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Synthesis, characterization, photophysical and photochemical properties of tetra-2-[2-(benzothiazolylthio)]ethoxy substituted phthalocyanine derivatives

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ABSTRACT

The metal-free and zinc (II) phthalocyanine compounds tetra substituted with 2-(2-benzothiazolylthio) ethoxy groups have been synthesized for the first time in this study for comparison central metal effect on photophysical and photochemical properties. The new compounds have been characterized by IR, ¹H NMR, ¹³C NMR and MS spectra data. These compounds showed excellent solubility in most common organic solvents. The photophysical and photochemical properties of metal-free and zinc (II) phthalocyanine compounds have been studied in DMF and toluene in order to investigate of polar and non-polar solvent effect on these properties. The fluorescence quenching behaviour of the studied compounds by 1,4-benzoquinone (BQ) have also been studied in DMF and toluene.

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1. Introduction

Metal-free and metallophthalocyanines (MPcs) are one of the major types of tetrapyrrole derivatives showing a wide range of applications in various areas such as semiconductors, nonlinear optics, electro-chromic display devices and liquid crystals [1]. The exceptional chemical and physical properties of phthalocyanines are derived from various substituents on the phenyl rings [2]. Over 70 elements can be included into the phthalocyanine core, and its chemical versatility allows the introduction of many different substituents at peripheral positions on phthalocyanine framework [3,4]. The usual purification methods such as crystallization and chromatographic separation cannot be used in most phthalocyanines because of their extreme insolubility [5].

Their utility derives, in part from the ease with which their properties (solubility, electronic absorption, fluorescence etc.) can be modified through synthetic manipulation. Specificity in the applications of phthalocyanines can be introduced by modification of the benzenoid substituents or variation in the central metal ion [6-8]. Substituents provide the prime means of solubilizing the ring system in either aqueous media or in organic solvents and offer

0022-328X/\$ – see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2012.09.002 a useful way of tuning the wavelength of the visible region absorption band [9–16].

MPcs have also attracted sizeable curiosity in recent years as photosensitizers in photodynamic therapy (PDT). They show intense absorption towards the red end of the visible spectrum, which allows for deeper penetration into biological tissues. However, not all MPc derivatives are applicable in PDT; in principle, only Pcs containing diamagnetic metal ions [17] are ideal for this purpose as their triplet properties (quantum yield and lifetime) are high, resulting in efficient generation of singlet oxygen, $O_2(^1\Delta_g)$, the key mediator in tumour destruction. The triplet states of paramagnetic central metal ions, on the other hand, are very short lived, limiting their use in PDT. Accordingly, MPc derivatives incorporating non-transition metal (or metalloid) ions like Al^{3+} , Zn^{2+} , Si^{4+} , Ge^{4+} and Sn^{4+} have been studied [18–20] due to their potential applicability in PDT.

The aim of our ongoing research is to synthesis soluble metalfree and metallophthalocyanine complexes to be used in some application areas. Recently, we reported that metal-free and metallophthalocyanine derivatives functionalized with substituents such as 2-[2-(1-naphthyloxy)ethoxy]ethanol, 2-[2-(2-naphthyloxy) ethoxy]ethanol [21,22], 2-[2-(dimethylamino)ethoxy]ethanol [23] groups in peripheral and non-peripheral positions on the phthalocyanine ring, compounds offered PDT and electrochemical properties due to their interesting properties. Our previous studies





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regarding synthesis, photophysical and photochemical properties of various substituted phthalocyanines have already been reported [24–31]. These phthalocyanine complexes show interesting photophysical and photochemical properties especially high singlet oxygen quantum yields which are very important for PDT of cancer. In this work, 2-(2-benzothiazolylthio)ethoxy tetra-substituted metal free (**4**) and zinc (II) (**5**) phthalocyanines have been synthesized as potential PDT agents. Furthermore, to determine PDT activity of photosensitizers, the photophysical and photochemical properties of studied phthalocyanine compounds **4** and **5** has been examined in both DMF and toluene.

2. Experimental

2.1. Materials

2-(2-Benzothiazolylthio)ethanol **1** [32], 4-nitrophthalonitrile **2** [33] were synthesized according to literature. 1,3-Diphenylisobenzofuran (DPBF) and unsubstituted zinc phthalocyanine (**Std-ZnPc**) were purchased from Aldrich. All chemicals, solvents, and reagents were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified as described by Perrin and Armarego [34].

