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Synthesis, photophysical, photochemical and electrochemical properties of crown ether bearing coumarin substituted phthalocyanines

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ABSTRACT

Zinc (II), cobalt (II) and copper (II) phthalocyanines substituted at the peripheral (complexes **5**, **6** and **7**) and non-peripheral (complexes **8**, **9** and **10**) positions with 7,8-(15-crown-5)-3-(4-oxyphenyl)coumarin groups have been prepared and characterized. The photophysical and photochemical properties of zinc (II) Pc complexes (**5** and **8**) were also described. The singlet oxygen quantum yields (0.54 for **5**, 0.65 for **8**) are indicating the potential of the complexes as photosensitizers in applications of PDT. The redox processes of the complexes were identified by voltammetry and *in situ* spectroelectrochemistry. Alpha and beta-substituted complexes displayed metal- and/or phthalocyanine ring-based redox processes. It was found that the kind of substitution affects the redox processes of the phthalocyanine complexes considerably, due to the difference in their aggregation behaviors.

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1. Introduction

Phthalocyanines (Pcs) are planar aromatic macrocycles consisting of four isoindole units presenting an 18π -electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms [1]. Pcs have been an important class of dyes and pigments since their first synthesis early in the last century [2]. Other areas of current interest include applications in catalysis [3], chemical sensors [4], electrochromism [5], photodynamic therapy (PDT) [6], nonlinear optical (NLO) materials [7] and liquid crystals [8] as a result of newly synthesized compounds [9].

Coumarin (2H-1-benzopyran-2-one) is the simplest naturally occurring phenolic substance possessing fused benzene and α -pyrone rings. The coumarin derivatives exist in a variety of forms, due to the various substitutions possible in their basic structure, which modulate their biological activities [10,11]. Coumarins possess anti-inflammatory [12], antioxidant [13], antithrombotic [14], antiviral [15], antimicrobial [16] and anti-carcinogenic [17] properties. Coumarins exhibit large Stokes shifts, which prevent the overlap between the excitation and emission spectra, and they usually have excellent fluorescence quantum yields [18]. Another interesting group of compounds used as biological models are crown ethers. Crown-ether derivatives bearing coumarin chromophores have been extensively studied as fluorescent metal indicators, especially for alkaline and alkaline-earth metal ions [18]. Crown ether containing Pcs have been shown to possess a combination of three very useful properties [19], namely, they have an extended π -conjugated core which plays a key role in the charge transfer properties of stacked Pcs, they contain crown ethers which can host alkaline ions and they possess alkyl side chains which can induce liquid crystalline behavior. Furthermore, crown ethersubstituted Pcs can be stacked to create ion-conducting channels [20-22]. 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 multifunctional properties have 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 [23,24].

MPc complexes have been proved as highly promising photosensitizers for PDT due to their intense absorption in the red region of the visible light. High triplet state quantum yields and long triplet lifetimes are required for efficient sensitization of them. The photophysical properties of the Pc dyes are strongly influenced by the presence and nature of the central metal ion. Complexes of Pc with transition metals give short triplet lifetimes to these dyes. Closed shell and diamagnetic ions, such as Zn^{2+} , Al^{3+} and Si^{4+} , give Pc complexes with both high triplet yields and long



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lifetimes and they are good candidate for photocatalytic reactions such as PDT [25–28].

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, photochemical and electrochemical properties of Zn(II), Co(II) and Cu(II) Pcs. The main feature of the crown ether groups is that they can hold the alkali cations within their cavity. Crown ether groups have been preferred as substituent on the Pc ring because they can penetrate easily into the cell. The photophysical (fluorescence lifetime and guantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties were investigated only on the Zn(II) Pc complexes. Other studied Co(II) and Cu(II) Pc complexes exhibited weak photophysical and photochemical properties due to the transition metal nature of Co(II) and Cu(II) atoms. This work also explores the effects of ring substitutions and position on the fluorescence auenching of zinc(II) Pcs by 1.4-benzoquinone (BO) 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 [29]. The understanding of the redox properties of the Pc complexes is important in terms of their applications in many areas. The redox or electron transfer processes of these complexes occur at either the Pc ring or the metal center. However, it is not possible to distinguish such processes by voltammetry alone. In situ spectroelectrochemistry provide additional support for the assignment of these redox processes. Moreover, spectroelectrochemical studies of Pcs are also important in identifying the effect of aggregation-disaggregation equilibrium of Pcs on their redox behavior. Therefore, we also investigate the electrochemical and in situ spectroelectrochemical behavior of the synthesized Pc complexes.

2. Experimental

2.1. Materials and equipment

Unsubstituted zinc (II) phthalocyanine (ZnPc), 1,3-diphenylisobenzofuran (DPBF), tetrabutylammonium hydroxide (TBAOH) and 2,3,4-trihydroxybenzaldehyde were purchased from Aldrich. Zinc (II) acetate, cobalt (II) acetate, copper (II) acetate, sodium carbonate (Na₂CO₃), sodium acetate (NaOAc) and tetraethylene glycol ditosylate were purchased from Fluka. All solvents were dried as described by Perrin and Armarego [30] before use. p-(2',3'-Dicyanophenoxy)phenylacetic acid [31], 7,8-dihydroxy-3-[p-(3',4'dicyanophenoxy)phenyl]coumarin (1) [32] and 7,8-dihydroxy-3-[p-(2',3'-dicyanophenoxy)phenyl]coumarin (2) [33] were synthesized and purified according to literature procedures.

Infrared spectra (IR) 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. ¹H 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/cm³ in THF) as matrix. MALDI samples were prepared by mixing the complex (0.02 g/cm³ in DMF) with the matrix solution (1:10 v/v) in a 0.5 cm^3 Eppendorf micro tube. Finally, 1×10^{-3} cm³ 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.

