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Chromenone 12-crown-4 substituted zinc phthalocyanine complexes: Investigation of spectral, photophysical and photochemical properties

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ABSTRACT

The synthesis of novel 6,7-[(12-crown-4)-3-[*p*-(3,4-dicyanophenoxy)phenyl]coumarin (**1**), 6,7-[(12-crown-4)-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin (**2**), and their corresponding tetra-(chromenone 12-crown-4)-substituted zinc (II) phthalocyanine complexes (**3** and **4**) have been prepared. These new compounds have been characterized by elementel analysis, ^{1}H NMR (**1** and **2**), MALDI-TOF, IR and UV–Vis spectral data. The fluorescence intensity changes for **1** and **2** by addition of Na^+ or K^+ ions have been determined at 25 °C in THF. Intensity of the binding Na^+- and K^+-complexes (**1** and **2**) have decreased. The effects of the chromenone crown ether on the phthalocyanine molecule concerning photophysical and photochemical properties are also investigated. Photodegredation, singlet oxygen, fluorescence quantum yields, and fluorescence lifetimes of zinc phthalocyanine complexes (**3** and **4**) are also examined in DMSO.

1. Introduction

Since their accidental discovery over seventy years ago and subsequent structural elucidation, the phthalocyanines (Pcs) have been one of the most studied class of functional materials [1,2]. Pcs, remarkably robust and versatile compounds first developed as industrial pigment, have been applied in a wide range of area such as photovoltaic devices [3], catalysts [4], gas sensors [5,6], electrochromic displays [7], and photodynamic therapy (PDT) agents [8,9]. These properties may be modulated by central metals and huge variety of substitutions attached to the Pc cores [10,11]. By controlling such parameters, diverse functionalities can be obtained. For example, Pcs containing macrocycles such as crown ethers show potential applications as ion conducting channel or heavy metal extraction agents [12,13].

Another interesting group of compounds used as biological models are crown ethers. Crown ethers, which are capable of selectively binding alkali metal ions, are important building blocks for constructing specific devices while metal complexation can lead to a specific response, e.g. a change in electrical conductivity [14–16].

Crown ether substituted phthalocyanines were first synthesized in 1986 [17–19]. The introduction of crown ether substituents into Pc molecules makes it possible to optimize the properties of the materials used in the semiconductor technology and electrochromic devices. The unique ability of crown substituted Pcs to the cation induced formation of supramolecular heteronuclear ensembles with ionic conductivity can be used for the design of materials with new properties [20]. Among crown substituted Pcs, the tetra crown substituted compounds and their transition metal complexes are studied the most extensively [21–23].

The aim of the ongoing research is to synthesize and investigate photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegredation) properties of zinc phthalocyanine complexes substituted with chromenone crown ether as potential PDT agent. The biological importance of both crown ether and Pc's it is worthwhile to combine these two functional molecules into a single compound via synthetic methology which may also exhibit biological activities and maybe a potential canditate molecule in the application of PDT. The crown ether groups as substituents on the Pc framework can penetrate the cancer cell easily for PDT activation to realize Na^+/K^+ ion equilibrium. The investigation of photophysical and photochemical properties, especially singlet oxygen generation, are very important for PDT of cancer. In this work, we also report on the effects of the crown ether functionalized chromenon group as substituent on the photophysical and photochemical parameters. The objective is the preparation and characterization of zinc phthalocyanines containing four crown ether moieties on the periphery through oxy bridges have shown to be good candidate for new fluorescence sensor to Na^+ and K^+ ions.

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This work also explores the effects of ring substitutions on the fluorescence quenching of zinc phthalocyanine by 1,4-benzoquinone (BQ) using the Stern–Volmer relationship.

2. Experimental

2.1. Materials

Unsubstituted zinc (II) phthalocyanine (ZnPc) and 1,3-diphenylisobenzofuran (DPBF) were purchased from Aldrich. Potassium carbonate (K_2CO_3) was purchased from Fluka. Acetonitrile (CH_3CN), triethyleneglycolditosylate, N,N-dimethylaminoethanol (DMAE), sodium carbonate (Na_2CO_3), calcium chloride ($CaCl_2$) and anhydrous zinc acetate ($Zn(OAc)_2$) were purchased from Acros. Quinoline, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were dried as described by Perrin and Armarego [24] before use. Methanol, n-hexane, chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), acetone and ethanol were freshly distilled. 4-Nitrophthalonitrile [25], 3-nitrophthalonitrile [26], 6,7-dihidroksi-3-[*p*-(3-4-dicyanophenoxy)phenyl]coumarin and 6,7-dihidroksi-3-[*p*-(2-3-dicyanophenoxy)phenyl]coumarin [27] were synthesized according to reported procedures.

2.2. Equipment

The IR spectra were recorded on a Shimadzu FTIR-8300 using KBr pellets. ^{1}H NMR spectra were recorded on a Varian 500 MHz spectrometer in DMSO-d_6 for compounds **1** and **2**. Mass spectra were performed on a Bruker Daltonics Autoflex III MALDI-TOF spectrometer. Absorption spectra in the UV–Visible region were recorded with a Shimadzu 2001 UV and Shimadzu UV-1601 spectrophotometers. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature.

Photo-irradiations were done using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. (1) [28,29]

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**3** and **4**) 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 samples and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [30] was employed as the standard. 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 [31]. 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 (**3** and **4**) were determined in DMSO by using the photo-irradiation set-up described in the literature [32,33]. Typically, 2 ml portion of the sample solution (concentration = 1×10^{-5} M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with ZnPc as standard and DPBF as chemical quencher. The Eq. (3) was used for calculation singlet oxygen quantum yield.