2.2. Equipment

FT-IR spectra were obtained on a Perkin Elmer 1600 FTIR spectrophotometer with the samples prepared as KBr pellets. NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl₃ and chemical shifts were reported (δ) relative to TMS as an internal standard. Mass spectra were recorded on a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer. Melting points were measured on an electrothermal apparatus. Domestic microwave oven was used for synthesis of zinc (II) phthalocyanine compound. Absorption spectra in the UV-vis region were recorded with a Shimadzu 2101 UV spectrophotometer. 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 (Mollectron detector incorporated) power metre.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined in DMF and toluene by the comparative method using equation (1) [35,36]

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

where *F* and *F*_{Std} are the areas under the fluorescence emission curves of the samples **4** and **5** and the standard, respectively. *A* and *A*_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [37] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program [38] which uses the Strickler–Berg equation. The fluorescence lifetimes (τ_F) were evaluated using equation (2).

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

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_{Δ}) determinations were carried out by using the experimental set-up described in the literature [19,39,40]. Typically, a 3 mL portion of the respective unsubstituted (**Std-ZnPc**), metal-free **4** and zinc **5** phthalocyanine solutions ($C = 1 \times 10^{-5}$ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references [19,39,40]. Singlet oxygen quantum yields (Φ_{Δ}) were determined in DMF and toluene using the relative method with unsubstituted ZnPc (**Std-ZnPc**) as reference. DPBF was used as chemical quencher for singlet oxygen in DMF and toluene. Equation (3) was employed for the calculations:

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

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard unsubstituted ZnPc (**Std-ZnPc**) ($\Phi_{\Delta}^{\text{Std}} = 0.56$ in DMF [41] and 0.58 in toluene [42]). *R* and R_{Std} are the DPBF photobleaching rates in the presence of the samples **4** and **5** and standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples **4** and **5** and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of quencher (DPBF) was lowered to ~3 × 10⁻⁵ mol dm⁻³ [41]. Solutions of sensitizers ($C = 1 \times 10^{-5}$ M) containing 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 6.48×10^{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 the literature [19,39,40]. Photodegradation quantum yields were determined using equation (4),

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

where C_0 and C_t are the samples **4** and **5** concentrations before and after irradiation respectively, *V* is the reaction volume, N_A is the Avogadro's constant, *S* is the irradiated cell area and *t* is the irradiation time. I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**4** and **5**). A light intensity of 2.16 $\times 10^{16}$ photons s⁻¹ cm⁻² was employed for Φ_d determinations.

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

Fluorescence quenching experiments on the metal-free **4** and zinc (II) **5** Pc compounds were carried out by the addition of different concentrations of BQ to a fixed concentration of the compounds, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 mol dm⁻³. The fluorescence spectra of the substituted metal-free **4** and zinc (II) **5** Pc compounds at each BQ concentration were recorded, and the

changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) equation [43] using equation (5):

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

where I_0 and I are the fluorescence intensities of samples in the absence and presence of BQ, respectively. K_{SV} is the Stern–Volmer constant; and this is the product of the bimolecular quenching constant (k_0) and the fluorescence lifetime τ_F (equation (6)):

$$K_{\rm SV} = k_{\rm q} \tau_F \tag{6}$$

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

2.5. Synthesis

2.5.1. 2-(2-Benzothiazolylthio)ethoxy phthalonitrile (3)