The cyclic and differential pulse voltammetry measurements were carried out with a PAR VersoStat II Model potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt plate with a surface area of 0.10 cm². The surface of the working electrode was polished with H₂O suspension of Al₂O₃ before each run. The last polishing was done with a particle size of 50 nm of Al₂O₃. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.10 moldm⁻³. High purity N₂ was used for deoxygenating the solution at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. In situ spectroelectrochemical measurements were carried out by an Agilent Model 8453 diode array spectrophotometer equipped with the potentiostat/ galvanostat and utilizing an optically transparent thin layer cell with three-electrode configuration at 25 °C. The working electrode was transparent Pt gauze. Pt wire counter electrode and a SCE reference electrode separated from the bulk of the solution by a double bridge were used.

2.2. Synthesis

2.2.1. Generel procedure for the synthesis of phthalonitriles $({f 3} \mbox{ and } {f 4})$

A mixture of 7,8-dihydroxy-3-[p-(3',4'-dicyanophenoxy) phenyl]coumarin (1) or 7,8-dihydroxy-3-[p-(2',3'-dicyanophenoxy)phenyl]coumarin (2) (1.00 g, 2.52 mmol), tetraethylene glycol ditosylate (1.269 g, 2.52 mmol) and anhydrous Na₂CO₃ (0.535 g, 5.05 mmol) in acetonitrile (CH₃CN) (100 ml) was heated to reflux for 5 days under nitrogen atmosphere. After the removal of solution by distillation, the precipitate was dissolved in chloroform (CHCl₃), washed with water and dried on Na₂SO₄. The crude products were purified by column chromatography on silica gel with CHCl₃ as eluent.

2.2.1.1. 7,8-(15-Crown-5)-3-[p-(3',4'-dicyanophenoxy)phenyl]coumarin (**3**). Yield: 0.509 g (37%). M.p.: 185 °C. FT-IR (KBr), v_{max} /(cm⁻¹): 3085–3050 (Ar–CH), 2950-2885 (aliphatic –CH), 2225 (C \equiv N), 1720 (C=O, lactone), 1605 (C=C), 1578–1450 (Ar C=C), 1295–1245 (Ar–O–Ar), 1184-1112 (Ar–O–C). ¹H NMR (CDCl₃, 500 MHz): 7.85 (s, 1H, coumarin 4-H), 7.82 (dd, J = 8 and 2 Hz, 2H, Ar–H), 7.79 (d, J = 8 Hz, 1H, Ar–H), 7.39 (d, J = 2 Hz, 1H, Ar–H), 7.35 (dd, J = 8 and 2 Hz, 2H, Ar–H), 7.79 (d, J = 8 Hz, 1H, Ar–H), 6.93 (d, J = 8 Hz, 1H, Ar–H), 7.18 (dd, J = 8 and 2 Hz, 2H, Ar–H), 6.93 (d, J = 8 Hz, 1H, Ar–H), 4.44 (t, J = 6 Hz, 2H, –OCH₂), 4.29 (t, J = 6 Hz, 2H, –OCH₂), 4.04–4.01 (m, 4H, –OC(CH₂)₂), 3.83–3.78 (m, 8H, –OCCO(CH₂)₂O(CH₂)₂). UV–Vis (CHCl₃) λ_{max} (nm) (log ε): 341 (4.03). MS (MALDI-TOF); calc. for C₃₁H₂₆N₂O₈: m/z 554 [M]⁺, found: *m*/z 577 [M+Na]⁺. *Anal.* Calc. for C₃₁H₂₆N₂O₈: C, 67.15; H, 4.69; N, 5.05. Found: C, 67.18; H, 4.65; N, 5.07%.

2.2.1.2. 7,8-(15-Crown-5)-3-[p-(2',3'-dicyanophenoxy)phenyl]coumarin (**4**). Yield: 0.340 g (24%). M.p.: 170 °C. FT-IR (KBr), v_{max} /(cm⁻¹): 3070–3052 (Ar–CH), 2915-2870 (aliphatic –CH), 2230 (C \equiv N), 1718 (C \equiv O, lactone), 1606 (C \equiv C), 1507–1457 (Ar C \equiv C), 1292-272 (Ar–O–Ar), 1119–1074 (Ar–O–C). ¹H NMR (CDCl₃, 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), 7.27 (d, J = 8 Hz, 1H, Ar–H), 7.20 (dd, J = 8 and 2 Hz, 2H, Ar–H), 6.93 (d, J = 8 Hz, 1H, Ar–H), 4.43 (t, J = 6 Hz, 2H, –OCH₂), 4.29 (t, J = 6 Hz, 2H, –OCH₂), 4.04–4.01 (m, 4H, –OC(CH₂)₂), 3.83–3.78 (m, 8H, –OCCO(CH₂)₂O(CH₂)₂). UV–Vis (CHCl₃) λ_{max} (nm) (log ε): 340 (4.06). MS (MALDI-TOF); calc. for $C_{31}H_{26}N_2O_8$: m/z 554 [M]⁺, found: m/z 577 [M+Na]⁺. *Anal.* Calc. for $C_{31}H_{26}N_2O_8$: C, 67.15; H, 4.69; N, 5.05. Found: C, 67.20; H, 4.73; N, 5.07%.

2.2.2. General procedure for the metallo phthalocyanines (5-7, 8-10)

A mixture of **3** or **4** (0.100 g, 0.181 mmol) and metal salt [Zn(A-cO)₂·2H₂O (0.010 g, 0.045 mmol), Co(AcO)₂.4H₂O (0.012 g, 0.048 mmol) and Cu(AcO)₂ (0.009 g, 0.049 mmol] in dry 2-dimethylaminoethanol (DMAE) (1.5 ml) was refluxed with stirring for 24 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 products were purified by column chromatography on silica gel with CHCl₃ as eluent.