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

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{Std} = 0.67$ in DMSO) [34]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the sample and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen the concentration of quencher was lowered to $\sim 3 \times 10^{-5}$ M [35]. Solutions of sensitizer containing DPBF was prepared in the dark and irradiated in the Q band region using the photo-irradiation set-up. DPBF degradation at 417 nm was monitored. The light intensity was 6.66×10^{15} photons/s cm^2 for Φ_Δ determinations.

2.4.2. Photodegredation quantum yields

Determination of photodegredation quantum yields (Φ_d) was carried out as previously described in the literature [32,33]. Φ_d was determined using Eq. (4),

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

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

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

Fluorescence quenching experiments on the substituted zinc phthalocyanine complexes (**3** and **4**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complexes (**3** and **4**), and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence spectra of substituted ZnPc complexes (**3** and **4**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation [36] as shown in Eq. (5):

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

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

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

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

2.5. Synthesis

2.5.1. 6,7-[(12-Crown-4)-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (**1**)

6,7-Dihydroxy-3-[*p*-(3,4-dicyanophenoxy)phenyl]coumarin (1.00 g, 2.50 mmol) and triethylenglycol ditosylate (1.26 g, 2.50 mmol) were dissolved in dry CH_3CN (150 ml) under nitrogen atmosphere and anhydrous Na_2CO_3 (0.53 g, 5 mmol) was added. This mixture was stirred for 7 days at 85–90 °C and then solvent was evaporated in vacuum. Diluted HCl was added to the residue and the mixture was extracted with $CHCl_3$ (4×30 ml). The combined organic extracts were washed with water, dried over $CaCl_2$ and evaporated in vacuum. Crude product was purified by column chromatography passing through silica gel 60 with chloroform as eluent and pure chromenone crown ether was obtained. The compound is soluble in ethanol, methanol, tetrahydrofuran (THF), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Yield: 0.10 g (8%). m.p.: 134–138 °C. IR ν(cm^{-1}): 3100–3050 (Ar-CH), 2980–2800 (aliphatic CH), 2200 (C≡N), 1705 (C=O), 1600 (Ar C=C), 1245 (Ar-O-Ar). ^{1}H NMR (DMSO-d$_6$, 500 MHz, δ ppm): 8.32 (s, 1H, lactone-H$_3$), 8.19 (d, 1H, Ar-H$_6$), 8.14 (d, *J* = 8 Hz, 1H, Ar-H$_8$), 7.86 (dd, *J* = 8 Hz, 2H, Ar-H$_4$), 7.47 (d, *J* = 8 Hz, 1H, Ar-H$_7$), 7.30 (d, *J* = 8 Hz, 2H, Ar-H$_5$), 7.21 (s, 1H, Ar-H$_1$), 7.12 (s, 1H, Ar-H$_2$), 4.18 (m, 4H, OCH$_2$), 3.80 (m, 4H, OCH$_2$), 3.71 (m, 4H, OCH$_2$). UV–Vis λ_{max} (nm) (log ε) (THF) (1×10^{-5} M): 363 (5.32). Anal. calcd. for $C_{29}H_{22}N_2O_7$: C 68.23; H 4.34; N 5.49%. Found: C 68.19; H 4.27; N 5.51%. MS (MALDI-TOF): *m/z* 510.8 [M]$^+$.

2.5.2. 6,7-[(12-Crown-4)-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (**2**)

Synthesis and purification were as outlined for **1** except 6,7-dihydroxy-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin was employed instead of 6,7-dihydroxy-3-[*p*-(3,4-dicyanophenoxy) phenyl]coumarin. The amounts of the reagents employed were: 6,7-dihydroxy-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin (1.00 g, 2.50 mmol), triethylenglycol ditosylate (1.26 g, 2.50 mmol), anhydrous Na_2CO_3 (0.53 g, 5 mmol) in DMF (150 ml). Yield: 0.13 g (10%). m.p.: 180–184 °C. IR ν(cm^{-1}): 3055 (Ar-CH), 2928–2864 (aliphatic CH), 2228 (C≡N), 1714 (C=O), 1619–1570 (Ar C=C), 1242 (Ar-O-Ar). ^{1}H NMR (DMSO-d$_6$, 500 MHz, δ ppm): 8.28 (s, 1H, lakton-H$_3$), 7.98 (d, *J* = 8 Hz, 2H, Ar-H$_4$), 7.92 (t, 1H, Ar-H$_7$), 7.78 (d, *J* = 8 Hz, 1H, Ar-H$_6$), 7.55 (d, *J* = 8 Hz, 1H, Ar-H$_8$), 7.41 (d, *J* = 8 Hz, 2H, Ar-H$_5$), 7.20 (s, 1H, Ar-H$_1$), 7.17 (s, 1H, Ar-H$_2$), 4.11 (m, 4H, OCH$_2$), 3.82 (m, 4H, OCH$_2$), 3.55 (m, 4H, OCH$_2$). UV–Vis λ_{max} (nm) (log ε) (THF) (1×10^{-5} M): 355 (3.97), 320 (3.84). Anal. calcd. for $C_{29}H_{22}N_2O_7$: C 68.23; H 4.34; N 5.49%. Found: C 68.11; H 4.17; N 5.49%. MS (MALDI-TOF): *m/z* 510.1 [M]$^+$, 511.2 [M+1]$^+$.