2-(2-Benzothiazolylthio)ethanol (1) (2 g, 9.52 mmol) was dissolved in dry DMF (40 mL) under N2 atmosphere and 4nitrophthalonitrile (2) (1.90 g, 9.52 mmol) was added to the solution. The solution was stirred up to 10 min and finely ground anhydrous K₂CO₃ (4.14 g, 28.56 mmol) was added portion wise within 2 h with efficient stirring. Stirred the reaction mixture under inert atmosphere at 50 °C for 3 days. Solution was then poured into ice-water (100 mL). The resultant precipitates were filtered off, washed with water (for neutralization), diethyl ether and dried in vacuum over P₂O₅. The crude product was crystallized from ethanol. Yield: 2.50 g (78%), mp: 134–135 °C. IR (KBr tablet) ν_{max} / cm⁻¹: 3077 (Ar−H), 2948–2852 (Aliph. C−H), 2227 (C≡N), 1594, 1500, 1458, 1428, 1318, 1256, 1171, 1093, 1020, 994, 835, 767, 727, 523. ¹H NMR (CDCl₃), (δ : ppm): 7.95 (d, 1H, J = 8.2 Hz, ArH), 7.75 (t, 2H, J = 10.9 Hz, ArH), 7.46 (m, 2H, ArH), 7.31 (m, 2H, Ar-H), 4.51 (t, 2H, J = 6.6 Hz, CH₂-O), 3.74 (t, 2H, J = 7.0 Hz, CH₂-S). ¹³C NMR $(CDCl_3)$, (δ : ppm): 165.02, 161.33, 152.66, 135.15, 126.25, 124.61, 121.48, 121.08, 119.66, 119.51, 117.38, 115.58, 115.22, 107.54, 67.13, 30.71. MS (ES⁺), m/z: Calc. for C₁₇H₁₁N₃S₂O: 337.43; Found: 338 $[M + H]^+$.

2.5.2. Synthesis of metal-free phthalocyanine (4)

The mixture of 2-(2-benzothiazolylthio)ethoxy phthalonitrile (3) (0.6 g, 1.78 mmol), n-pentanol (3 mL) and 12 drops of 1.8diazabicyclo[5,4,0]undec-7-ene (DBU) was placed in Schlenk tube at 160 °C, for 24 h. After cooling to room temperature the reaction mixture was refluxed with ethanol (45 mL) in order to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. After that the crude product was purified by column chromatography which is placed silicagel using chloroform as eluent. Yield: 103 mg (41%). mp > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1} : 3292 (N–H), 3063 (Ar-H), 2923-2852 (Aliph. C-H), 1603, 1541, 1486, 1457, 1427, 1312, 1281, 1238, 1117, 1018, 996, 833, 756, 726. ¹H NMR (CDCl₃) (δ: ppm): 7.96 (d, J = 7.8 Hz, 4H, ArH), 7.72 (m, 8H, ArH), 7.40 (m, 8H, ArH), 7.30 (m, 8H, Ar-H), 4.47 (m, 8H, CH₂-O), 3.72 (m, 8H, CH₂-S). MS (ES⁺), *m*/*z*: Calc. for C₆₈H₄₆N₁₂S₈O₄: 1351.72; Found: 1374 $[M + Na]^+$. UV/vis: λ , nm (log ε): in DMF; 702 (4.31), 670 (4.40), 639 (4.26), 335 (4.56), in toluene; 704 (4.76), 666 (4.72), 641 (4.51), 340 (4.67).

2.5.3. Synthesis of zinc (II) phthalocyanine (5)

A mixture of compound **3** (0.6 g, 1.78 mmol), $Zn(CH_3COO)_2$ (0.080 g, 0.44 mmol) and 2-(dimethylamino)ethanol (6 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After the mixture was cooled to the room temperature, it was stirred in EtOH (30 mL) addition for overnight and filtered off. The crude

product was also refluxed in EtOH (50 mL) for 6 h. The obtained dark-green product was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* over P₂O₅. After cooling to room temperature, the reaction mixture was precipitated in hot ethanol (40 mL), then the product was filtered off. The green solid product was purified through alumina column using CHCl₃:MeOH (90:10) as eluting solvent system. The light-green solid product is soluble in CHCl₃, CH₂Cl₂, DMSO, DMF, THF, pyridine. Yield: 0.282 g (45%), mp > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1} : 3085 (Ar–H), 2933–2867 (Aliph. C–H), 1738, 1642, 1092, 915, 846, 793. ¹H NMR (CDCl₃) (δ : ppm): 7.74 (m, 12H, ArH), 7.30 (m, 16H, ArH), 4.55 (m, 8H, CH₂–O), 3.73 (m, 8H, CH₂–S). MS (ES⁺), *m/z*: Calc. for C₆₈H₄₄N₁₂S₈O₄Zn: 1415.09; Found: 1438 [M + Na]⁺. UV/vis: λ , nm (log ε): in DMF; 678 (5.26), 611 (4.56), 355 (4.93), in toluene; 682 (5.26), 615 (4.66), 360 (4.94).

