^{-6} (B), 8×10^{-6} (C), 6×10^{-6} (D), 4×10^{-6} (E), 2×10^{-6} (F) M (inset: Plot of absorbance versus concentration).

for etheric (–OCH_2CH_2O–) protons at δ 4.46–3.70 ppm for **3** and 4.46–3.75 ppm for **4** each a triplet. The singlets at δ 7.85 ppm for **3** and 7.83 ppm for **4** indicated the presence the proton of coumarin at position 4. In addition the chemical shifts of the aromatic protons are observed at δ 7.83–6.94 ppm for compound **3** and 7.81–6.94 ppm for compound **4**. Molecular ion peaks were easily identified at $m/z = 533$ [M+Na]$^+$ for **3** and **4**.

The sharp vibration for the C≡N groups in the FT-IR spectra of phthalonitriles **3** and **4** at 2227 and 2232 cm^{-1}, respectively, disappeared after conversion into metal-free (**3a** and **4a**) and zinc (II) (**3b** and **4b**) Pcs. Characteristic NH stretching band of the metal-free Pcs (**3a** and **4a**) appeared at 3292 cm^{-1} for **3a** and 3288 cm^{-1} for **4a**. The FT-IR spectra of the metal-free (**3a** and **4a**) and zinc (II) (**3b** and **4b**) Pcs are very similar, except the ν(NH) vibrations of the inner Pc core in the metal-free molecule. The ^{1}H NMR spectra of complexes showed ring protons between 7.66 and 7.32 ppm for **3a**, 7.60 and 7.43 ppm for **3b**, 7.63 and 7.38 ppm for **4a** and 7.68 and 7.45 ppm for **4b** as multiplets. The NH protons of complexes **3a** and **4a** could not be observed owing to the probable strong aggregation of the molecules. Etheric (–OCH_2CH_2O–) protons were observed between 4.37 and 3.62 ppm for **3a**, 4.42 and 3.71 ppm for **3b**, 4.34 and 3.65 ppm for **4a** and 4.45 and 3.78 ppm for **4b** as multiplets. The MALDI-TOF mass spectra of Pcs (**3a**–**b** and **4a**–**b**) confirmed the proposed structures; molecular ions were easily identified at m/z: 2042 [M]$^+$, 2065 [M+Na]$^+$ for **3a** (Fig. 1) and **4a**, at m/z: 2105 [M]$^+$, 2065 [M+Na]$^+$ for **3b** and **4b**. The elemental analyses for complexes **3a**–**b** and **4a**–**b** gave satisfactory results that were close to calculated values.

3.2. Electronic absorption spectra

The electronic spectra of the peripherally and non-peripherally tetra-substituted Pc complexes (**3a**–**b**, **4a**–**b**) showed characteristic Q band absorptions in $CHCl_3$. The π–π^* transitions for Q band absorptions were observed at 665, 700 (**3a**), 675 (**3b**), 684, 717 (**4a**) and 692, 736 nm (**4b**) (Fig. 2) in $CHCl_3$. The substitution of the crown ether and coumarin substituents on the Pc ring increased the wavelength of the Q band compared to unsubstituted zinc (II) Pc. The Q bands of the non-peripherally metal-free (**4a**) and zinc (II) (**4b**) Pc complexes were red-shifted 19, 17 nm (between **3a** and **4a**) and 17 nm (between **3b** and **4b**) compared to the peripherally metal-free (**3a**) and zinc (II) (**3b**) Pc complexes in $CHCl_3$ (Fig. 2). The observed red spectral shifts are typical of Pcs with substituents at the non-peripheral positions and have been explained [44,45] 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 (Soret) bands of these complexes exist at 341 nm for **3a**, 342 nm for **3b**, 339 nm for **4a** and 337 nm for **4b**.

The aggregation behaviour of the Pc complexes (**3a**–**b**, **4a**–**b**) was investigated at different concentrations in DMSO (Fig. 3 for complex **3b**). In DMSO, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands due to the aggregated species for zinc (II) Pc complexes (**3b** and **4b**). Beer–Lambert law was obeyed for all Pc complexes in the concentrations ranging from 1.2×10^{-5} to 2×10^{-6} M. While metal-free Pc complexes (**3a** and **4a**) showed doublet Q bands in $CHCl_3$, they showed a Q band around 665 nm together with a