2.2.2.1. 2(3),9(10),16(17),23(24)-Tetra[7,8-(15-crown-5)-3-(4-oxyphenyl)coumarin]-phthalocyaninato zinc (II) (**5**). Yield: 0.089 g (86%). M.p. >300 °C. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3078–3036 (Ar-CH), 2925–2863 (aliphatic CH), 1719 (C=O, lactone), 1605 (C=C), 1508–1463 (Ar C=C), 1291–1233 (Ar–O–Ar), 1122–1077 (Ar–O–C). ¹H NMR (CDCl₃, 500 MHz): 7.83–7.59 (m, 40H, Ar–H), 4.40–3.75 (m, 64H, –OCH₂). UV–Vis λ_{max} (DMSO) (nm) (log ε): 355 (5.25), 619 (shoulder, 4.55), 681 (5.07). MS (MALDI-TOF, DHB as matrix); calc. for C₁₂₄H₁₀₄N₈O₃₂Zn: *m*/*z* 2281 [M]⁺, found: *m*/*z* 2281 [M]⁺, 2304 [M+Na]⁺. Anal. Calc. for C₁₂₄H₁₀₄N₈O₃₂Zn: C, 65.23; H, 4.56; N, 4.91. Found: C, 65.28; H, 4.61; N, 4.85%.

2.2.2.2. 2(3),9(10),16(17),23(24)-Tetra[7,8-(15-crown-5)-3-(4-oxyphenyl)coumarin]-phthalocyaninato cobalt (II) (**6**). Yield: 0.063 g (61%). M.p. >300 °C. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3085–3050 (Ar-CH), 2958–2874 (aliphatic CH), 1720 (C=O, lactone), 1601 (C=C), 1512–1465 (Ar C=C), 1295–1240 (Ar–O–Ar), 1120–1040 (Ar–O–C). UV–Vis λ_{max} (DMSO) (nm) (log ε): 339 (4.95), 595 (shoulder, 4.14), 665 (4.76). MS (MALDI-TOF, DHB as matrix); calc. for C₁₂₄H₁₀₄N₈O₃₂Co: m/z 2275 [M]⁺, found: m/z 2275 [M]⁺, 2298 [M+Na]⁺. Anal. Calc. for C₁₂₄H₁₀₄N₈O₃₂Co: C, 65.41; H, 4.57; N, 4.92. Found: C, 65.48; H, 4.54; N, 4.96%.

2.2.2.3. 2(3),9(10),16(17),23(24)-Tetra[7,8-(15-crown-5)-3-(4-oxyphenyl)coumarin]-phthalocyaninato copper (II) (**7**). Yield: 0.063 g (61%). M.p. >300 °C. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3080–3065 (Ar-CH), 2960–2848 (aliphatic CH), 1722 (C=O, lactone), 1601 (C=C), 1510–1445 (Ar C=C), 1295–1238 (Ar–O–Ar), 1120–1040 (Ar–O–C). UV–Vis λ_{max} (DMSO) (nm) (log ε): 341 (4.99), 603 (shoulder, 4.24), 673 (4.64). MS (MALDI-TOF, DHB as matrix); calc. for C₁₂₄H₁₀₄N₈O₃₂Cu: *m/z* 2280 [M]⁺, found: *m/z* 2280 [M]⁺, 2303 [M+Na]⁺, 2319 [M+K]⁺. Anal. Calc. for C₁₂₄H₁₀₄N₈O₃₂Cu: C, 65.26; H, 4.56; N, 4.91. Found: C, 65.23; H, 4.60; N, 4.95%.

2.2.2.4. 1(4),8(11),15(18),22(25)-Tetra[7,8-(15-crown-5)-3-(4-oxy-phenyl)coumarin]-phthalocyaninato zinc (II) (**8**). Yield: 0.057 g (55%). M.p. >300 °C. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3068–3053 (Ar-CH), 2915–2863 (aliphatic CH), 1719 (C=O, lactone), 1606 (C=C), 1507–1479 (Ar C=C), 1292–1244 (Ar–O–Ar), 1122–1076 (Ar–O–C). ¹H NMR (CDCl₃, 500 MHz): 7.78–7.60 (m, 40H, Ar–H), 4.43-3.81 (m, 64H, –OCH₂). UV–Vis λ_{max} (DMSO) (nm) (log ε): 352 (5.19), 632 (shoulder, 4.52), 697 (5.22). MS (MALDI-TOF, DHB as matrix); calc. for C₁₂₄H₁₀₄N₈O₃₂Zn: m/z 2281 [M]⁺, found: m/z 2281 [M]⁺, 2304 [M+Na]⁺. Anal. Calc. for C₁₂₄H₁₀₄N₈O₃₂Zn: C, 65.23; H, 4.56; N, 4.91. Found: C, 65.28; H, 4.59; N, 4.95%.

2.2.2.5. 1(4),8(11),15(18),22(25)-Tetra[7,8-(15-crown-5)-3-(4-oxy-phenyl)coumarin]-phthalocyaninato cobalt (II) (**9**). Yield: 0.076 g (74%). M.p. >300 °C. FT-IR (KBr), v_{max}/(cm⁻¹): 3065–3048 (Ar–CH), 2948–2868 (aliphatic CH), 1718 (C=O, lactone), 1608 (C=C),

1508–1478 (Ar C=C), 1292–1247 (Ar–O–Ar), 1122–1076 (Ar–O–C). UV–Vis λ_{max} (DMSO) (nm) (log ε): 336 (4.76), 604 (shoulder, 3.82), 676 (4.51). MS (MALDI-TOF, DHB as matrix); calc. for C₁₂₄H₁₀₄N₈O₃₂Co: *m/z* 2275 [M]⁺, found: *m/z* 2275 [M]⁺, 2298 [M+Na]⁺. Anal. Calc. for C₁₂₄H₁₀₄N₈O₃₂Co: C, 65.41; H, 4.57; N, 4.92. Found: C, 65.36; H, 4.51; N, 4.90%.