3. Results and discussion

3.1. Synthesis and characterization

The general route for the syntheses of new metal-free (**4**) and zinc (II) (**5**) phthalocyanine compounds is given in Scheme 1. The synthesis of the phthalonitrile compound **3** was based on the reaction of 4-nitrophthalonitrile (**2**) with 2-(2-benzothiazolylthio) ethanol (**1**) in the presence of dry K_2CO_3 as a base in dry DMF at 50 °C. The self-condensation of the phthalonitrile compound **3** in a high-boiling solvent in the presence of a few drops of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a strong base at reflux temperature under a nitrogen atmosphere afforded the metal-free phthalocyanine (**4**) in 41% yield as a dark green solid after purification by column chromatography which is placed aluminium oxide using CHCl₃:CH₃OH (9:1) as solvent system. Zinc (II) phthalocyanine (**5**) was obtained in the presence of the anhydrous Zn(CH₃COO)₂ in 2-(dimethylamino)ethanol as solvent using microwave irradiation.

In the IR spectra, the formation of compound **3** was clearly confirmed by the disappearance of the -OH and $-NO_2$ bands and appearance of $-C \equiv N$ band at 2227 cm⁻¹. In the ¹H NMR spectra of **3**, the proton signals corresponding to OH group for compound **1** appeared as expected. ¹H NMR spectrum of **3** showed new signals at $\delta = 7.95$, 7.75, 7.46 and 7.31 ppm for aromatic protons. The ¹H NMR signals belong to aliphatic protons were observed at $\delta = 4.51$, 3.74 ppm. The ¹³C NMR spectra of **3** showed signals for carbon atoms at $\delta = 165.02$, 161.33, 152.66, 135.15, 126.25, 124.61, 121.48, 121.08, 119.66, 119.51, 117.38, 115.58, 115.22, 107.54, 67.13, 30.71. The MS spectrum of compound **3** showed a molecular ion peak at m/z = 338 [M + H]⁺ support the proposed formula for this compound.

The sharp peak in the IR spectra for the C=N vibration of phthalonitrile compound (**3**) at 2227 cm⁻¹ disappeared after conversion into metal-free phthalocyanine, indicative of metal-free phthalocyanine formation. The characteristic N–H stretching for the metal-free phthalocyanine ring was observed at 3292 cm⁻¹. The IR spectra of metal-free (**4**) and zinc (II) (**5**) phthalocyanines are very similar, except these ν (NH) vibrations of the inner phthalocyanine core in the metal-free molecule. In the ¹H NMR spectrum of compound **4**, aromatic protons were observed at δ = 7.96, 7.72, 7.40 and 7.30 ppm. The aliphatic protons were observed at δ = 4.47 and 3.72 ppm. The NH protons of compound **4** could not be observed owing to the probable strong aggregation of the molecules [44]. In the mass spectrum of compound **4**, the presence of the characteristic molecular ion peak at m/z = 1374 [M + Na]⁺ confirmed the proposed structure.

In the IR spectrum of zinc (II) phthalocyanine, the sharp vibration for the $-C \equiv N$ groups in the IR spectra of phthalonitrile compound **3** at 2227 cm⁻¹, disappeared after conversion into zinc



Scheme 1. The synthetic route of the phthalonitrile and its metal-free and zinc phthalocyanine derivatives. Reagents and conditions: (i) dry DMF, K₂CO₃, 50 °C, 72 h; (ii) *n*-pentanol, DBU, 160 °C, (iii) Zn(CH₃COO)₂, DMAE, 175 °C, 350 W.



Fig. 1. Absorption spectra of compound 4 and 5 (a) in toluene and (b) in DMF.

Table 1

Absorption, excitation and emission spectral data for substituted metal-free (4) zinc (5) and unsubstituted zinc (Std-ZnPc) phthalocyanine compounds in DMF and toluene.

| Compound | Solvent | Q band λ_{max} , (nm) | $\log \epsilon$ | Excitation λ_{Ex} , (nm) | Emission $\lambda_{\rm Em}$, (nm) | Stokes shift Δ_{Stokes} , (nm) |
|----------|---------|-------------------------------|-------------------|----------------------------------|------------------------------------|--|
| 4 | DMF | 670, 702 | 4.40, 4.31 | 673, 704 | 711 | 9 |
| | Toluene | 666, 704 | 4.72, 4.76 | 668, 705 | 710 | 6 |
| 5 | DMF | 678 | 5.26 | 680 | 690 | 12 |
| | Toluene | 682 | 5.26 | 686 | 694 | 12 |
| Std-ZnPc | DMF | 670 ^a | 5.37 ^a | 670 ^a | 676 ^a | 6 ^a |
| | Toluene | 672 ^b | 5.14 ^b | 672 ^c | 676 ^d | 6 ^d |

Data from reference [52]. b

Data from reference [29].

