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# Self-assembling novel phthalocyanines containing a rigid benzothiazole skeleton with a 1,4-benzene linker: Synthesis, spectroscopic and spectral properties, and photochemical/photophysical affinity

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# ABSTRACT

A novel benzothiazole containing phthalonitrile derivative and its peripherally tetra substituted metal free (4), Ni(II) (5), Zn(II) (6), Cu(II) (7) and Ti(IV) (8) phthalocyanines have been synthesized. The novel compounds were characterized by elemental analysis, IR, UV-Vis, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy. Zn(II)Pc (**6**) showed monomeric behavior in THF up to  $7 \times 10^{-5}$  mol dm<sup>-3</sup> concentration and in various solvents (pyridine, dichloromethane, DMF and DMSO) up to  $4 \times 10^{-5}$  mol dm $^{-3}$  concentration. On the other hand, Cu(II)Pc (7) formed aggregates in THF at concentrations higher than  $3.6 \times 10^{-5}$  mol dm<sup>-2</sup> and showed monomeric behavior in THF, DMF and DMSO at  $2.4 \times 10^{-5}$  mol dm<sup>-3</sup>. Furthermore, the photochemical and photophysical properties of the metal free (4), Zn(II) (6) and Ti(IV) (8) phthalocyanines were investigated in THF. All the investigated phthalocyanines showed similar fluorescence behavior in THF. The synthesized Ni(II) (5) and Cu(II) (7) phthalocyanines were not evaluated for this purpose because of the paramagnetic behavior of the central metals in the cavity of these complexes. Singlet oxygen generation properties of these phthalocyanine compounds were also investigated and the order of singlet oxygen quantum yields were found as: Zn(II) Pc (6) > Ti(IV) Pc (8) > unsubstituted Zn(II) Pc (ZnPc) > metal free Pc (4). The degradation of the studied compounds was studied under light irradiation and the oxotitanium (IV) phthalocyanine derivative was found to be very sensitive to light irradiation. The fluorescence quenching behavior of the studied novel peripherally tetra 4-(1,3-benzothiazol-2yl)phenoxy substituted metal free (4), Zn(II) (6) and Ti(IV) (8) phthalocyanines by the addition of 1,4benzoquinone was also studied.

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# 1. Introduction

Phthalocyanines (Pcs) have been under systematic study for more than 70 years due to their glorious functional properties [1]. Pcs are used in a number of applications due to their high stability, diverse coordination properties and improved spectroscopic characteristics. Possible application areas of Pcs are electrophotography, molecular electronics, photovoltaic and solar cells, Langmuir–Blodgett films, gas sensors, electrochromic display devices, NLO, optical discs and photosensitizers in photodynamic therapy of cancer (PDT) [2,3].

On the other hand, nitrogen and sulfur containing aromatic heterocyclic compounds, called benzothiazole and its derivatives, are very important species [4]. They are popular molecules due to their pharmaceutical and biological activities, such as antitumor [5], local anesthetic [6], antimicrobial [7] and antiglutamate/ antiparkinson agents. Recently, these compounds have been widely used for the preparation of anti-inflammatory drugs and analgesics [8], organic optoelectronic materials, second-order non-linear optical (NLO) materials [9], calcium channel antagonists [10], liquid crystals [11], fluorophores [12], inhibitors of several enzymes, azo dyes [13,14] and corrosion inhibitors [15–17].

Pcs are useful photosensitizers due to their high molar absorption coefficients, long lifetimes of the photoexcited triplet states and photostabilities [18,19]. One of the most important problems related to Pcs is their low solubility in common organic solvents, such as chloroform, methanol, acetone, THF, diethylether and ethyl acetate. Their insolubility does not allow scientists to investigate them. Locating bulky groups or long alkyl, alkoxy or alkylthio chains to peripheral areas or quaternary ion formation enhances the solubility of phthalocyanine products in many solvents [20]. In view of the biological importance of both benzothiazoles and phthalocyanines, it is worthwhile to combine these two functional structures into a single compound.

In the last decade, microwave heating technology has arisen as a strategic alternative to thermal energy due to advantages such as selectivity, rapidity in heating and cooling, decreased reaction





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time, increased yields and easy improved controllability [21–23]. From this perspective, microwave assisted synthesis of phthalocyanines is even more important [23–25].