2.2.2.6. 1(4),8(11),15(18),22(25)-Tetra[7,8-(15-crown-5)-3-(4-oxy-phenyl)coumarin]-phthalocyaninato copper (II) (**10**). Yield: 0.052 g (50%). M.p. >300 °C. FT-IR (KBr), $v_{max}/(cm^{-1})$: 3065–3053 (Ar-CH), 2924–2870 (aliphatic CH), 1719 (C=O, lactone), 1605 (C=C), 1506–1474 (Ar C=C), 1291–1248 (Ar–O–Ar), 1125–1076 (Ar–O–C). UV–Vis λ_{max} (DMSO) (nm) (log ε): 339 (4.92), 615 (shoulder, 3.98), 691 (4.73). MS (MALDI-TOF, DHB as matrix); calc. for C₁₂₄H₁₀₄N₈O₃₂Cu: *m/z* 2280 [M]⁺, found: *m/z* 2280 [M]⁺, 2303 [M+Na]⁺, 2319 [M+K]⁺. Anal. Calc. for C₁₂₄H₁₀₄N₈O₃₂Cu: C, 65.26; H, 4.56; N, 4.91. Found: C, 65.20; H, 4.52; N, 4.86%.

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]:

$$\Phi_F = \Phi_F(\text{Std}) \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2}$$
(1)

where *F* and *F*_{Std} are the areas under the fluorescence emission curves of the samples (**5** and **8**) 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 (Φ_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 (**5** and **8**) were determined as previously explained in detail [38–40]. Typically, 2 cm³ portion of the samples (**5** and **8**) solutions (concentration = 1 × 10⁻⁵ mol dm⁻³) 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):

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

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard ($\Phi_{\Delta}^{\text{Std}} = 0.67$ for unsubstituted ZnPc in DMSO) [41]; *R* and *R*^{Std} are the DPBF photobleaching rates in the presence of the samples (**5** and **8**) and standard, respectively; *I*_{abs} and *I*_{abs}^{Std} are the rates of light absorption by the samples (**5** and **8**) 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 ~3 × 10⁻⁵ moldm⁻³. Solutions of sensitizer containing 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.

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:

$$\Phi_{\rm d} = \frac{C_0 - C_t \cdot V \cdot N_A}{I_{\rm abs} \cdot S \cdot t} \tag{4}$$

where C_0 and C_t are the samples (**5** and **8**) concentrations before and after irradiation, respectively. *V* is the reaction volume; *S* is the irradiated cell area (2.0 cm²); *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 (**5** and **8**) 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 moldm⁻³. The fluorescence spectra of Pc complexes (**5** and **8**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) Eq. (5) [43]:

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

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.

3. Results and discussion

3.1. Synthesis and characterization

The general synthetic routes for the synthesis of new phthalonitriles (3 and 4), Zn(II), Co(II) and Cu(II) Pcs tetra-substituted at the peripheral (complexes 5, 6 and 7) and non-peripheral (complexes 8, 9 and 10) positions are given in Scheme 1. 7,8-Dihydroxy-3-[p-(3',4'-dicyanophenoxy)phenyl]coumarin (1) and 7,8dihydroxy-3-[p-(2',3'-dicyanophenoxy)phenyl]coumarin (2) were reacted with tetraethylene glycol ditosylate giving the crown ethers (3 and 4) in the presence of Na₂CO₃ in CH₃CN. The crude products (3 and 4) were purified by column chromatography on silica gel with CHCl₃ as eluent. The Zn(II), Co(II) and Cu(II) Pcs (5-7 and 8-10) were obtained from the dicyano derivatives (3 and **4**) and metal salts [Zn(AcO)₂·2H₂O, Co(AcO)₂·4H₂O and Cu(AcO)₂, respectively] 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 spectra of **3** and **4** showed vibration peaks for their aliphatic CH stretching frequency at 2950–2885 and 2915–

2870 cm⁻¹, respectively. The characteristic vibration peaks of the nitrile (C \equiv N) and carbonyl groups (C \equiv O, lactone) appeared at 2225, 2230 cm⁻¹ and 1720, 1718 cm⁻¹, respectively. The ¹H NMR spectra of **3** and **4** in CDCl₃ showed characteristic signals for etheric ($-OCH_2CH_2O_-$) protons at 4.44-3.78 ppm for **3** and 4.43–3.78 ppm for **4** indicated the presence the proton of coumarin at position of 4. In addition the chemical shifts of the aromatic protons are observed at 7.82–6.93 ppm for compound **3** and 7.81–6.93 ppm for compound **4**. Molecular ion peaks were easily identified at m/z = 577 [M+Na]⁺ for **3** and **4**.