Data from reference [30]

^d Data from reference [53].

(II) phthalocyanine. In the ¹H NMR spectrum of zinc (II) phthalocyanine, the aromatic ring protons were observed at $\delta = 7.74$ ppm as multiplet and aromatic protons on the substituents were also observed at δ = 7.30 ppm as multiplet. The aliphatic protons were observed at δ = 4.55 and 3.73 ppm. In the mass spectrum of compound **5**, the presence of molecular ion peaks at m/z = 1438 $[M + Na]^+$, confirmed the proposed structures.

3.2. Ground state electronic absorption spectra and fluorescence spectra

UV-vis spectroscopy is one of the best indicator to confirm the formation of phthalocyanines in their dilute solutions. The UV-vis spectra of the studied metal-free **4** and zinc (II) **5** phthalocyanine compounds in DMF and toluene were given in Fig. 1. The Q band of the metal-free phthalocyanine was observed as split two bands due to D_{2h} symmetry [45] in both studied solvents. The splitting Q band was observed at λ_{max} 702 and 670 nm in DMF and at λ_{max} 704 and 666 nm in toluene (Table 1), indicating the structure with nondegenerate D_{2h} symmetry [45]. The ground state electronic absorption spectrum of zinc (II) phthalocyanine compound 5 showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes, Fig. 1 [46]. The Q band of this complex was observed at 678 nm in DMF and 682 in toluene, Table 1. The B bands of studied phthalocyanine compounds 4 and 5 were observed at around 340-360 nm in DMSO (Fig. 1).

Aggregation is highly depends on a number of parameters such as concentration, temperature, nature of the substituents, nature of solvents and complex metal ions [47,48]. Aggregation behaviour of metal-free 4 and zinc 5 phthalocyanine compounds were investigated in different solvents (DMSO, THF and chloroform).

Aggregation behaviour of these compounds was also studied at different concentrations in DMF and toluene. The compound **5** did not show any aggregation in all these solvents while the compound **4** showed a little aggregation in DMSO. Beer–Lambert law could be obeyed for studied phthalocyanine complexes in the concentrations ranging from 1.2×10^{-5} to 2×10^{-6} M (Fig. 2).

The fluorescence behaviour of the studied phthalocvanine complexes was examined in DMF and toluene. Fig. 3 shows fluorescence emission, absorption and excitation spectra of compound 4 in toluene (Fig. 3a) and compound 5 in DMF (Fig. 3b) as examples. The observed Stokes shifts ($\sim 5-15$ nm) were within the region observed for Pc complexes. Metal-free 4 and zinc 5 phthalocyanine compounds showed similar fluorescence behaviour in DMF and toluene. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for both compounds **4** and **5** in both DMF and toluene. The proximity of the wavelength of the Q-band absorption and the Q band maxima of the excitation spectra for all studied compound suggested that the nuclear configurations of the ground and excited states are similar and not affected by excitation.

Fluorescence emission and excitation peaks in DMF and toluene are listed in Table 1. The observed Stokes shifts of substituted metal-free 4 and zinc 5 phthalocyanine compounds are higher than standard ZnPc in both DMF and toluene (Table 1). The observed Stokes shift of the substituted zinc phthalocyanine complex 5 is higher than substituted metal-free **4** phthalocyanine compound in both DMF and toluene (Table 1).

3.3. Photophysical properties

3.3.1. Fluorescence quantum yields and lifetimes

The fluorescence quantum yield (Φ_F) values of metal-free **4** and zinc (II) 5 phthalocyanine compounds in DMF and toluene are given in Table 2. The Φ_F values of the studied phthalocyanine compound **4** and 5 are higher than unsubstituted zinc Pc (Std-ZnPc) in both DMF and toluene. Especially, the Φ_F values of substituted phthalocyanine compounds are quite higher than unsubstituted zinc Pc (Std-ZnPc) in toluene. The increasing in the Φ_F values for substituted phthalocyanine complexes in the presence of the ring substituents suggests that the substituents less quench the excited singlet state than the fluorescence. The substituted metal-free Pc (4) complex shows larger Φ_F values in both studied solvents. Fluorescence quantum yield (Φ_F) values of studied phthalocyanines complexes (4 and 5) are almost similar values compared to metal free and zinc phthalocyanine derivatives studied in the literature [49].