In this study, the synthesis, characterization and structural investigation of metal-free and Ni(II), Zn(II), Cu(II) and Ti(IV) metallo phthalocyanines containing nitrogen, sulfur and oxygen donor atoms on the periphery are described. They are discussed below on the basis of their spectroscopic characteristics. The photophysical and photochemical properties of the novel metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines were also investigated in THF and results are compared.

## 2. Experimental

# 2.1. Materials

4-(1,3-Benzothiazol-2-yl)phenol (1) [26] and 4-nitrophthalonitrile (2) [27] were prepared according to literature procedures. All reactions were carried out under an atmosphere of dry, oxygenfree nitrogen, using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [28].

#### 2.2. Equipment

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in CDCl<sub>3</sub>, and chemical shifts are reported  $(\delta)$  relative to Me<sub>4</sub>Si as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer Spectrum one FT-IR spectrometer using KBr pellets. The mass spectra were measured with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer equipped with chloroform-methanol as the solvent. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument and the obtained values agreed with the calculated ones. A Beko MD 1500, 2.45 MHz domestic microwave oven was used in the synthesis of all the phthalocyanines, except for metal-free and Ti(IV) Pc. Melting points were measured on an electrothermal apparatus and were uncorrected. UV-Vis spectra were recorded by means of Unicam UV2-100 and Shimadzu 2101 UV-Vis spectrophotometers, using 1 cm path length cuvettes at room temperature. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. A General Electric quartz line lamp (300 W) was used for photoirradiation studies. A 600 nm glass cut off filter (Intor) 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 ( $\Phi_F$ ) were determined by the comparative method using Eq. (1) [29].

$$\Phi_{\rm F} = \Phi_{\rm F}({\rm Std}) \frac{F \cdot A_{\rm Std} \cdot n^2}{F_{\rm Std} \cdot A \cdot n_{\rm Std}^2} \tag{1}$$

where *F* and *F*<sub>std</sub> are the areas under the fluorescence emission curves of the samples (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines) and the standard, respectively. *A* and *A*<sub>std</sub> are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. *n* and *n*<sub>std</sub> are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc ( $\Phi_F = 0.20$ ) [30] was employed as the standard

in DMSO. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes ( $\tau_0$ ) were determined using the PhotochemCAD program [31] which uses the Strickler–Berg equation. The fluorescence lifetimes ( $\tau_F$ ) were evaluated using Eq. (2).

$$\Phi_{\rm F} = \frac{\tau_{\rm F}}{\tau_0} \tag{2}$$

## 2.4. Photochemical parameters

#### 2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) determinations were carried out using the experimental set-up described in the literature [32–34] in THF. Typically, a 3 mL portion of the respective substituted phthalocyanine (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**)) 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 the references [32–34].

Singlet oxygen quantum yields ( $\Phi_{\Delta}$ ) were determined in air using the relative method with unsubstituted ZnPc (in THF) as the reference. DPBF was used as a chemical quencher for singlet oxygen in THF. Eq. (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  $\Phi_{\Delta}^{Std}$  is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ( $\Phi_{\Delta}^{Std} = 0.53$  in THF) [35]. *R* and  $R_{Std}$  are the DPBF photobleaching rates in the presence of the respective samples (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines) and standards, respectively.  $I_{abs}$  and  $I_{abs}^{Std}$  are the rates of light absorption by the samples and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [36], the concentration of the quencher was lowered to  $\sim 3 \times 10^{-5}$  M. Solutions of sensitizer ( $1 \times 10^{-5}$  M) containing DPBF was prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm was monitored. A light intensity of  $6.39 \times 10^{15}$  photons s<sup>-1</sup> cm<sup>-2</sup> was used for  $\Phi_{\Delta}$  determinations.

#### 2.4.2. Photodegradation quantum yields

Photodegradation quantum yield ( $\Phi_d$ ) determinations were carried out using the experimental set-up described in the literature [32–34]. Photodegradation quantum yields were determined using Eq. (4),

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

where  $C_0$  and  $C_t$  are the sample (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanines) concentrations before and after irradiation respectively, V is the reaction volume,  $N_A$  is Avogadro's constant, S is the irradiated cell area, t is the irradiation time and  $I_{abs}$  is the overlap integral of the radiation source light intensity and the absorption of the samples. A light intensity of  $2.13 \times 10^{16}$  photons s<sup>-1</sup> cm<sup>-2</sup> was employed for  $\Phi_d$  determination.