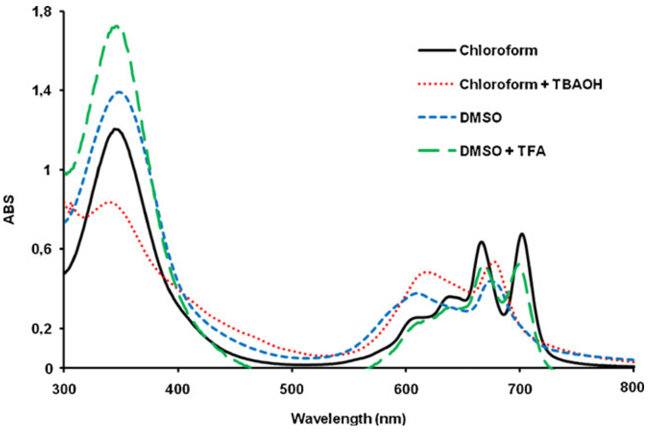


Fig. 4. Absorption spectra of **3a** in $CHCl_3$, DMSO, the addition of TBAOH in $CHCl_3$ solution and the addition of TFA in DMSO solution (concentration: 12×10^{-6} M).

blue shifted band around 600 nm in DMSO (Fig. 4 for complex **3a**). Firstly, we thought that this corruption could be due to the aggregation of the Pc molecules. Triton X-100, which is a surfactant for reducing of aggregation, was added to the metal-free Pc solutions, but any changes were not observed after addition of triton X-100. Metal-free Pcs contain four pyrolle nitrogen atoms, all of which theoretically capable of undergoing protonation/deprotonation reactions [46]. We thought that this modification could be due to the deprotonation of the pyrolle nitrogens in the Pc core due to basic nature of using solvent (DMSO, solvent basicity: 0.647 [47]). TBAOH which is an organic base was also used for proving of the deprotonation phenomenon. The metal-free Pcs showed Q band around 665 nm together with a blue shifted band around 600 nm after addition of TBAOH in $CHCl_3$ solution, resulting completely deprotonation of the pyrolle nitrogens in the Pc core (Fig. 4 for complex **3a**). The protonation of the pyrolle nitrogens in the Pc core by the addition of the TFA caused doublet Q bands in DMSO (Fig. 4 for complex **3a**).

Generally in metallo Pc complexes, the peak due to aggregation is blue shifted with respect to the monomer (called H-type aggregation). However, a less common type of aggregation in solution (called J-type aggregation) results in a red-shifted peak [48]. While complex **4b** showed a single Q band in DMSO and THF, it showed a new peak at 736 nm in $CHCl_3$ and CH_2Cl_2 (Fig. 5). The peak at 736 nm is not due to aggregation. We suggest that this new peak is a result of the splitting in the Q band due to lowering in symmetry observed [49] because of the protonation. In solvents which contain small amounts of acid such as dichloromethane and chloroform (which contain small amount of HCl), protonation of the inner nitrogen atoms may occur forming protonated metallo Pc derivatives which are of lower symmetry than the parent metallo Pc molecule, hence the Q band is split [50,51]. The split is not observed in DMSO which is basic and THF which is neither acidic nor basic. **4b** showed a single Q band after addition of TBAOH in $CHCl_3$ solution, resulting completely deprotonation of the nitrogen atoms in the Pc core (Fig. 6). **4b** also showed a single Q band in $CHCl_3$ which is neutralized with basic Al_2O_3 (Fig. 6). Complex **4b** contains electron donating groups at the alpha position, hence close to the nitrogen atoms, making the latter more basic than for **3b**, so protonation occurs in **4b** but not in **3b**. There is no change in the electronic spectra of the metal-free Pcs (**3a** and **4a**) in $CHCl_3$. The strong coordinating ability of zinc atom to the inner nitrogen atoms causes the outer nitrogen atoms more basic than inner nitrogen atoms. So protonation occurs easily in $CHCl_3$ for non-peripherally substituted zinc (II) Pc (**4b**).

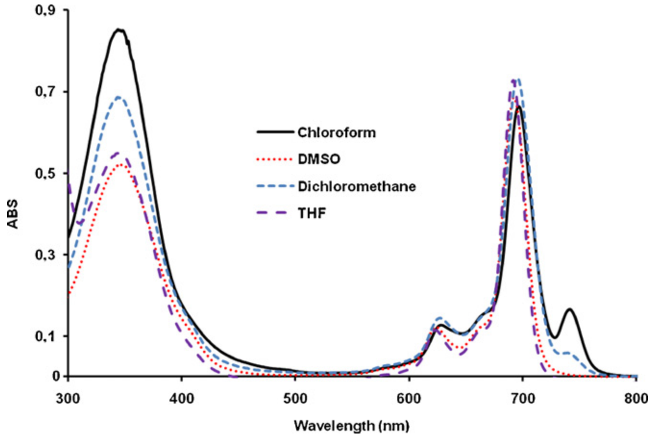


Fig. 5. Absorption spectra of **4b** in $CHCl_3$, CH_2Cl_2, THF and DMSO (concentration: 1×10^{-5} M).