Fluorescence lifetime (τ_F), directly related to Φ_F value, refers to the average time a molecule stays in its excited state before emission. The value of Φ_F could be indirectly reduced by such factors



Fig. 2. Absorption spectra: (a) for compound 4 in toluene and (b) for compound 5 in DMF at different concentrations. (Inset: Plot of absorbance versus concentration).



Fig. 3. Absorption, excitation and emission spectra of (a) compound 4 in toluene and (b) compound 5 in DMF. Excitation wavelength: 640 for compound 4 and 650 nm for compound 5.

shortening the fluorescence lifetime of a fluorophore, including internal conversion and intersystem crossing. Lifetimes of fluorescence were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been found [36] between experimentally and the theoretically determined lifetimes for the unaggregated molecules as is the case in this work. Generally, the τ_F values are within the range reported for MPc complexes [50]. The τ_F values of metal-free **4** and zinc (II) **5** phthalocyanine compounds are higher than unsubstituted zinc Pc (**Std-ZnPc**). Among the substituted phthalocyanine compounds, the τ_F values of metal-free compound **4** are higher than zinc phthalocyanine compound **5** in both studied solvents. Fluorescence lifetime (τ_F) values of employed phthalocyanines complexes (**4** and **5**) are almost similar values compared to metal free and zinc phthalocyanine derivatives studied in the literature [49].

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also given in Table 2. The τ_0 values of metal-free **4** and zinc **5** phthalocyanine compounds are higher than unsubstituted ZnPc (**Std-ZnPc**) in DMF but the τ_0 values of these compounds are lower than unsubstituted ZnPc (**Std-ZnPc**) in toluene. The k_F values of these compounds (**4** and **5**) are higher than unsubstituted ZnPc (**Std-ZnPc**) in both DMF and toluene.

3.4. Photochemical properties

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3.4.1. Singlet oxygen quantum yields

In PDT applications, it is worth saying that the most important parameter is the efficiency in singlet oxygen generation of the

| Table 2 |
|--|
| Photophysical and photochemical parameters of substituted metal-free (4), zinc (5) |
| and unsubstituted zinc (Std-ZnPc) phthalocyanine compounds in DMF and toluene. |

| Compound | Solvent | Φ_F | $\tau_F(\mathbf{ns})$ | τ_0 (ns) | $k_F(s^{-1}) \ (imes 10^7)^a$ | $\begin{array}{c} \Phi_d \\ (\times 10^{-5}) \end{array}$ | $\Phi\Delta$ |
|--------------------|---|---|---|---|---|---|---|
| 4 5 Std-ZnPc | DMF Toluene DMF Toluene DMF | 0.31 0.23 0.23 0.21 0.17 ^b | 7.58 3.02 1.71 1.16 1.03 ^b | 24.21 12.95 7.57 5.60 6.05 ^b | 4.13 7.72 13.20 17.87 1.65 ^b | 0.52 9.65 0.21 6.72 2.3 ^b | 0.26 0.36 0.73 0.61 0.56 ^b |
| | Toluene | 0.07 ^c | 0.90 ^d | 12.97 ^d | 7.70 ^d | 6.19 ^e | 0.58 ^c |

^a k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F / \tau_F$.

^b Data from reference [52].

^c Data from reference [53]. ^d Data from reference [30].

^e Data from reference [20].

^e Data from reference [28].

photosensitizer. Energy transfer from the triplet state of a photosensitizer to ground state molecular oxygen leads to the production of singlet oxygen. There is a necessity of high efficiency of transfer of energy between excited triplet state of photosensitizer and ground state of oxygen to generate large amounts of singlet oxygen, essential for PDT. The singlet oxygen quantum yield (Φ_{Δ}) value gives the amount of the singlet oxygen generation and this value is an indication of potential of the complexes as photosensitizers in applications where singlet oxygen is required. The Φ_{Λ} values were determined using a chemical method (in DMF and toluene using DPBF as quenchers). The disappearance of DPBF was monitored using UV-vis spectrophotometer (Fig. 4 as examples: (a) for compound **4** in toluene and (b) for compound **5** in DMF) Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen including such as triplet excited state energy, nature of substituents and solvents, 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 decrease in the Q band of formation of the studied metal-free **4** and zinc (II) **5** phthalocyanine derivatives during Φ_{Δ} determinations.