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

Fluorescence quenching experiments on the substituted phthalocyanine compounds (metal-free (**4**), Zn(II) (**6**) and Ti(IV) (**8**)) 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 M. The fluorescence spectra of the substituted phthalocyanine compounds at each BQ concentration were recorded, and the changes in fluorescence intensity were related to the BQ concentration by the Stern–Volmer (SV) equation [37] (Eq. (5)):

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

where  $I_0$  and I are the fluorescence intensities of the 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  $\tau_F$  (Eq. (6)):

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

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

## 2.5. Synthesis

## 2.5.1. 4-[4-(1,3-Benzothiazol-2-yl)phenoxy]phthalonitrile (3)

A mixture of 4-(1,3-benzothiazol-2-yl)phenol (1) (500 mg, 2.2 mmol) and dry DMF (20 ml) was charged into a 100 ml onenecked flask and stirred at room temperature under an inert nitrogen atmosphere. 4-Nitrophthalonitrile (2) (381 mg, 2.2 mmol) was added to the solution and the temperature was increased up to 55-60 °C. Powdered dry K<sub>2</sub>CO<sub>3</sub> (456 mg, 3.3 mmol) was added to the system in eight equal portions at 15 min intervals, with efficient stirring, and the reaction system was stirred at the same temperature for 4 days. Aliquots were taken and checked periodically for completeness of the reaction and observed by thin layer chromatography (TLC) (chloroform). The reaction system was cooled and poured into ice-water and then mixed for 24 h. The mixture was filtered and dried in vacuum over P<sub>2</sub>O<sub>5</sub> for 4 h and recrystallized from ethanol to give a light orange crystalline powder. Yield: 67 mg, (86%), mp: 90-92 °C. Anal. Calc. for C<sub>21</sub>H<sub>11</sub>N<sub>3</sub>OS: C, 71.31; H, 3.11; N, 11.88. Found: C, 71.43; H, 2.95; N, 11.53. IR (KBr tablet) v<sub>max</sub>/cm<sup>-1</sup>: 3044 (Ar−CH), 2232 (C≡N), 1594–1562 (C=N/C=C), 1477-1434 (=C-S), 1087-1013 (C-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), (δ, ppm): 8.22–8.15 (dt, 2H/Ar–H<sub>e(e')</sub>, J = 9.00 and 2.60 Hz), 8.10–8.05  $(dt, 1H/Ar-H_f, I = 7.60 \text{ and } 0.80 \text{ Hz}), 7.95-7.91 (dt, 1H/Ar-H_a)$ I = 7.80 and 0.80 Hz), 7.78–7.74 (d, 1H/Ar-H<sub>b</sub>, I = 7.60 Hz), 7.56– 7.48 (td, 1H/Ar- $H_i$ , J = 7.80 and 1.60 Hz), 7.46-7.41 (dd, 1H/Ar- $H_g$ , J = 7.60 and 1.60 Hz), 7.38–7.31 (dd, 1H/Ar–H<sub>h</sub>, J = 7.40 and 1.80 Hz), 7.28-7.26 (m, 1H/Ar-H<sub>c</sub>), 7.23-7.16 (dt, 2H/Ar-H<sub>d(d')</sub>, J = 9.00 and 2.60 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ( $\delta$ , ppm): 166.23 (C<sub>3</sub>-NS), 160.92 (C<sub>1</sub>-O), 155.75 (C<sub>2</sub>-O), 154.02 (C<sub>4</sub>-N), 135.56 (C<sub>5</sub>-S), 135.06, 131.58, 129.89, 126.58, 125.53, 123.30, 122.09, 121.84, 121.72, 120.90, 117.81, 115.24 (C=N), 114.78 (C=N), 109.55. MS (ESI), (*m*/*z*): Calculated: 353.40; Found: 353.97 [M]<sup>+</sup>.