2.5.3. 2(3),9(10),16(17),23(24)-Tetrakis[6,7-(12-crown-4)-3-(4-oxyphenyl)coumarin)]-phthalocyaninato zinc(II) complex (**3**)

6,7-[(12-Crown-4)-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (**1**) (0.05 g, 0.098 mmol), Zn(AcO)$_2$ (0.0054 g, 0.024 mmol) and dry N,N-dimethylamino ethanol (DMAE) (2 ml) were refluxed with stirring under N_2 atmosphere for 24 h. After cooling to room temperature, the mixture was treated with methanol, and then the precipitated product was filtered off; washed with water, methanol, ethanol, acetonitrile, ethyl acetate, aceton, acetic acid and diethyl ether. The compound **3** is soluble in DMF and DMSO. Yield: 0.041 g (79%), m.p.: > 300 °C. IR ν(cm^{-1}): 3100–3050 (Ar-H), 2985–2800 (aliphatic-CH), 1725 (C=O lactone), 1625 (C=C), 1230 (Ar-O-Ar). UV–Vis λ_{max} (nm) (log ε) (DMSO) (1×10^{-5} M): 679 (5.02), 648 (4.43), 355 (5.01). Anal. calcd. for $C_{116}H_{86}N_8O_{28}Zn$: C 66.18; H 4.12; N 5.32%. Found: C 66.22; H 4.14; N 5.30%. MS (MALDI-TOF, 2,5-dihydroxybenzoic acid as matrix): *m/z* 2105 [M]$^+$.

2.5.4. 1(4),8(11),15(18),22(25)-Tetrakis[6,7-(12-crown-4)-3-(4-oxyphenyl)coumarin)]-phthalocyaninato zinc(II) complex (**4**)

Synthesis and purification were as outlined for **3** except 6,7-[(12-crown-4)-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (**2**) was employed instead of 6,7-[(12-crown-4)-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (**1**). The amounts of the reagents employed were: 6,7-[(12-crown-4)-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (**2**) (0.05 g, 0.098 mmol), Zn(AcO)$_2$ (0.0054 g, 0.024 mmol) dry DMAE (2 ml). The compound **4** is soluble in DMF and DMSO. Yield: 0.045 g (80%), m.p.: > 300 °C. IR ν(cm^{-1}): 3053 (Ar-H), 2918–2861 (aliphatic-CH), 1717 (C=O lactone), 1614–1569 (C=C), 1246 (Ar-O-Ar). UV–Vis λ_{max} (nm) (log ε) (DMSO) (1×10^{-5} M): 699 (4.83), 669 (4,12), 363 (4.82). Anal. calcd. for $C_{116}H_{86}N_8O_{28}Zn$: C 66.18; H 4.12; N 5.32%. Found: C 66.15; H 4.12; N 5.28%. MS (MALDI-TOF, 2,5-dihydroxybenzoic acid as matrix): *m/z* 2105 [M]$^+$, 2197 [M+4Na]$^+$.