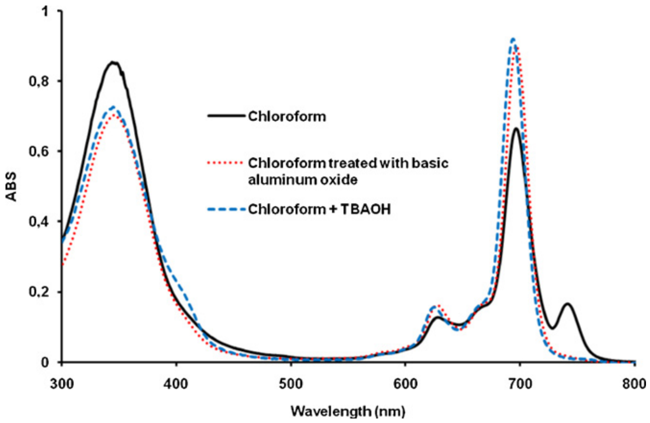


Fig. 6. Absorption spectra of **4b** in $CHCl_3$, $CHCl_3$ treated with basic Al_2O_3 and the addition of TBAOH in $CHCl_3$ solution (concentration: 1×10^{-5} M).

3.3. Fluorescence spectra, fluorescence quantum yields and lifetimes

Fig. 7 (as an example for complex **4a**) shows the fluorescence emission and excitation spectra for the metal-free Pc complexes in DMSO and $CHCl_3$ (concentration = 2×10^{-6} M). While the excitation spectra of **3a** and **4a** showed splitting Q band in $CHCl_3$ (Fig. 7A), they showed non-splitting Q band in DMSO (Fig. 7B) due to the deprotonation of inner nitrogen protons on the phthalocyanine core in DMSO. Fluorescence emission peaks were observed at 709 nm for **3a** and 719 nm for **4a** (Table 1). Zinc (II) Pc complexes (**3b** and **4b**) showed excitation spectra in DMSO which were similar to absorp-

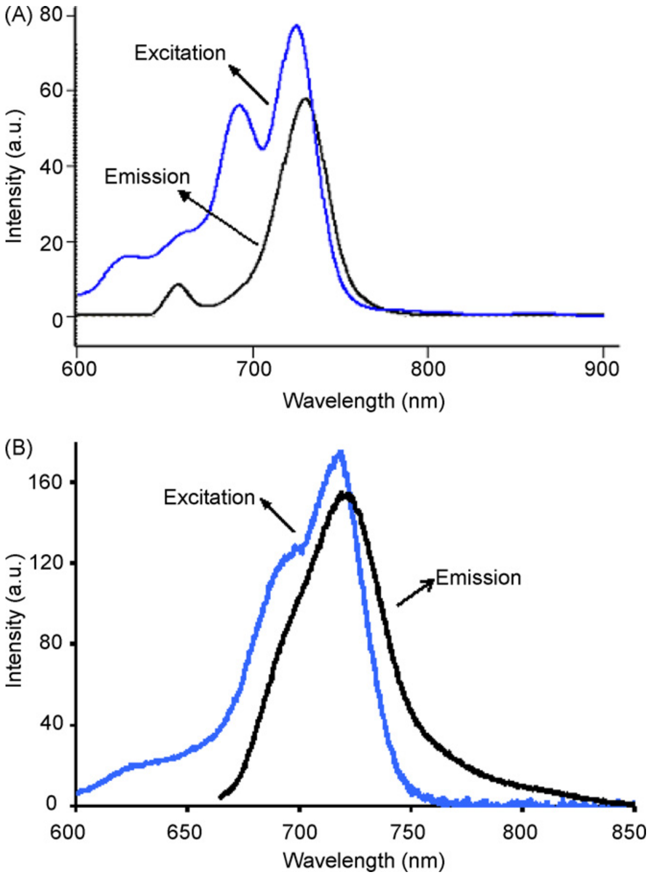


Fig. 7. Excitation and emission spectra of complex **4a**: (A) in $CHCl_3$ and (B) in DMSO (concentration: 2×10^{-6} M). Excitation wavelength = 657 nm.