## 2.5.2. Metal-free phthalocyanine (4)

A standart Schlenk tube was charged with (212 mg, 0.65 mmol) of 3, 3 ml of N,N-dimethylaminoethanol (DMAE) and (0.23 ml, 1.51 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under a nitrogen atmosphere. The reaction mixture was stirred at 160 °C for 24 h. Then, the reaction mixture was cooled and evaporated to dryness. The remaining dark green solid was stirred with methyl alcohol for 24 h. The product was filtered and washed with hot methyl alcohol and diethyl ether successively, and dried in vacuum over P2O5. Purification of the solid crude product was accomplished by preparative silicagel plate (0.5 mm) with THF as the eluent to give a dark green powder. Crude yield: 85 mg, (36.56%), after purification of 25 mg, yield: 6.5 mg, (26%), mp: 230-233 °C (decomposition). Anal. Calc. for C<sub>84</sub>H<sub>46</sub>N<sub>12</sub>O<sub>4</sub>S<sub>4</sub>: C, 71.27; H, 3.25; N, 11.88. Found: C, 71.09; H, 3.53; N, 12.01. IR (KBr tablet) v<sub>max</sub>/cm<sup>-1</sup>: 3286 (-NH), 3050 (Ar-CH), 1600-1517 (CH=N/C=C), 1474, 1435 (=C-S), 1234-1165, 1092-1011 (=C-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), ( $\delta$ , ppm): 8.04–7.91 (m, 12H/Ar-H<sub>e(e'),f</sub>), 7.89–7.80 (m, 8H/Ar-H<sub>a,b</sub>), 7.39-7.27 (m, 12H/Ar-H<sub>i,g,h</sub>), 7.24-6.99 (m, 12H/

Ar-H<sub>c,d(d')</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ( $\delta$ , ppm): 173.99 (C<sub>3</sub>-NS), 168.01 (C<sub>1</sub>-O), 161.51 (C<sub>2</sub>-O), 158.0 (C<sub>4</sub>-N), 156.01 (C<sub>5</sub>-S), 154.32 (C<sub>isoiminoindoline</sub>), 146.12, 140.0, 138.55, 135.21, 131.11, 129.81, 127.19, 126.60, 125.50, 123.44, 121.93, 107.89. UV-Vis (THF)  $\lambda_{max}/nm$  [(10<sup>-5</sup> log  $\varepsilon$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 320(4.36), 607(3.63), 644(3.86), 663(4.23), 697(4.30). MS (ESI), (*m/z*): Calculated: 1414.26; Found: 1415.89 [M+H]<sup>+</sup>.

## 2.5.3. Ni(II) phthalocyanine (5)

A mixture of compound **3** (100 mg, 0.283 mmol), anhydrous Ni(CH<sub>3</sub>COO)<sub>2</sub> (12.5 mg, 0.071 mmol), dry DMAE (3 ml) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.067 ml, 0.44 mmol) was irradiated in a microwave oven at 1000 W for 15 min. Then the mixture was diluted with hot methyl alcohol and stirred for 12 h. The product was filtered and then washed with hot methyl alcohol, diethyl ether and dried in vacuum over P<sub>2</sub>O<sub>5</sub>. Purification of the solid crude product was accomplished by preparative silicagel plate (0.5 mm) with THF-chloroform (95:5) as eluents to give a dark green powder. Crude yield: 40 mg (38.46%), after purification of 25 mg, yield: 7.5 mg, (30%), mp: 210-213 °C (decomposition). Anal. Calc. for C<sub>84</sub>H<sub>44</sub>N<sub>12</sub>O<sub>4</sub>S<sub>4</sub>Ni: C, 68.56; H, 2.99; N, 11.43; Ni, 3.99. Found: C, 68.85; H, 2.84; N, 11.77; Ni, 4.20. IR (KBr tablet) v<sub>max</sub>/cm<sup>-1</sup>: 3060 (Ar-CH), 1599–1514 (CH=N/C=C), 1472–1432 (=C-S), 1234-1164, 1093-1053 (=C-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), (δ, ppm): 9.02-8.51 (m, 12H/Ar-H<sub>e(e'),f</sub>), 8.24-8.18 (m, 8H/  $Ar-H_{a,b}$ ), 7.88–7.69 (m, 12H/Ar- $H_{i,g,h}$ ), 7.51–7.46 (m, 12H/ Ar- $H_{c,d(d')}$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ( $\delta$ , ppm): 177.20 (C<sub>3</sub>-NS), 166.98 (C1-O), 161.42 (C2-O), 159.00 (C4-N), 156.19 (C5-S), 150.45 (Cisoiminoindoline), 144.71, 142.98, 140.27, 134.51, 127.69, 125.74, 124.54, 122.43, 121.51, 120.39, 115.0, 103.0. UV-Vis (THF)  $\lambda_{\text{max}}/\text{nm}$  [(10<sup>-5</sup> log  $\varepsilon$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 324(4.67), 613(4.04), 680(4.79). MS (ESI), (m/z): Calculated: 1470.18; Found: 1506.54  $[M+2H_2O]^+$ .