3. Result and discussion

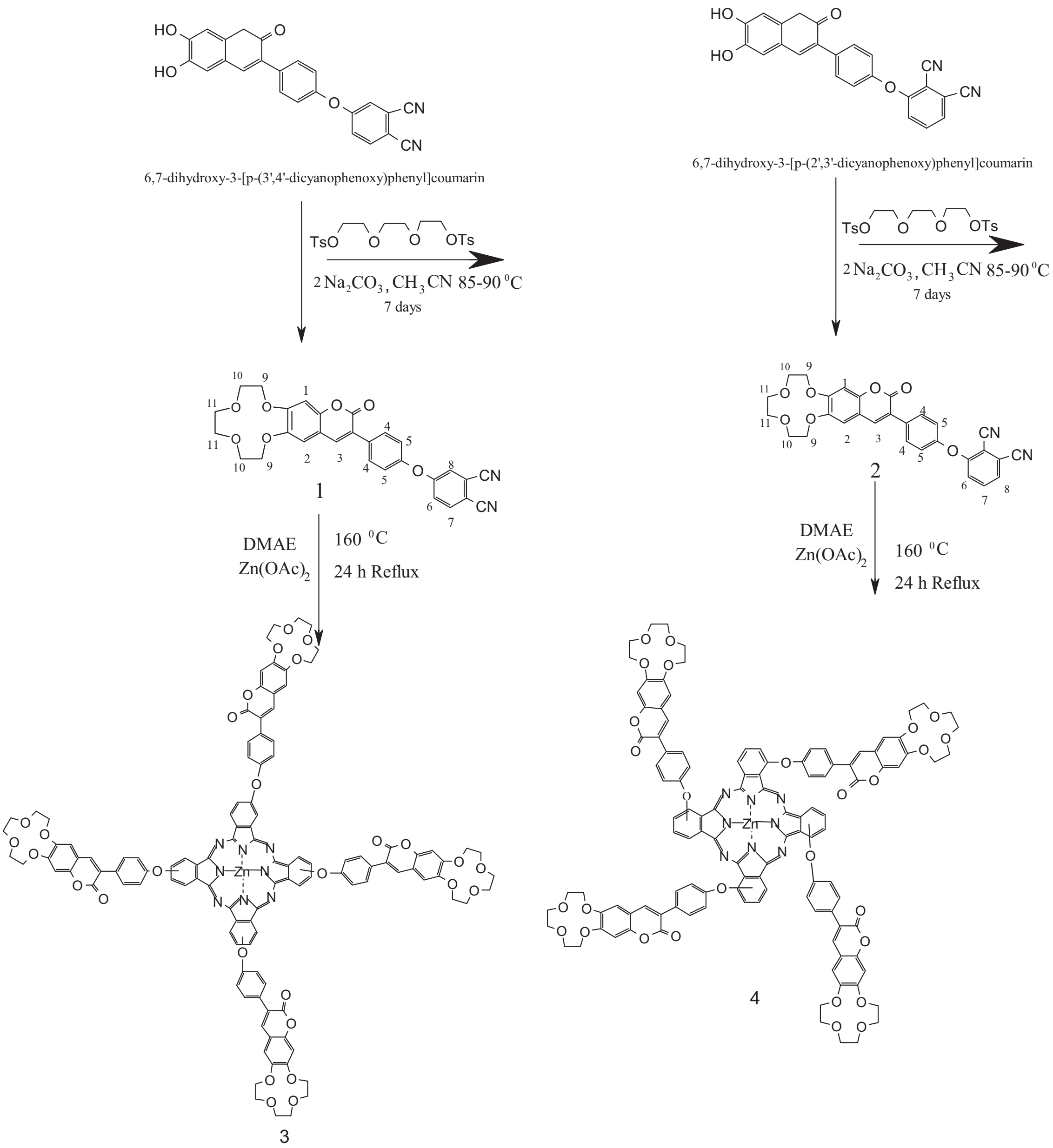
3.1. Synthesis and characterization

6,7-Dihydroxy-3-[*p*-(3,4-dicyanophenoxy)phenyl]coumarin and 6,7-dihydroxy-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin were reacted with triethylenglycol ditosylate to give the crown ether analogues (**1** and **2**) in the presence of Na_2CO_3 as base in CH_3CN, respectively. The crude products were purified by column chromatography over silica gel using $CHCl_3$ as eluent and the chromenone crown ether compounds were obtained in 8% yield for **1** and in 10% yield for 2 (Scheme 1). The ZnPc complexes show good solubility in solvents such as DMF and DMSO. The novel compounds have been characterized by elemental analysis IR, ^{1}H NMR and MALDI-MS spectroscopy.

The IR spectra showed two vibration peaks at ca. 2980–2800 cm^{-1} for compound **1** and 2982–2864 cm^{-1} for compound **2** due to aliphatic C–H stretching frequency. The characteristic vibrational peaks of the carbonyl (C=O) was appeared in the region 1705–1714 cm^{-1}. The vibration peaks corresponding to C–O–C ether chain was appeared in the range 1245–1242 cm^{-1}. The characteristic C≡N peaks were also showed at 2220 cm^{-1} for compound **1** and 2228 cm^{-1} for compound **2**.

The ^{1}H NMR spectra showed the expected peak resonances and peak integrals due to the protons of chromenone crown ether derivatives (**1** and **2**) in DMSO-d$_6$. The ^{1}H NMR spectra of **1** and **2** showed characteristic signals for etheral (–O–CH$_2$–CH$_2$–O–) protons at δ 3.71–4.18 ppm for compound **1** and 3.55–4.11 ppm for compound **2** as multiplets. The singlet peak at δ 8.32 ppm for compound **1** and 8.28 ppm for compound **2** indicated the presence of lacton protons. In addition, the chemical shifts of the aromatic protons were observed at between 7.12–8.19 ppm and 7.17–8.28 ppm for compounds **1** and **2**, respectively.

2(3),9(10),16(17),23(24)-Tetrakis[6,7-(12-crown-4)-3-(4-oxyphenyl)coumarin)]-phthalocyaninato zinc (**3**) and 1(4),8(11),15(18),22(25)-tetrakis[6,7-(12-crown-4)-3-(4-oxyphenyl)coumarin)]-phthalocyaninato zinc (**4**) complexes have been prepared by cyclotetramerization of novel 6,7-[(12-crown-4)-3-[*p*-(3,4-dicyanophenoxy)phenyl] coumarin (**1**) and 6,7-[(12-crown-4)-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin (**2**), respectively. Cyclotetramerization of the dinitril compounds (**1** and **2**) to the ZnPc complexes (**3** and **4**) was confirmed by the disappearance of the sharp C≡N vibration at 2200 and 2228 cm^{-1} for compounds **1** and **2**, respectively. The IR spectra showed characteristic vibrational peaks at 3050 cm^{-1} for complex **3** and



Scheme 1. Synthesis route of the 6,7-[(12-crown-4)-3-[*p*-(3,4-dicyanophenoxy)phenyl]coumarin (**1**) 6,7-[(12-crown-4)-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin (**2**) and the chromenone crown ether substituted zinc (II) phthalocyanine complexes (**3** and **4**).

3053 cm^{-1} for complex **4** due to aromatic C–H stretching, and 2985–2800 cm^{-1} for complex **3** and 2918–2861 cm^{-1} for complex **4** due to their aliphatic C–H stretching frequency. The characteristic vibrational peaks of the carbonyl groups (C=O) were appeared at 1725 cm^{-1} and 1717 cm^{-1} for complexes (**3** and **4**), respectively. The vibrational peaks were observed at 1230 cm^{-1} for complex **3** and 1246 cm^{-1} for complex **4** corresponding to C–O–C ether chains. The mass spectra of complexes (**3** and **4**) confirmed the proposed structure. The mass spectral study by the MALDI-TOF technique on the newly synthesized phthalocyanine complexes (**3** and **4**) were identified at *m*/*z*: 2105 [M]$^+$ (Fig. 1 for complex **4**) in the presence of 2,5-dihydroxybenzoic acid (DHB) (20 mg/ml in THF) as a matrix.