Table 1
Absorption, excitation and emission spectral data for peripherally and non-peripherally substituted metal-free and zinc (II) Pcs in DMSO.

Compound	Q band λ_{max} (nm)	log ε	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift Δ_{Stokes} (nm)
3a	674, 702	4.11, 4.11	674, 703	709	7
3b	681	5.05	682	692	11
4a	693, 716	4.63, 4.67	694, 717	719	3
4b	697	5.15	698	709	12
ZnPc[a]	672	5.14	672	682	10

[a] Data from Ref. [52].

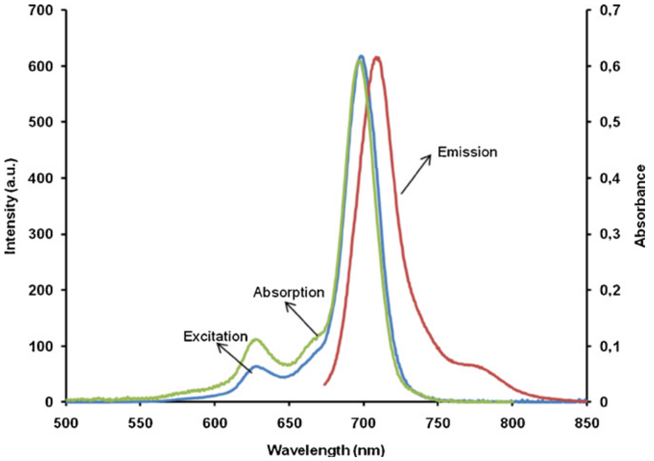


Fig. 8. Absorption, excitation and emission spectra of complex **4b** in DMSO (concentration: 2×10^{-6} M). Excitation wavelength = 674 nm.

tion spectra with both being mirror images of emission (Fig. 8 as an example for complex **4b**). The proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for all complexes suggests that the nuclear configurations of the ground and excited states were similar and not affected by excitation in DMSO. Fluorescence emission peaks were observed at 692 nm for **3b** and 709 nm for **4b** in DMSO (Table 1). The observed Stokes shifts (Table 1) are typical of Pc complexes in DMSO.

The fluorescence quantum yield (Φ_F) values for the complexes were found to range from 0.09 to 0.15, with complex **3b** having the highest quantum yield, Table 2. The Φ_F values of all studied Pc complexes are lower than unsubstituted zinc (II) Pc in DMSO. The Φ_F values of the zinc (II) Pc complexes (**3b** and **4b**) are higher than for metal-free Pc complexes (**3a** and **6a**). The error in the determination of Φ_F was ~10% (determined from several Φ_F values).

Lifetimes of fluorescence (τ_F) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been [35] found for the experimentally and theoretically determined fluorescence lifetimes in this work for Pc complexes in DMSO. Thus, we suggest that the values which were obtained using this equation are a good measure of fluorescence lifetimes. Complexes **3a** and **3b** showed highest lifetime of fluorescence among the studied Pc complexes, Table 2. τ_F values were longer for peripheral Pc complexes (1.53 for **3a** and 1.78 for **3b**) when compared to unsubstituted zinc (II) Pc (1.22) in DMSO. The τ_F values of the zinc (II) Pc complexes (**3b** and **4b**) were longer than for metal-free Pc complexes (**3a** and **4a**). The natural radiative lifetime (τ_0) values of all substituted Pc complexes (**3a**, **3b**, **4a** and **4b**) were longer when compared to unsubstituted zinc (II) Pc in DMSO. The τ_0 values of metal-free Pc complexes (**3a** and **4a**) were also longer when compared to zinc (II) Pc complexes (**3b** and **4b**) in DMSO and complex **3a** showed highest natural radiative lifetime. Also the peripheral Pc complexes (**3a** and **3b**) show higher natural radiative lifetime (τ_0) values compared to the non-peripheral Pc complexes (**4a** and **4b**). The rate constant for fluorescence (k_F) value for complex **4b** showed highest and k_F values for all substituted Pc complexes (**3a**, **3b**, **4a** and **4b**) were lower than unsubstituted zinc (II) Pc in DMSO.