The sharp vibration for the C \equiv N groups in the FT-IR spectra of phthalonitriles **3** and **4** at 2225 and 2230 cm⁻¹, respectively, disappeared after conversion into metallo Pcs (**5–7** and **8–10**). The ¹H NMR spectra of complexes showed ring protons between 7.83–7.59 ppm for **5** and 7.78–7.60 ppm for **8** as multiplets. Etheric (– OCH₂CH₂O–) protons were observed between 4.40–3.75 ppm for **5** and 4.43–3.81 ppm for **8** as multiplets. The MALDI-TOF mass spectra of Pcs (**5–7** and **8–10**) confirmed the proposed structures; molecular ions were easily indentified at m/z: 2281 [M]⁺ for **5** and **8**, 2275 [M]⁺ for **6** and **9**, 2280 [M]⁺ for **7** and **10**. The elemental analyses for complexes **5–7** and **8–10** 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 (5-7, 8-10) showed characteristic Q band absorptions in DMSO, Fig. 1. The π - π * transitions for Q band absorptions were observed at 681 (5), 665 (6), 679 (7), 697 (8), 676 (9) and 695 nm (10) in DMSO, Table 1. The substitution of the crown ether and coumarin substituents on the Pc ring increased the wavelength of the Q band. The Q bands of the nonperipherally metallo Pc complexes were red-shifted 16 nm (between 5 and 8), 11 nm (between 6 and 9) and 16 nm (between 7 and 10) compared to the peripherally metallo Pc complexes in DMSO (Fig. 1). 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 \sim 20 nm bathochromic shift. The B (Soret) bands of these complexes exist at 355 nm for 5, 339 nm for 6, 341 nm for 7, 352 nm for 8, 336 nm for 9 and 339 nm for 10.

The aggregation behavior of the Pc complexes (**5–7**, **8–10**) was investigated at different concentrations in DMSO. 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. Beer–Lambert law was obeyed for all Pc complexes in the concentrations ranging from 1.2×10^{-5} to 2×10^{-6} moldm⁻³.

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 [46]. While complex **8** showed a single Q band in DMSO and THF, it showed a new peak at 739 nm in CHCl₃ and CH₂Cl₂ (Fig. 2). The peak at 739 nm is not due to aggregation. We suggest that this peak is a result of the splitting in the Q band due to lowering in symmetry observed [47] because of the protonation. In solvents such as dichloromethane and chloroform (which contain small amounts of HCl), protonation of the inner nitrogen atoms may occur forming



Scheme 1. Synthesis route of new phthalonitriles (3 and 4), zinc (II), cobalt (II) and copper (II) Pc complexes (5-7 and 8-10).

protonated metallo Pc derivatives which are of lower symmetry than the parent metallo Pc molecule, hence the Q band is split [48]. The split is not observed in DMSO which is basic and THF which is neither acidic nor basic. **8** showed a single Q band after addition of TBAOH (which is an organic base) in CHCl₃ solution, resulting completely deprotonation of the nitrogen atoms in the Pc core (Fig. 3). **8** also showed a single Q band in CHCl₃ which is neutralized with basic Al₂O₃ (Fig. 3). Complex **8** contains electron donating groups at the alpha position, hence close to the nitrogen atoms, making the latter more basic than for **5**, so protonation occurs in **8** but not in **5**.

3.3. Fluorescence spectra, fluorescence quantum yields and lifetimes

The studied Co(II) (**6** and **9**) and Cu(II) (**7** and **10**) phthalocyanine complexes did not show fluorescence due to the paramagnetic nature of the Co(II) and Cu(II) metals. Fig. 4 shows the absorption, fluorescence emission and excitation spectra for Zn(II) Pc complexes (**5** and **8**) in DMSO (concentration = $2 \times 10^{-6} \text{ mol dm}^{-3}$). Zn(II) Pc complexes (**6** and **9**) showed excitation spectra in DMSO which were similar to absorption spectra with both being mirror images of emission. 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 **5** and 708 nm for **8** 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 be 0.09 for **5** and 0.14 for **8** in DMSO, Table 2. The Φ_F values of Zn(II) Pc complexes (**5** and **8**) are lower than unsubstituted Zn(II) Pc in DMSO. The fluorescence quantum yield (Φ_F) value of non-peripheral Zn(II) Pc complex (**8**) was higher than peripheral Zn(II) Pc complex (**5**).

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



Fig. 1. Absorption spectra of substituted zinc (II), cobalt (II) and copper (II) Pc complexes: (A) 5, 6 and 7, (B) 8, 9 and 10 in DMSO. Concentrations: 1 × 10⁻⁵ moldm⁻³.

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bsorption, excitation and emission spectral data for peripherally and non-peripherally substituted Zn(II), Co(II) and Cu(II) Pcs in DMSO.

Compound	Q band λ_{max} (nm)	$\log \varepsilon$	Excitation λ_{Ex} (nm)	Emission λ_{Em} , (nm)	Stokes shift Δ_{Stokes} , (nm)
5	681	5.07	682	692	11
6	665	4.76	-	-	-
7	679	4.64	-	-	-
8	697	5.22	698	708	11
9	676	4.80	-	-	_
10	695	4.73	-	-	_
ZnPc ^a	672	5.14	672	682	10

^a Data from Ref. [64].

 $\varPhi_{\rm F\!-}$ Such factors include internal conversion and intersystem crossing. As a result, the nature and the environment of a fluorophore

determine its fluorescence lifetime. τ_F values (Table 2) were calculated using the Strickler–Berg equation. Lifetimes of fluorescence



Fig. 2. Absorption spectra of 8 in CHCl₃, CH₂Cl₂, THF and DMSO (concentration: 1×10^{-5} mol dm⁻³).



Fig. 3. Absorption spectra of 8 in CHCl₃, CHCl₃ treated with basic Al₂O₃ and the addition of TBAOH in CHCl₃ solution (concentration: 1 × 10⁻⁵ moldm⁻³).

 (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 for the unaggregated molecules as is the case in this work for **5** and **8** in DMSO. Thus we suggest that the values which obtained using this equation are a good measure of fluorescence lifetimes. The τ_F values of the Zn(II) Pc complexes (**5** and **8**) were lower than unsubstituted Zn(II) Pc complex in DMSO, suggesting more quenching by substitution.