## 2.5.4. Zn(II) phthalocyanine (6)

A mixture of compound **3** (100 mg, 0.283 mmol), anhydrous Zn(CH<sub>3</sub>COO)<sub>2</sub> (12.9 mg, 0.071 mmol), dry DMAE (3 mL) and 1,8diazabycyclo[5.4.0]undec-7-ene (DBU) (0.166 ml, 1.09 mmol) was irradiated in a microwave oven at 1000 W for 10 min. Then the mixture was diluted with hot methyl alcohol and stirred for 12 h. The product was filtered and then washed with hot methyl alcohol, diethyl ether and dried in vacuum over P<sub>2</sub>O<sub>5</sub>. Purification of the solid crude product was accomplished by preparative silicagel plate (0.5 mm) with THF-chloroform (95:5) as eluents to give a dark green powder. Crude yield: 71 mg, (67.98%), after purification of 25 mg, yield: 10 mg (40%), mp: 270-274 °C (decomposition). Anal. Calc. for C<sub>84</sub>H<sub>44</sub>N<sub>12</sub>O<sub>4</sub>S<sub>4</sub>Zn: C, 68.28; H, 2.98; N, 11.38; Zn, 4.43. Found: C, 67.93; H, 2.85; N, 11.88; Zn, 4.74. IR (KBr tablet) v<sub>max</sub>/ cm<sup>-1</sup>: 3058 (Ar-CH), 1600 (C=N/C=C), 1480-1435 (=C-S), 1232–1165, 1088–1045 (=C–O–C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), (δ, ppm): 8.03-7.26 (m, 44H/Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>), (δ, ppm): 177.12 (C<sub>3</sub>-NS), 167.88 (C1-O), 161.32 (C2-O), 161.19 (C4-N), 158.17 (C5-S), 154.45 (Cisoiminoindoline), 147.61, 143.98, 142.17, 135.31, 129.79, 127.84, 126.64, 123.33, 121.91, 120.79, 113.0, 105.0. UV-Vis (THF)  $\lambda_{\text{max}}/\text{nm}$  [(10<sup>-5</sup> log  $\varepsilon$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 316(4.60), 613(3.87), 675(4.61). MS (ESI), (*m*/*z*): Calculated: 1476.18; Found: 1476.19 [M]<sup>+</sup>.

### 2.5.5. Cu(II) phthalocyanine (7)

A mixture of compound **3** (100 mg, 0.283 mmol), anhydrous  $CuCl_2$  (9.5 mg, 0.071 mmol), dry DMAE (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.166 ml, 1.09 mmol) was irradiated in a microwave oven at 1000 W for 15 min. Then the mixture was diluted with hot methyl alcohol and stirred for 12 h. The dark green product was filtered and then washed with hot methyl alcohol, diethyl ether and dried in vacuum over  $P_2O_5$ . Purification of the solid crude product was accomplished by preparative silicagel plate (0.5 mm) with THF-chloroform (95:5) as eluents to give a dark green powder. Crude yield: 91 mg, (87%), after purification of 25 mg, yield: 9.5 mg (38%), mp: 240–245 °C (decomposition). *Anal.* Calc. for C<sub>84</sub>H<sub>44</sub>N<sub>12</sub>O<sub>4</sub>S<sub>4</sub>Cu: C, 68.33; H, 2.98; N, 11.39; Cu, 4.31. Found: C, 68.47; H, 3.24; N, 11.58; Cu, 4.08. IR (KBr tablet)  $v_{max}/cm^{-1}$ : 3044 (Ar–CH), 1601 (C=N/C=C), 1479–1429 (=C–S), 1234–1164, 1093–1043 (=C–O–C). UV–Vis (THF)  $\lambda_{max}/nm$  [(10<sup>-5</sup> log  $\varepsilon$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 318(4.73), 612(3.87), 680(4.41). MS (ESI), (*m*/*z*): Calculated: 1475.18; Found: 1521.16 [M+2Na]<sup>2+</sup>.