Table 2 gives the Φ_{Δ} values of substituted metal-free 4, substituted zinc (II) 5 phthalocyanines and unsubstituted zinc phthalocyanine (Std-ZnPc) which is used as standard for singlet oxygen studies of phthalocyanine compounds for comparison. While the Φ_{Δ} values of substituted zinc (II) phthalocyanine compound **5** are higher, the Φ_{Δ} values of substituted metal-free **4** phthalocyanine compound are lower than unsubstituted zinc (II) phthalocyanine in both DMF and toluene. The Φ_{Δ} values of substituted zinc (II) phthalocyanine compound 5 are higher than the Φ_{Δ} values of substituted metal-free **4** phthalocyanine compound in both DMF and toluene. The singlet oxygen quantum yield (Φ_{Δ}) values of employed phthalocyanines complexes (**4** and **5**) are almost similar values compared to metal free and zinc phthalocyanine derivatives studied in the literature [49]. In general, zinc phthalocyanine compounds which could be generated highly singlet oxygen possess high triplet yields duo to the d¹⁰ configuration of the central Zn^{2+} ion, giving an excellent candidate as a photosensitizers for PDT applications.

3.4.2. Photodegradation studies

Degradation of the compounds under light irradiation can be used to study their stability and this is especially important for those compounds intended for use in photocatalysis. The collapse of the absorption spectra without any distortion of the shape confirms photodegradation not associated with



Fig. 4. Absorbance changes during the determination of singlet oxygen quantum yield: (a) for compound **4** in toluene and (b) for compound **5** in DMF at a concentration of 1.0×10^{-5} M. (Inset: Plots of DPBF absorbance versus time).

phototransformation into different forms of photosensitizers absorbing light in the visible region. The spectral changes observed for metal-free **4** and zinc (II) **5** Pc complexes during confirmed photodegradation occurred without phototransformation (Fig. 5 as examples: (a) for compound **4** in DMF and (b) for compound **5** in toluene).

The photodegradation quantum yield (Φ_d) values of metal-free **4** and zinc 5 phthalocvanine compounds as well as unsubstituted zinc (II) phthalocvanine (**Std-ZnPc**) in DMF and toluene are given in Table 2. All the studied complexes showed about the same stability with Φ_d of the order of 10^{-5} . The Φ_d values, found in this study, are similar with zinc Pc complexes having different substituents on the phthalocyanine ring in literature [50]. The Φ_d values have been reported as low as 10⁻⁶ for stable zinc phthalocyanine complexes and the Φ_d values of the order of 10^{-3} for unstable zinc phthalocyanine complexes [49]. The metal-free 4 and zinc 5 phthalocyanine compounds showed lower Φ_d values when compared to the unsubstituted ZnPc (Std-ZnPc) in DMF but studied compounds showed slightly higher in Φ_d values toluene. The substitution of the phthalocyanine framework with 2-(2-benzothiazolylthio)ethoxy groups slightly increased the stability of studies phthalocyanine compounds in DMF but slightly decreased in toluene. However, studied Pc complexes could be classified as stable compounds. The photodegradation quantum yield (Φ_d) values of studied phthalocyanines complexes (4 and 5) are almost similar values compared to metal free and zinc phthalocyanine derivatives studied in the literature [49].

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

The fluorescence quenching of metal-free 4 and zinc 5 phthalocyanine compounds by BQ was found to obey Stern-Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions in both DMF and toluene. Fig. 6 shows the quenching of metal-free (4) (Fig. 6a) and zinc (II) (5) (Fig. 6b) Pc compounds by BQ in toluene and DMF, respectively. The slopes of the plots were given as insets in Fig. 6a and b. These plots gave Stern-Volmer constants (K_{SV}) values of studied phthalocvanine compounds 4 and **5** and listed in Table 3. The linearity of these plots indicates that fluorescence guenching is reasonably described by a collisional quenching mechanism. The K_{SV} values of the substituted phthalocyanine complexes 4 and 5 are lower than unsubstituted ZnPc (Std-**ZnPc**) in DMF and toluene. The K_{SV} values of zinc phthalocyanine compound 5 are slightly lower than metal-free phthalocyanine compound 4 in both DMF and toluene. These two compounds compared in terms of solvent effect, K_{SV} values are higher in toluene than in DMF. The bimolecular guenching rate constant $(k_{\rm q})$ values of the substituted phthalocyanine complexes 4 and 5 are also lower than unsubstituted ZnPc (Std-ZnPc) in DMF and toluene, thus substitution of phthalocyanine framework with 2-(2benzothiazolylthio)ethoxy groups seems to decrease the k_{a} values of the compounds in both DMF and toluene. Moreover, studied zinc (II) **5** phthalocyanine has higher k_q value than metal-free **4** Pc complex in both solvents. The k_q values are near $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and in agreement with the theoretical Smoluchowski-Stokes-Einstein approximation at 298 K [51].