3.2. Ground state electronic absorption behavior

The ground state electronic spectra of the compounds showed characteristic absorption bands in the Q band region at 679 nm for **3** and 699 nm for **4** in DMSO. The B band region was observed around 355 nm for **3** and 363 nm for **4** in DMSO, (Table 1). The UV–Vis spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical for metallated phthalocyanine complexes [37]. Thus substitution of the ZnPc with chromenon crown ether substituents increased the wavelength of the Q band. The Q band of the peripherally and non-peripherally tetra-substituted ZnPc complexes (**3** and **4**) were red-shifted 7 nm and 27 nm compared to the unsubstituted ZnPc in DMSO. Non-peripherally tetra-substituted complex **4** was red-shifted 20 nm compared to the peripherally substituted ZnPc complex **3** (Fig. 2). The observed red spectral shift is typical of phthalocyanines with substituents at the non-peripheral positions and has been explained [38,39] 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 on the Pc framework. Essentially, the energy gap

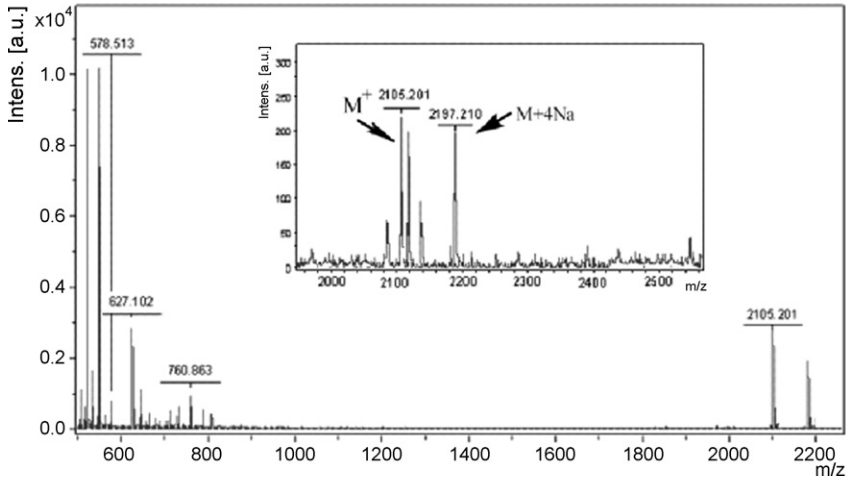


Fig. 1. The positive ion and linear mode MALDI-TOF MS spectrum of non-peripherally substituted zinc Pc complex (**4**). Inset spectrum shows expanded molecular mass region of the complex.

Table 1
Absorption, excitation and emission spectral data for unsubstituted (**ZnPc**), and the chromenone crown ether substituted zinc Pc complexes (**3** and **4**) in DMSO.

Compound	Q band λ_{max} (nm)	(Log ε)	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift Δ_{Stokes} (nm)
ZnPc[a]	672	5.14	672	682	10
3	679	5.02	683	689	10
4	699	4.96	698	710	11

[a] Data from Ref [43].

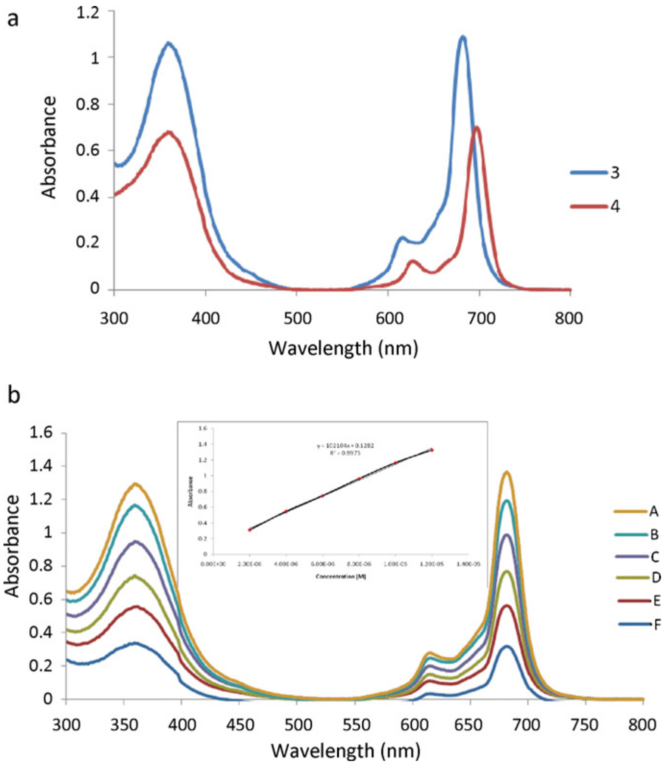


Fig. 2. (a) Absorption spectra of peripherally (**3**) and non-peripherally (**4**) substituted zinc Pc complexes in DMSO. Concentration = 1×10^{-5} M. (b) Aggregation behavior of **3** in DMSO at different concentrations: 12×10^{-6} (F), 10×10^{-6} (E), 8×10^{-6} (D), 6×10^{-6} (C), 4×10^{-6} (B), 2×10^{-6} (A) M. (Inset: Plot of absorbance versus concentration.)