3.4. Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using a chemical method using DPBF as a quencher. The disappearance of DPBF absorption was monitored using UV–vis spectrophotometer. Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen including; triplet excited state energy, ability of substituents and solvents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen. There was no change in the Q band intensity during the Φ_Δ determinations, confirming that complexes were not degraded during singlet oxygen studies (Fig. 9 as an example for complex **4b**). The Φ_Δ value of non-peripheral zinc (II) complex (0.80, **4b**) was higher when compared to unsubstituted zinc (II) Pc (0.67) in DMSO. The Φ_Δ values of zinc (II) Pc complexes (**3b** and **4b**) were higher when compared to metal-free Pc complexes (**3a** and **4a**) in DMSO, suggesting that closed shell d^{10} configuration and the heavy atom effect of the zinc as central metal in the Pc complexes. Zinc (II) Pcs (**3b** and **4b**) gave good singlet oxygen quantum yields (Φ_Δ) (0.51 for **3b** and 0.80 for **4b**, respectively, Table 2) which are indicating the potential of the complexes as photosensitizers in applications of PDT.

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

Table 2
Photophysical and photochemical parameters of peripherally and non-peripherally substituted metal-free and zinc (II) Pcs in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	k_F[a] (ns)	Φ_d ($\times 10^{-5}$)	Φ_Δ	K_{SV} (M^{-1})	$k_q/10^{10}$ ($M^{-1}\,s^{-1}$)
3a	0.09	1.53	17.00	0.06	0.7	0.18	16.11	1.05
3b	0.15	1.78	11.87	0.08	1.0	0.51	18.32	1.03
4a	0.08	0.93	11.46	0.09	0.8	0.11	15.27	1.65
4b	0.12	1.19	10.53	0.10	1.0	0.80	19.46	1.64
ZnPc[b]	0.20	1.22	6.80	14.70	2.6	0.67	31.90	2.61

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Data from Ref. [52].

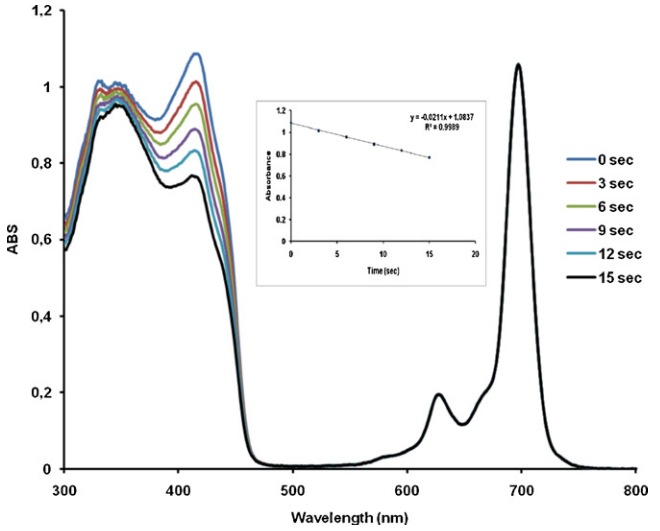


Fig. 9. A typical spectra for the determination of singlet oxygen quantum yield. This determination was for complex **4b** in DMSO at a concentration of 1 × 10^{-5} M (inset: Plot of DPBF absorbance versus time).

clean photodegradation not associated with phototransformation. The spectral changes observed for all the studied Pc complexes (**3a**, **3b**, **4a** and **4b**) during confirmed photodegradation occurred without phototransformation.

The photodegradation quantum yield (Φ_d) values of the Pc complexes (**3a**, **3b**, **4a** and **4b**) in DMSO are given in Table 2. Table 2 shows that all substituted complexes (**3a**, **3b**, **4a** and **4b**) were more stable to degradation compared to unsubstituted zinc (II) Pc in DMSO. Thus, the substitution of Pc with crown ether bearing coumarin groups seems to increase the stability of the complexes in DMSO.

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

The fluorescence quenching of Pc complexes by 1,4-benzoquinone (BQ) in DMSO was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 10 shows the quenching of zinc (II) Pc complex (**4b**) by BQ in DMSO as an example. The slope of the plots shown in Fig. 11 gave K_{SV} values, listed in Table 2. The K_{SV} values of the substituted Pc complexes (**3a**, **3b**, **4a** and **4b**) were lower than unsubstituted zinc (II) Pc in DMSO. The K_{SV} values of zinc (II) Pc complexes (**3b** and **4b**) were higher when compared to metal-free Pc complexes (**3a** and **4a**). The substitution with crown ether bearing coumarin groups seems to decrease the K_{SV} values of the complexes in DMSO suggesting that the steric effect of the substituents. The bimolecular quenching constant (k_q) values of the substituted Pc complexes (**3a**, **3b**, **4a** and **4b**) were lower than for unsubstituted zinc (II) Pc in DMSO, thus substitution with crown ether bearing coumarin groups seems to decrease the k_q values of the complexes. Also the non-peripheral Pc complexes (**4a** and **4b**) showed higher k_q values compared to the peripheral Pc complexes (**3a** and **3b**).