Fig. 5. Absorbance changes during the photodegradation study: (a) for compound 4 in DMF and (b) for compound 5 in toluene showing the disappearance of the Q-band at 5 and 2.5 min intervals, respectively. (Inset: Plot of Q band absorbance versus time).



Fig. 6. Fluorescence emission spectral changes of: (a) compound **4** and (b) compound **5** ($C = 1.00 \times 10^{-5}$ M) on addition of different concentrations of BQ in toluene and DMF respectively. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M and saturated with BQ. (Insets: Stern–Volmer plots for benzoquinone (BQ) quenching of compounds **4** and **5** in DMF and toluene).

Table 3

Fluorescence quenching data for substituted metal-free (**4**), zinc (**5**) and unsubstituted zinc (**Std-ZnPc**) phthalocyanine compounds in DMF and toluene.

| Compound | Solvent | $K_{\rm SV}^{\rm BQ}/({\rm M}^{-1})$ | $k_{\rm q}/10^{10}~({ m M}^{-1}~{ m s}^{-1})$ |
|----------|----------------------|--------------------------------------|---|
| 4 | DMF | 36.79 | 0.49 |
| | Toluene | 61.40 | 2.03 |
| 5 | DMF | 32.02 | 1.87 |
| | Toluene | 60.57 | 5.22 |
| Std-ZnPc | DMF ^a | 57.60 | 5.59 |
| | Toluene ^b | 61.53 | 6.83 |

^a Data from reference [52].

^b Data from reference [28].

4. Conclusion

The novel metal-free **4** and zinc (II) **5** phthalocyanines bearing four 2-(2-benzothiazolylthio)ethoxy groups at peripheral position have been synthesized for the first time in this study. The studied compounds were characterized by elemental analysis, UV-vis, FT-IR, ¹H NMR and ESI mass spectroscopies. Both studied Pc complexes are very soluble in most organic solvents such as chloroform, dichloromethane, toluene, THF etc. The photophysical and photochemical properties of studied metal-free 4 and zinc 5 phthalocyanines compounds have also been described in both DMF and toluene for comparison of solvent effect. In solution, the absorption spectra showed monomeric behaviour evidenced by a single (narrow) Q band for the zinc phthalocyanine compound 5 due to $D_{4\rm h}$ symmetry of this compound. But the metal-free phthalocyanine compound **4** showed a doublet O band in different solvents due to D_{2h} symmetry of this compound. The substitution of the 2-(2-benzothiazolylthio)ethoxy substituents on the phthalocyanine ring increased the wavelength of the Q band. In both DMF and toluene, the fluorescence behaviour of the phthalocyanine complexes indicated that the metal-free 4 and zinc 5 Pc complex are more fluorescent than unsubstituted ZnPc (Std-ZnPc). The substituted zinc Pc 5 complex has good singlet oxygen quantum yields (Φ_{Δ}) in compared to the metal free **4** Pc complex and unsubstituted ZnPc (**Std-ZnPc**) in both solvents. The value of Φ_{Δ} ranged from 0.26 (for complex 4 in DMF) to 0.73 (for complex 5 in DMF) indicates that there is a considerable potential of these compounds as photosensitizers in PDT applications. The substitution of the phthalocyanine framework with 2-(2-benzothiazolylthio)ethoxy groups slightly increased the stability of studies phthalocyanine compounds in DMF but slightly decreased in toluene. The substituted phthalocyanine compounds **4** and **5** showed slightly lower K_{SV} values in toluene but showed quite lower values in DMF when compared to unsubstituted ZnPc (**Std-ZnPc**) according to the results of fluorescence quenching studies.

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