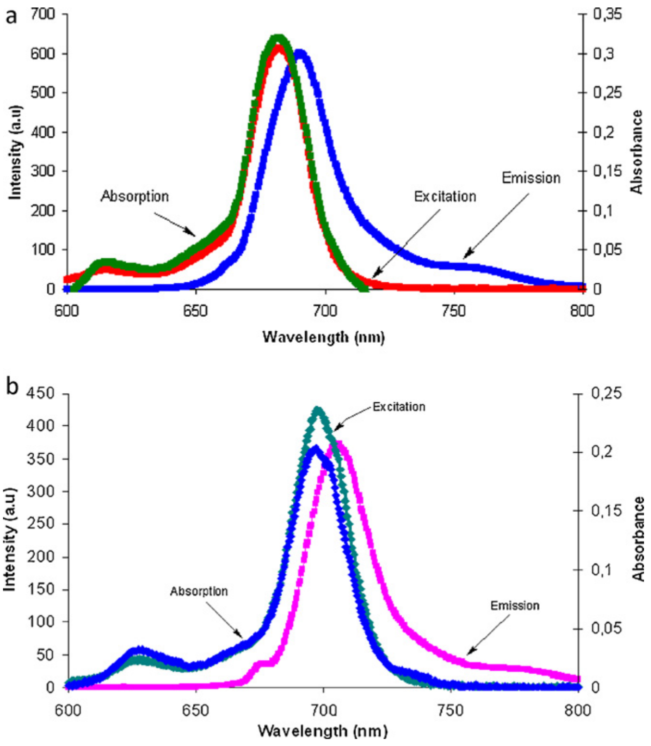


Fig. 3. Absorption, excitation and emission spectra of: (a) for complex **3**, (b) for complex **4** in DMSO. Excitation wavelength = 648 nm for **3**, 669 nm for **4** in DMSO.

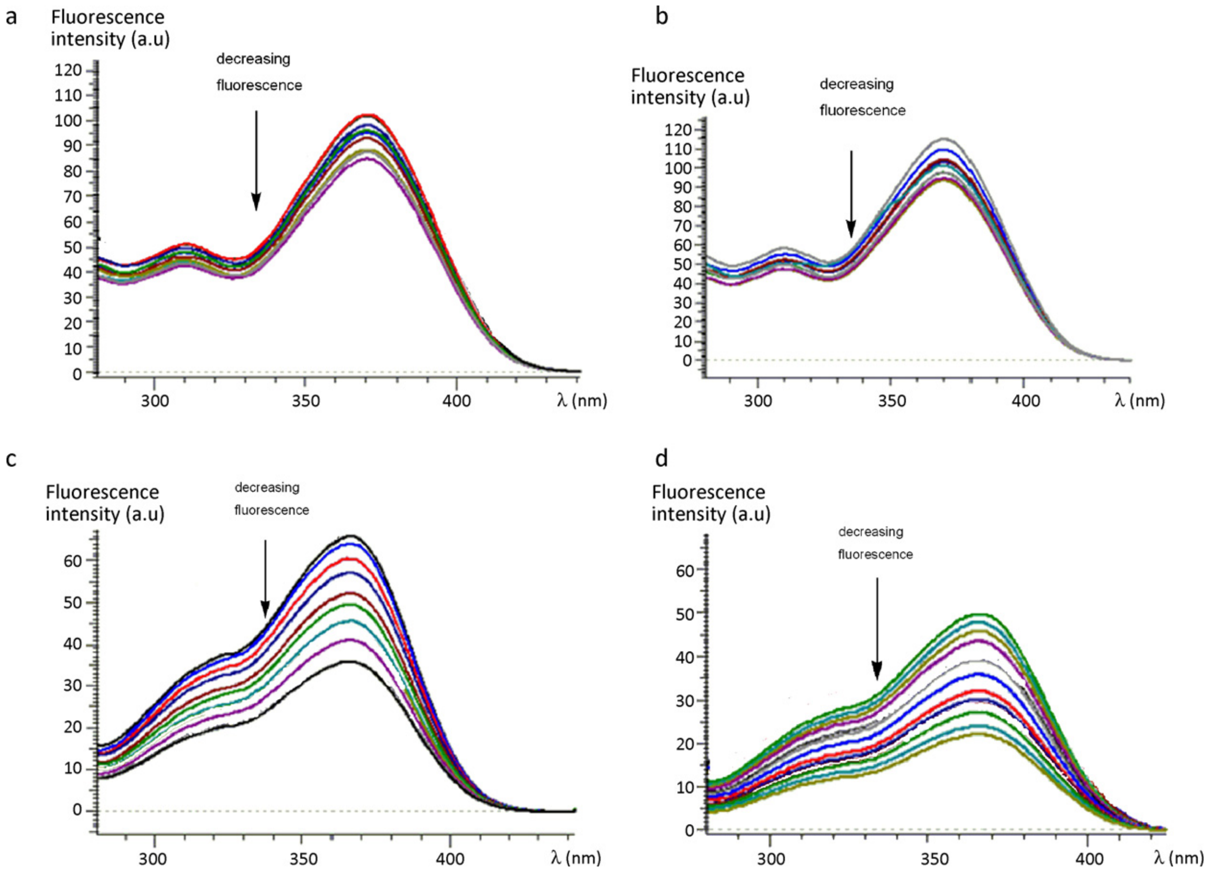


Fig. 4. The effect of alkali cations on the fluorescence intensity (a) for **1** and (b) for **2** during the gradual addition of KSCN, (c) for **1** and (d) for **2** addition of NaSCN in THF.

(ΔE) between the HOMO and lowest unoccupied molecular orbital (LUMO) becomes smaller, resulting in a ~20 nm bathochromic shift. Beer-Lambert low was obeyed for all studied ZnPc complexes in the concentrations ranging from 12×10^{-6} to 2×10^{-6} M and both ZnPc complexes did not show aggregation in these concentrations.

3.3. Fluorescence quantum yields and lifetimes

Fluorescence emission spectra were recorded for compounds (**1** and **2**) in THF, and in DMSO for zinc Pc complexes (**3** and **4**). The emission peaks were observed at 443 nm for **1**, 445 nm for **2**, 689 nm for **3** and 711 nm for 4 (Table 1). The excitation spectra of the zinc Pc complexes (**3** and **4**) are similar to that of absorption spectra, and they are mirror images of the fluorescence emission spectra. Fig. 3 shows the absorption, fluorescence emission and excitation spectra for zinc complexes (**3** and **4**) in DMSO.