#### 2.5.6. Ti(IV) phthalocyanine (8)

A mixture of compound 3 (275 mg, 0.78 mmol), urea (23.3 mg, 0.39 mmol), and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.17 ml, 1.12 mmol) were mixtured in dry *n*-amyl alcohol and heated to 120 °C. At that temperature, titanium (IV) butoxide  $Ti(OBu)_4$  (0.081 ml) was added through a syringe and the reaction mixture was heated at reflux at 155 °C for 7 h. After cooling to room temperature, the mixture was poured into n-hexane and stirred for 12 h. Then the dark green product was filtered, washed with hot diethyl ether and dried in vacuum over P<sub>2</sub>O<sub>5</sub>. Purification of the solid crude product was accomplished by preparative silicagel plate (2 mm) with chloroform-methanol (95:5) as eluents to give a dark green powder. Crude yield: 109 mg, (94%), after purification of 55 mg, yield: 14.0 mg (25.5%), mp: >300 °C (decomposition). Anal. Calc. for C<sub>84</sub>H<sub>44</sub>N<sub>12</sub>O<sub>5</sub>S<sub>4</sub>Ti: C, 68.25; H, 2.98; N, 11.38; Ti, 3.24. Found: C, 68.20; H, 3.05; N, 11.18; Ti, 3.32. IR (KBr tablet) v<sub>max</sub>/cm<sup>-1</sup>: 3049 (Ar-CH), 1630 (C=N/C=C), 1474-1432 (=C-S), 1234-1163, 1067-1006 (=C-O-C), 965 (Ti=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>), ( $\delta$ , ppm): 8.05–7.30 m, (44H/Ar–H). UV–Vis (THF)  $\lambda_{max}/nm$  $[(10^{-5} \log \varepsilon \,\mathrm{dm^3 \,mol^{-1} \, cm^{-1}})]$ : 319(4.34), 611(4.66), 636(3.93), 666(4.19), 698(4.46). MS (ESI), (*m*/*z*): Calculated: 1476.91; Found: 1477.89 [M+H]<sup>+</sup>.

## 3. Results and discussion

## 3.1. Outlook of the synthesized compounds

The preparation of 4-(1,3-benzothiazol-2-yl)phenoxy substituted phthalonitrile (**3**) and its target metal-free (**4**) and metallophthalocyanine (**5**, **6**, **7** and **8**) derivatives is shown in Fig 1. The structures of the novel compounds were characterized by a combination of  ${}^{1}\text{H}/{}^{13}\text{C}$  NMR, IR, UV–Vis, elemental analysis and mass spectral data.

### 3.2. Spectroscopic characterization via complementary techniques

Compound 3 was obtained from the reaction of 4-(1,3-benzothiazol-2-yl) phenol (1) with 4-nitrophthalonitrile (2) in dry K<sub>2</sub>CO<sub>3</sub>/dry DMF under N<sub>2</sub> atmosphere at 55–60 °C in a Schlenk system over 4 days. This was accomplished by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with compound 1 [38-42]. A comparison of the IR spectral data clearly indicates the formation of compound **3** by the disappearance of the O-H band of **1** at 3401 cm<sup>-1</sup>, and by the appearance of a new vibration band at 2228 cm<sup>-1</sup> for ( $C \equiv N$ ) stretching and at 1287–1207 and 1087–1013 cm<sup>-1</sup> for =C-O-C vibration bands. In the <sup>1</sup>H NMR spectrum of compound **3**, the disappearance of the resonance at 10.25 ppm belonging to the -OH group also confirms the existence of the expected compound 3. The functionalized phthalonitrile **3** seems to be a very good resonance (Fig. 2). In the <sup>1</sup>H NMR spectrum of this compound, the  $H_{d(d')}$  and  $H_{e(e')}$ ,  $H_f$ ,  $H_g$ ,  $H_h$ , and H<sub>i</sub> protons possess AA'XX' and AA'BB' spin systems, respectively, and the H<sub>a</sub>, H<sub>b</sub> and H<sub>c</sub> protons associated with nitrile show an ABX spin system, as expected [43,44]. The  $H_{d(d')}$  and  $H_{e(e')}$  protons have been split into a pseudo-doublet of triplets, instead of double doublets, due to the long-range interactions, (meta and/or para positioned couplings), therefore they were each not able to affect the other sufficiently, as shown in Fig. 2 [43–45]. As a consequence of the strong electron-withdrawing effect of the cyano group with sp hybridisation and azomethine groups with sp<sup>2</sup> hybridisation, the lowest shifted signals at 8.15-8.22, 8.05-8.10, 7.91-7.95 and 7.74–7.78 ppm have been assigned to exterior aromatic protons of the fragment with related terminal groups. Five sets of resonances have been observed at 7.48-7.56, 7.41-7.46, 7.31-7.38, 7.26-7.28 and 7.16-7.23 ppm, integrating for five protons each, making a total of 24 protons expected for the periphery protons of each phthalocyanine ring. While the <sup>1</sup>H NMR spectra of **1** and **3** are mostly similar, the proton-decoupled <sup>13</sup>C NMR spectrum indicates the presence of a nitrile carbon atom in **3** at  $\delta$  = 115.24 and 114.78 ppm. In addition, the mass spectrum of **3** shows a molecular ion peak at  $m/z = 353.97 \text{ [M]}^+$ , supporting the proposed formula for this compound.