The natural radiative lifetime (τ_0) values of Zn(II) Pc complexes (**5** and **8**) were longer when compared to unsubstituted Zn(II) Pc in DMSO. Also the peripheral Pc complex (**5**) show higher natural radiative lifetime (τ_0) value compared to the non-peripheral Pc complex (**8**). The rate constant for fluorescence (k_F) values for Zn(II) Pc complexes (**5** and **8**) were lower than unsubstituted Zn(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 by 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



Fig. 4. Absorption, excitation and emission spectra of (A) complex **5** (excitation wavelength = 645 nm) and (B) complex **8** (excitation wavelength = 665 nm) in DMSO (concentration: $2 \times 10^{-6} \text{ mol dm}^{-3}$).

Photophysical and photochemical parameters of peripherally and non-peripherally substituted Zn(II) Pcs in DMSO.	ible 2
	notophysical and photochemical parameters of peripherally and non-peripherally substituted Zn(II) Pcs in DMSO.

Compound	$arPsi_F$	$\tau_F(ns)$	τ_0 (ns)	k_{F}^{a} (ns)	$arPsi_d (imes 10^{-5})$	Φ_Δ	$K_{\rm SV}({ m M}^{-1})$	$k_{ m q}/10^{10}~({ m M}^{-1}{ m s}^{-1})$
5	0.09	0.94	10.65	0.10	0.3	0.54	16.91	1.81
8	0.14	1.20	8.92	0.11	1.0	0.65	19.67	1.63
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. [64].

intensity during the Φ_{Δ} determinations, confirming that complexes were not degraded during singlet oxygen studies (Fig. 5 for complex **8**). Zn(II) Pcs (**5** and **8**) gave good singlet oxygen

quantum yields (Φ_{Δ}) (0.54 for **5** and 0.65 for **8**, respectively, Table 2) which are indicating the potential of these complexes as photosensitizers in applications of PDT.



Fig. 5. A typical spectra for the determination of singlet oxygen quantum yield. This determination was for complex **8** in DMSO at a concentration of 1×10^{-5} moldm⁻³. (Inset: plot of DPBF absorbance versus time.)

3.5. Photodegradation studies

Degradation of the molecules under irradiation can be used to study their stability and this is especially important for those molecules intended for use as photocatalysts. The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation to visible region absorbing materials. The spectral changes observed for zinc (II) Pc complexes (**5** and **8**) during confirmed photodegradation occurred without phototransformation. Phthalimide was found to be the photooxidation product following degradation of MPcs according to the literature [49].

The photodegradation quantum yield (Φ_d) values of the Pc complexes (**5** and **8**) in DMSO are given in Table 2. The substituted

Zn(II) Pc complexes (**5** and **8**) were more stable to degradation compared to unsubstituted Zn(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. 6 shows the quenching of non-peripherally substituted Zn(II) Pc complex (**8**) by BQ in DMSO as an example. The slope of the plots for substituted Zn(II) Pc complexes (**5** and **8**) shown in Fig. 6 gave K_{SV} values, listed in Table 2. The K_{SV} values of the



Fig. 6. Fluorescence emission spectral changes of **8** (concentration: $1 \times 10^{-5} \text{ mol dm}^{-3}$) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, and 0.040 mol dm⁻³. (Inset: Stern–Volmer plots for BQ quenching of zinc (II) Pc complexes (**5** and **8**).)

substituted Pc complexes (**5** and **8**) were lower than unsubstituted Zn(II) Pc in DMSO. The substitution with crown ether bearing coumarin groups on the phthalocyanine framework seems to decrease the K_{SV} values of these complexes in DMSO. The bimolecular quenching constant (k_q) values of the substituted Pc complexes (**5** and **8**) were lower than for unsubstituted Zn(II) Pc in DMSO, thus substitution with crown ether bearing coumarin groups seems to decrease the k_q values of the complexes.

3.7. Electrochemistry and in situ spectroelectrochemistry

Voltammetry and *in situ* spectroelectrochemistry of the complexes were carried out in de-aerated DMSO containing TBAP. The voltammetric data of the Pc complexes, including the half-wave redox potential value versus SCE ($E_{1/2}$) and anodic-to-cathodic peak potential separation (ΔE_p) are listed in Table 3. The number of electrons transferred is usually unity for all redox processes. Anyway, in monophthalocyanines, multi-electron processes occurring in one step are not common.

Fig. 7 shows typical cyclic voltammograms of beta- and alphasubstituted ZnPc complexes, **5** and **8** respectively, at 0.100 Vs⁻¹ scan rate in DMSO/TBAP. As shown in Fig. 7A, beta-substituted ZnPc, 5 displays four reduction (R1, R2, R3 and R4) and two oxidation (O1' and O1") couples. It is clear from the well-known electrochemistry of metallophthalocyanines that Zn(II) at the center of Pc core is redox-inactive and thus, these redox couples are Pc ligandbased [50,51]. The redox signals of 5 are remarkably broad. This may be due to the presence of aggregated species. The aggregation of Pc molecules is usually a coplanar association, which results mainly from the π - π ^{*} interactions between the π electron clouds of adjacent Pc macrocycles [52]. Some functionalities such as carboxylic acid, ester or alkylamide groups in Pc molecules may also increase the extent of aggregation, due to additional interactions such as hydrogen bonding. The coumarins can also build aggregation at carboxyl groups. On the other hand, the lactone carbonyl of coumarins can coordinate central metal cations. The presence of both aggregated and nonaggregated Pc species at equilibrium results generally in broadening of the redox signals, due to the differences in the redox potentials of these species. On the contrary of the redox signals of beta-substituted ZnPc, 5, those of alpha-substituted ZnPc, 8 are not broad (Fig. 7B). Thus, the redox signals of 8 are better defined than those of 5, probably due to the absence of aggregated species in TBAP/DMSO in the case of 8. The absence of aggregated species in solution in the case of alpha-substitution should be due to its nonperipheral nature, leading to nonplanarity of the complex.