With the aim of assessing the effect of alkali cations on the fluorescence behavior of the crown ether substituted coumarins by spectral methods, the chromenon crown ether compounds (**1** and **2**) were dissolved in THF and then an alkali metal salt (NaSCN or KSCN) solutions in ethanol was added. To avoid any effect arising from dilution due to the addition of the metal salts to the **1** and **2** solutions, the chromenone crown ether compounds (**1** and **2**) and metal salts were prepared at concentrations of 1.233×10^{-5} M for NaSCN and 1.029×10^{-5} M for KSCN in EtOH, respectively. However, the addition of NaSCN and KSCN to the chromenone crown ethers (**1** and **2**) solutions caused decreasing of the fluorescence intensity of these compounds indicate that the entrance of the binding Na^+ or K^+ cations in the crown ether cavitiy. The fluorescence intensities of complexes **1** and **2** are least decreased with addition of KSCN (Fig. 4a and b) but on the contrary, fluorescence intensities of these complexes are more decreased with addition of NaSCN (Fig. 4c and d); because the size of the Na^+ ion is more suitable for the cavity of 12-crown-4 than the size of K^+ cation.

The fluorescence quantum yields (Φ_F) of the studied zinc Pc complexes are given in Table 2. The Φ_F values of peripherally and non-peripherally substituted zinc Pc complexes are similar and typical of MPc complexes in DMSO. The Φ_F value of the substituted zinc Pc complex **3** is lower compared to unsubstituted zinc Pc complex but, complex **4** is higher compared to unsubstituted zinc Pc complex in DMSO which implies that the position effect of the chromenon crown ether substituents on the phthalocyanine framework. The non-peripherally substituted complex (**4**) show larger Φ_F value, suggesting less quenching of the excited singlet state by non-peripheral substitution compared to peripheral substitution.

Lifetimes of fluorescence (τ_F) are calculated using the Strickler–Berg equation. Using this equation, a good correlation has been [29] found for the experimentally and theoretically determined fluorescence lifetimes for the phthalocyanine molecules as is the case in this work for **3** and **4** in DMSO solution. While τ_F value of peripherally and non-peripherally zinc phthalocyanine complexes were higher than the τ_F value of unsubstituted ZnPc complex. The natural radiative lifetime (τ_0) values of peripherally and non-peripherally tetra-substituted zinc Pc complexes (**3** and **4**) were also longer when compared to unsubstituted ZnPc in DMSO. The rate constants for fluorescence (k_F) of tetra-substituted zinc Pc complexes (**3** and **4**) were lower than unsubstituted ZnPc complex in DMSO.

3.4. Singlet oxygen quantum yields

Energy transfer between the triplet state of phthalocyanines and ground state molecular oxygen molecules leads to the pro-

Table 2
Photophysical, photochemical and fluorescence quenching data for unsubstituted (**ZnPc**) and the chromenone crown ether substituted zinc Pc complexes (**3** and **4**) in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	[a]k_F (s^{-1}) ($\times 10^8$)	Φ_d ($\times 10^{-4}$)	$\Phi_($	K_{SV} (M^{-1})	$k_q/10^{10}$ (M^{-1} s^{-1})
ZnPc[b]	0.20	1.22	6.80	1.47	0.26	0.67	31.90	2.61
3	0.11	3.00	27.27	0.36	0.14	0.21	22.92	0.76
4	0.25	7.33	29.32	0.34	0.37	0.38	18.85	0.31

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] [43].

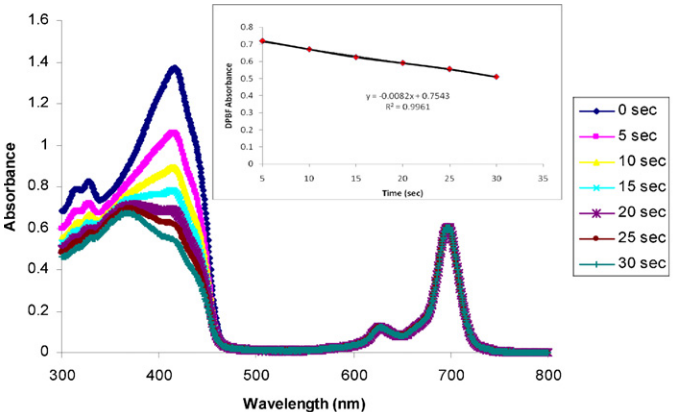


Fig. 5. A typical spectrum for the determination of singlet oxygen quantum yield. These determinations were for compound **4** in DMSO at a concentration of 1×10^{-5} M. (Inset: Plot of DPBF absorbance versus time.)

duction of singlet oxygen. There is a necessity of high efficiency of transferred of energy between excited triplet state of phthalocyanine and ground state of oxygen to generate large amounts of singlet oxygen, essential for photocatalytic reactions such as PDT.

Many factors are responsible for singlet oxygen including; triplet excited state energy, ability of substituents and solvents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen. It is believed that during photosensitization, the phthalocyanine molecule is first excited to the singlet state and through intersystem crossing forms the triplet state, and then transfers the energy to ground state oxygen, $O_2(^3\sum g)$, generating excited singlet state oxygen, $O_2(^1\Delta_g)$, the main cytotoxic species, which subsequently oxidizes the substrate by Type II mechanism.