In a microwave oven, all attempts to obtain the metal free (4) and Ti(IV) Pc (8) resulted in failure. So, the metal-free (4) and Ti(IV) Pc (8) derivatives were obtained directly by the reaction of the substituted phthalonitrile 3 with DMAE and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) [42] and of the substituted phthalonitrile **3** with dry *n*-amyl alcohol/urea/DBU/Ti(OBu)<sub>4</sub> mixtures, respectively. On the other hand, in the presence of metal salts, cyclotetramerization of the phthalonitrile based on 1,3-benzothiazol 3 gave the metal phthalocyanines 5, 6, 7, and 8 [42,46,47]. In the cases of 5, 6 and 7 metal salts, the solvent for the microwaveassisted method was DMAE (N,N-dimethylaminoethanol), and for 8 the solvent was dry *n*-amyl alcohol. In addition, in the microwave-assisted method, the reactions of 5, 6 and 7 were accomplished in DMAE/DBU mixtures at 1000 W in 15 min for Ni(II), 10 min for Zn(II) and 15 min for Cu(II), whereas in the classical method, the reaction of 8 was accomplished in dry *n*-amyl alcohol/urea/DBU media after 7 h.

The IR spectrum of the metal-free phthalocyanine **4** shows the known classical –NH band (inner –NH) at 3286 cm<sup>-1</sup>, as indicated in previous reports [42,46–51]. The rest of the spectrum of **4** is similar to that of **3**, except for the C $\equiv$ N group in **3**. The typical shielding of the inner core protons belonging to metal-free phthalocyanines, which are generally located in the negative ppm region were not observed in the <sup>1</sup>H NMR spectrum of compound **4** because of strong aggregation of this compound in the solution at the NMR concentration (especially, because of the crowded benzene moieties) [52,53]. The signals related to aromatic groups in the macrocyclic moieties and phthalocyanine skeleton gave a significant absorbance characteristic of the proposed structure. The mass spectrum of **4** shows a molecular ion peak at m/z = 1415.89 [M+H]<sup>+</sup>, supporting the proposed formula of this compound.

On the other hand, the studied metallophthalocyanines (**5**, **6**, **7** and **8**) were obtained from the substituted phthalonitrile derivative **3** and the corresponding anhydrous metal salts Ni(CH<sub>3</sub>COO)<sub>2</sub>, Zn(CH<sub>3</sub>COO)<sub>2</sub>, CuCl<sub>2</sub> and Ti(OBu)<sub>4</sub> respectively. In the IR spectra of all the metallophthalocyanines, the disappearance of the strong C=N stretching vibration of **3** at 2228 cm<sup>-1</sup> is an evidence for the formation of metalloPcs. In addition the presence of a Ti=O stretch at 960 cm<sup>-1</sup> confirmed the titanium phthalocyanine formation [54]. Due to the paramagnetic nature of **7**, the <sup>1</sup>H NMR spectrum of this compound could not be recorded. The molecular ion peaks were observed at m/z = 1506.54 [M+2H<sub>2</sub>O]<sup>+</sup> for Ni(II) (**5**), 1476.19 [M]<sup>+</sup> for Zn(II) (**6**), 1521.16 [M+2Na]<sup>2+</sup> for Cu(II) (**7**) and 1477.89 [M+H]<sup>+</sup> for Ti(IV) (**8**) phthalocyanines. These peak values confirm the proposed structures.



Fig. 1. The synthesis of metal-free and metallophthalocyanines.

### 3.3. Ground state electronic absorption spectra

In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one of them is observed in the UV region at ca. 300–500 nm and is called the B band, and the another is observed in the visible region at ca. 600–750 nm and is called the Q band [55]. The Q band absorptions of **4** in THF were observed at  $\lambda = 697$  and 663 nm. A shoulder band was also observed at  $\lambda = 607$  nm. The other absorption band (B) was observed at 320 nm, which is ascribed to deeper  $\pi \rightarrow \pi^*$  levels of LUMO transitions [52,53,56] (Fig 3). As can be seen in the spectrum, the splitting of the Q band absorption of **4** to Q<sub>x</sub> and Q<sub>y</sub> bands can be attributed to the fact that the D<sub>2h</sub> symmetry of the metal-free phthalocyanine is non-degenerate [38–42].