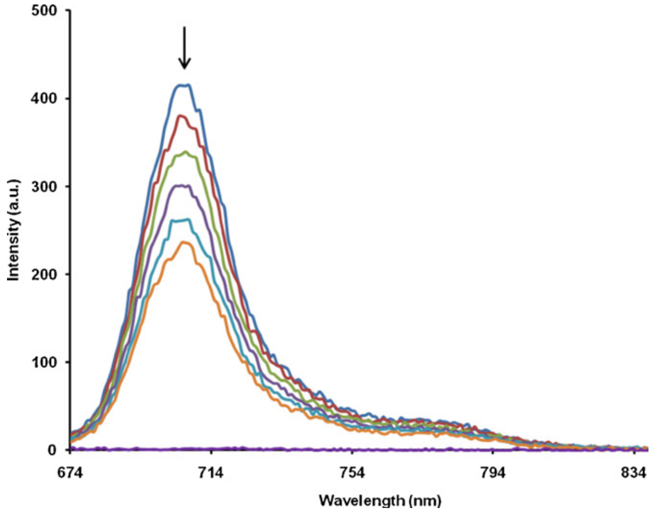


Fig. 10. Fluorescence emission spectral changes of **4b** (concentration: 1 × 10^{-5} M) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

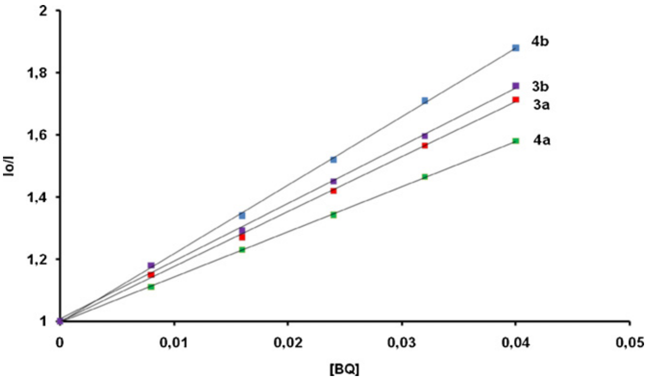


Fig. 11. Stern–Volmer plots for 1,4-benzoquinone (BQ) quenching of metal-free and zinc (II) Pc complexes (**3a**, **3b**, **4a** and **4b**). [MPc]: 1 × 10^{-5} M, [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M in DMSO.

4. Conclusion

In conclusion, we have prepared and characterized new metal-free and zinc (II) Pcs tetra-substituted at the peripheral (complexes **3a** and **3b**) and non-peripheral (complexes **4a** and **4b**) positions with 7,8-(12-crown-4)-3-(4-oxyphenyl)coumarin groups. The spectroscopic, photophysical and photochemical properties of Pc complexes (**3a**–**b**, **4a**–**b**) were also described. While metal-free Pc complexes (**3a** and **4a**) showed doublet Q bands in $CHCl_3$, they showed no splitting Q band due to the deprotonation of the pyrolle nitrogens in the Pc core due to basic nature of DMSO. On the other hand, while the absorption spectra of **4b** showed monomeric behaviour evidenced by a single (narrow) Q band in DMSO and THF, it showed a new peak at 736 nm in $CHCl_3$ and CH_2Cl_2. The red-shifted and split Q band of **4b** in $CHCl_3$ and CH_2Cl_2 due to lowering in symmetry observed because of the protonation. The singlet oxygen quantum yields, which give indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.11 to 0.80. Thus, these complexes show potential as Type II photosensitizers and can be used in photodynamic therapy. Substitution of Pc complexes with crown ether bearing coumarin groups seems to increase the stability of the complexes in DMSO. The fluorescences of the substituted Pc complexes are effectively quenched by 1,4-benzoquinone (BQ). The substituted complexes showed lower K_{SV} values when compared to the unsubstituted zinc (II) Pc in DMSO.

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