There was no change in the Q band intensity during the Φ_Δ determinations, confirming that complexes were not degraded during singlet oxygen studies (Fig. 5 as an example for complex **4** in DMSO). The Φ_Δ values of zinc phthalocyanine complexes (**3** and **4**) are lower when compared to unsubstituted ZnPc in DMSO.

3.5. Photodegradation studies

Degradation of the photosensitizers under light irradiation can be used to study their stability and this is especially important for those photosensitizers intended for use as photocatalysts. The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation into different forms of MPc.

Stable zinc phthalocyanine complexes show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [40]. It seems that synthesized zinc Pc complexes (**3** and **4**) also show similar Φ_d values and stability to the known zinc phthalocyanine complexes. The Φ_d values of the peripherally and non-peripherally zinc Pc complexes are lower than unsubstituted ZnPc and the Φ_d value of the non-peripherally substituted zinc Pc complex (**4**) is higher than peripherally substituted complex (**3**) in DMSO.

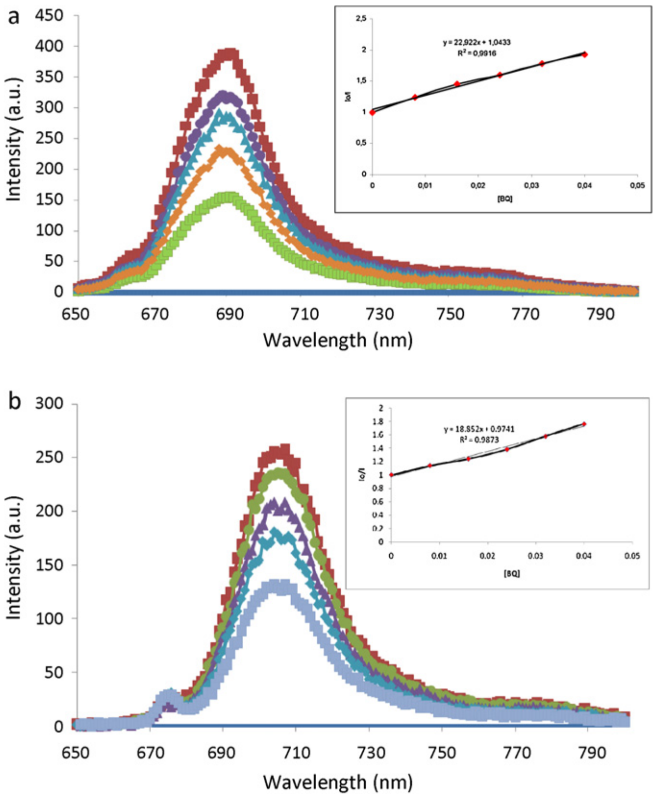


Fig. 6. Fluorescence emission spectral changes and Stern–Volmer plots for 1,4-benzoquinone (BQ) quenching of **3** (a) and **4** (b) (1.00×10^{-5} M) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

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

Phthalocyanine complexes may also be used as photosynthetic mimickers. An essential requirement for a good photosynthetic mimicker is the ability to undergo excited state charge transfer with ease, and Pc-quinone systems have proved to be favored candidates for understanding of energy transfer process [41,42].

The fluorescence quenching of zinc phthalocyanine 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 complexes **3** and **4** by BQ in DMSO solution. The slope of the plots shown in inset of Fig. 6 gave K_{SV} value, listed in Table 2. The K_{SV} values of the peripherally and non-peripherally zinc Pc complexes (**3** and **4**) were lower than unsubstituted ZnPc. The substitution with coumarin and crown ether groups seems to decrease the K_{SV} values of the complexes in DMSO. The bimolecular quenching constant (k_q) values of the substituted zinc phthalocyanine complexes (**3** and **4**) were also lower than for unsubstituted ZnPc, but generally, substitution with coumarin and crown ether groups seems to increase the k_q values of the complexes.

4. Conclusion

In the present work, novel 6,7-[(12-crown-4)-3-[*p*-(3,4-dicyanophenoxy)phenyl]coumarin (**1**) 6,7-[(12-crown-4)-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin (**2**) and their novel peripherally and non-peripherally substituted zinc Pc complexes (**3** and **4**) have been synthesized and characterized by elementel analysis, ^{1}H NMR (**1** and **2**), MALDI-TOF, IR, UV–Vis and fluorescence spectral data. The fluorescence intensity of the K^+-crown complexes compared to the Na^+-crown complexes in the THF, the K^+-crown complexes have least fluorescence intensity, because oxygen atoms in the crown ether binds least to the K^+ ion.

We found that the chromenone-crown ether derivatives (**1** and **2**) were not selective for K^+. Its binding affinity was $Na^+ > K^+$. The Na^+ selectivity of compounds **1** and **2** as a [12]-crown-4 derivatives were greater than its selectivity for K^+. Compounds **1** and **2** were quite selective for K^+, but had higher affinity for Na^+.

The photophysical and photochemical properties of the peripherally and non-peripherally tetra-substituted zinc Pc complexes (**3** and **4**) in DMSO were also described for comparison. In solutions, the absorption spectra showed monomeric behavior evidenced by a single (narrow) Q band for **3** and **4** in DMSO. The chromenone crown ether substituted zinc Pc complexes (**3** and **4**) have enough singlet oxygen quantum yields (Φ_Δ) for photocatalytic reactions. The peripherally and non-peripherally tetra-substituted zinc Pc complexes show similar Φ_d value and stabilities of these complexes applicable in PDT. The peripherally and non-peripherally tetra-substituted zinc Pc complexes (**3** and **4**) showed lower K_{sv} and k_q values when compared to the unsubstituted ZnPc in DMSO solution in the fluorescence quenching studies by BQ.

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