As shown in Table 3, the redox behavior of beta-substituted CuPc, **7** is similar to that of beta-substituted ZnPc **5**, with small

Table 3	Ta	bl	e	3	
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Vol	tammetric	data	on	Pt in	DMSO	/TBAP	for	5-7,	, 8-	10	J,
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Fig. 7. Cyclic and differential pulse (inset) voltammograms of 5×10^{-4} mol dm⁻³ (A) 5 (B) 9 in TBAP/DMSO.

differences in half-peak potentials, probably resulting from the difference in polarizing power of central metals. The similarity in their redox potentials is also observed for alpha-substituted CuPc, **10** and alpha-substituted ZnPc, **8**. However, similar to the case for **5** and **8**, the comparison of the shape of their redox signals suggested that there is equilibrium between the aggregated and nonaggregated species of beta-substituted CuPc, **7** in TBAP/DMSO while the solution of alpha-substituted CuPc, **10** in TBAP/DMSO does not involve its aggregated species. The redox processes of **7** and **10** are also Pc ligand-based as Cu(II) at the center of Pc core is redox-inactive (Table 3) [50].

Complex		Ring oxida	ations	M ^{II} /M ^{III}	M ^{II} /M ^I	Ring reducti	ons		
5 (β-ZnPc)	$E_{1/2}^{a}$ (V)	0.63	0.56			-0.81	-1.16	-1.42	-1.63
	$\Delta E_{\rm p}^{\rm b}$ (V)	-	0.060			0.060	0.120	0.080	-
8 (α-ZnPc)	$E_{1/2}^{a}$ (V)		0.74			-0.80	-1.26	-1.60	
	$\Delta E_{\rm p}^{\rm b}$ (V)		0.120			0.080	0.060	-	
7 (β-CuPc)	$E_{1/2}^{a}$ (V)	0.65	0.58			-0.79	-1.13	-1.40	-1.60
	$\Delta E_{\rm p}^{\rm b}$ (V)	-	0.060			0.070	0.110	0.090	-
10 (α-CuPc)	$E_{1/2}^{a}$ (V)		0.75			-0.78	-1.24	-1.57	
	$\Delta E_{\rm p}^{\rm b}({\rm V})$		0.100			0.080	0.070	-	
6 (β-CoPc)	${}^{a}E_{1/2}(V)$			0.36	-0.44	-1.06	-1.32	-1.72	
	$\Delta E_{\rm p}^{\rm b}$ (V)			0.080	0.200	-	0.040	-	
9 (α-CoPc)	$E_{1/2}^{a}$ (V)			0.37	-0.40	-1.35	-1.64		
	$\Delta E_{\rm p}^{\ \rm b}({\rm V})$			0.060	0.080	0.060	0.060		

^a $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.050 V s⁻¹.

^b $\Delta E_{\rm p} = E_{\rm pa} + E_{\rm pc}$ at 0.050 V s⁻¹.



Fig. 8. (A) Cyclic voltammograms of 5×10^{-4} mol dm⁻³ **6** in TBAP/DMSO. *In situ* UV–Vis spectral changes during the controlled potential electrolysis of **6** upon (B) the first reduction at -0.70 V vs. SCE, (C) the second reduction at -1.48 V vs. SCE and (D) the first oxidation at 0.55 V vs. SCE in TBAP/DMSO.

Figs. 8A and 9A shows the cyclic and differential pulse voltammograms of beta- and alpha-substituted cobalt(II) Pcs, 6 and 9, respectively, in DMSO/TBAP. The redox potentials of 6 or 9 are considerably different in comparison with those of 5, 7, 8 and 10 (Table 3). The first reduction and the first oxidation of 6 or 9 occur at the potentials much less negative than those of 5, 7, 8 and 10. This difference in the voltammetric behavior is due to the fact that MPcs, such as MnPc, CoPc and FePc, having a metal that possesses energy levels lying between the HOMO and the LUMO of the Pc ligand, in general exhibit redox processes centered on the metal [50,53-57]. For CoPc complexes, the first oxidation and first reduction processes usually occur on the metal center in polar solvents such as DMF and DMSO. However the first oxidation process usually occurs on the Pc ring in nonpolar solvents such as DCM and THF. Therefore, the first reduction (R1) and the first oxidation (O1) processes of **6** or **9** may be assigned to the [Co(II)Pc(-2)]/ $[Co(I)Pc(-2)]^-$ and $[Co(II)Pc(-2)]/[Co(III)Pc(-2)]^+$ redox couples, respectively. The second and the third reduction processes (R2 and R3) of these complexes are probably ligand-based and can be assigned to $[Co(I)Pc(-2)]^{-}/[Co(I)Pc(-3)]^{2-}$ and $[Co(I)Pc(-3)]^{2-}/[Co(I)Pc(-3)]$ $[Co(I)Pc(-4)]^{3-}$, respectively [50]. In the cyclic voltammogram of beta-substituted CoPc, 6, redox signals are remarkably broad (Fig. 8A), suggesting that complex 6 forms aggregated species in DMSO/TBAP. In situ spectroelectrochemical measurements in TBAP/DMSO provided strong support for both the assignment of the redox processes of **6** and the coupling of its electron transfer processes by aggregation-disaggregation equilibrium. Fig. 8B represents in situ UV-Vis spectral changes during the first reduction of 6 at -0.70 V versus SCE corresponding to the redox

process labeled R1. The concentration of the complexes was \sim 5.00 \times 10⁻⁵ moldm⁻³ in DMSO/TBAP for studies in optically transparent thin layer cell. The spectrum at the start of electrolysis indicates the presence of an equilibrium between the aggregated and monomer species, as judged by remarkably broad Q-band absorption. The broad Q-band at 665 nm decreases and nearly disappears, while two new bands at 706 and 474 nm appear. At the same time, the band at 344 nm shifts 332 nm. The red shifting of the Q-band from 665 to 706 nm and the formation of a new band at 474 nm indicate the formation of $[Co(I)Pc(-2)]^{-}$ species, confirming the voltammetric assignment of the couple R1 to $Co(II)Pc(-2)/[Co(I)Pc(-2)]^{-}$ process [58–62]. However, the Q-band obtained after the first reduction process is still broad and the accompanied spectral changes have not well-defined isosbestic points at specific wavelengths. These observations imply that the species obtained upon the reduction of aggregated species probably do not disaggregate after the first reduction process and thus, there is still equilibrium between aggregated and monomeric forms of mono-reduced species. During the second reduction, the O band decreases without shift (Fig. 8C) and the absorption within the range of 500-600 nm increases. These spectral changes at the potential of the couple R2 are characteristic for a ring-based second reduction in Co(II)Pc complex, $[Co(I)Pc(-2)]^{-}/[Co(I)Pc(-3)]^{2-}$. Fig. 8D displays in situ UV-Vis spectral changes during the first oxidation process. The broad Q band at 665 nm increases in intensity with red shift to 675 nm and becomes sharp. At the same time, the B bands decrease. The increase of the Q band with red shift is typical of a metal-based oxidation in CoPc complexes [58-63], and thus confirms the voltammetric assignment of Co(II)Pc(-2)/



Fig. 9. (A) Cyclic and differential pulse (inset) voltammograms of 2.5×10^{-4} mol dm⁻³ **9** in TBAP/DMSO. *In situ* UV–Vis spectral changes during the controlled potential electrolysis of **9** upon (B) the first reduction at -0.60 V vs. SCE and (C) the first oxidation at 0.55 V vs. SCE in TBAP/DMSO.

 $[Co(III)Pc(-2)]^+$ for couple O1 of **6**. In addition, the formation of a sharp Q-band after the first oxidation process implies that monooxidized species are not aggregated, i.e., disaggregation occurs immediately after the oxidation of aggregated species. As shown in Table 3, the first reduction and the first oxidation potentials of beta-substituted CoPc, 6 and alpha-substituted CoPc, 9 are very similar to each other with small shifts. However, Pc ring-based second and third reduction potentials of **9** are more negative than those of 6. On the contrary of the reduction couples of 6, those of **9** are not broad, probably due to the absence of aggregated species (Figs. 8A and 9A). It is known that the shape of the alpha-substituted Pc molecules deviate from planarity, which should be responsible for the absence of aggregated species since aggregation usually results from the π - π ^{*} interactions between the π electron clouds of adjacent Pc macrocycles [52]. Fig. 9B and C displays in situ UV-Vis spectral changes during the first reduction and the first oxidation processes of 9 at suitable potentials, respectively. The spectrum at the start of the electrolysis in Fig. 9B or Fig. 9C indicates the absence of aggregated species, as judged by relatively

sharper Q-absorption band at 680 nm, in comparison with the corresponding one for 6 in Fig. 8B or Fig. 8D. During the first reduction process, the Q-band at 680 nm shifts 692 nm and its shoulder at 614 nm decreases first, and then nearly disappears. At the same time, the absorption between 700 and 756 nm increases with the formation of a shoulder around 716 nm and a new band at 473 nm appears (Fig. 9B). These spectral changes are accompanied by the decrease in the B band at 342 nm and have well-defined isosbestic points at 310, 385, 563 and 701 and 756 nm. The formation of a new band at 473 nm and red shifting of the Q band indicate the formation of $[Co(I)Pc(-2)]^{-}$ species, confirming the CV assignment of the first reduction process, R1 to Co(II)Pc(-2)/ $[Co(I)Pc(-2)]^{-}$ process [58–62]. Upon the first oxidation process. the Q band at 680 nm increases slightly in intensity with red shift to 689 nm (Fig. 9C). The increase of the Q band with red shift is typical of a metal-based oxidation in CoPc complexes [58–63], and thus confirms the voltammetric assignment of Co(II)Pc(-2)/ $[Co(III)Pc(-2)]^+$ for the first oxidation process, O1, of **9**.

4. Conclusion

In conclusion, we have prepared and characterized new tetrasubstituted zinc (II), cobalt (II) and copper (II) Pcs at the peripheral (complexes 5, 6 and 7) and non-peripheral (complexes 8, 9 and 10) positions with 7,8-(15-crown-5)-3-(4-oxyphenyl)coumarin groups. The photophysical and photochemical properties of Zn(II) Pc complexes (5 and 8) were also described. The singlet oxygen quantum yields (0.54 for 5, 0.65 for 8), which give indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism). 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 Zn(II) Pc complexes are effectively quenched by 1,4-benzoquinone (BQ). The substituted complexes showed lower K_{SV} values when compared to the unsubstituted Zn(II) Pc in DMSO. Voltammetric and in situ spectroelectrochemical measurements indicated that aggregation tendency of beta-substituted phthalocyanine complexes in DMSO/TBAP is much higher than that of alpha-substituted ones. The difference in aggregation tendency of compounds can be attributed to the deviation from planarity in alpha-substituted molecules as a result of the non-peripheral substitution.

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