The UV–Vis absorption spectra of the studied metallophthalocyanines (**5**, **6**, **7** and **8**) are given in Figs. 3 and 4. These compounds showed the expected absorptions in THF at the main peaks of the Q and B bands, appearing at  $\lambda$  = 680 nm (corresponding to degenerate D<sub>4h</sub> symmetry), 324 nm (corresponding to the B region) for Ni(II), 675, 613 and 316 nm for Zn(II), 680, 612 and 318 nm for Cu(II), 698, 666, 636, 611 and 319 nm for Ti(IV) phthalocyanines, respectively. These results are typical for metal complexes of substituted and unsubstituted Pcs with D<sub>4h</sub> symmetry [38–42,50–55]. The absorption spectra of **5-8** in THF indicated that all compounds exist mainly as a monomeric species.

### 3.4. Aggregation studies

The high aggregation tendency of phthalocyanine compounds due to interactions between their 18  $\pi$ -electron systems often cause weak solubility or insolubility in many solvents. It also affects seriously their spectroscopic, photophysical, photochemical and electrochemical properties. It has been established that phthalocyanines can form H- and J-type aggregates, depending on the orientation of the induced transition dipoles of their constituent monomers [57–59]. In H-aggregates, the component monomers are arranged into a face-to-face conformation, and transition dipoles are perpendicular to the line connecting their centers. In contrast, in J-aggregates, the component monomers adopt a side-by-side conformation, and their transition dipoles are parallel to the line connecting their centers [60].

Aggregation is dependent on the concentration, nature of the solvent, nature and connection of the substituents, coordinated metal ions and temperature [61,62]. In aggregated species, the intensity of the Q-band starts to decrease, while the intensity of the blue-shifted shoulder starts to increase for H-type aggregation. Taking inspiration from this basic information, the aggregation behavior of the zinc(II) phthalocyanine (6) and copper(II) phthalocyanine (7) were investigated at different concentrations in THF and in different solvents (Figs. 5 and 6). As the concentration was increased, the intensity of the Q-band maxima increased and no new bands, that would be a sign of aggregation, were observed at the measured concentrations. The Zn(II) and Cu(II) phthalocvanine derivatives showed monomeric behavior and the Beer-Lambert law was obeyed between the concentrations  $2 \times 10^{-5}$ and  $7 \times 10^{-5}$  mol dm<sup>-3</sup>,  $1.2 \times 10^{-5}$  and  $3.2 \times 10^{-5}$  mol dm<sup>-3</sup>, respectively (Figs. 5a and 6a). However, Zn(II)Pc and Cu(II)Pc did show aggregation at concentrations higher than  $7 \times 10^{-5}$  and  $3.6 \times 10^{-5}$  mol dm<sup>-3</sup>, respectively. To investigate the effect of the solvents on the aggregation behavior of the Zn(II)Pc and Cu(II)Pc derivatives, the absorptions of the Zn(II)Pc and Cu(II)Pc derivatives were measured in different solvents at  $4 \times 10^{-5}$  and  $2.4 \times 10^{-5}$  mol dm<sup>-3</sup>, respectively. The Zn(II)Pc and Cu(II)Pc derivatives did not show aggregation in the used solvents (Figs. 5b and 6b).

#### 3.5. Fluorescence spectra

Fig 7 shows the fluorescence emission, absorption and excitation spectra of the studied phthalocyanine compounds **4**, **6** and **8** in THF. The fluorescence emission peaks are listed in Table 1. The observed Stokes shifts were within the region observed for A. Aktaş et al./Polyhedron 48 (2012) 80–91



Fig. 2. <sup>1</sup>H NMR spectrum of compound 3 in CDCl<sub>3</sub>.



0.7 0.6 Zn (II) Pc 0.5 Ni (II) Pc 0.4 Absorbance 0.3 0.2 0.1 0 700 300 400 500 600 800 Wavelength (nm)

Fig. 3. The absorption spectra of compound  $sH_2Pc$  (4), CuPc (7) and TiOPc (8) in THF at  $1\times10^{-5}$  mol dm  $^{-3}$  concentration.

phthalocyanine compounds. All the studied phthalocyanine compounds (**4**, **6** and **8**) showed similar fluorescence behavior in THF (Fig. 7). The excitation spectra are similar to absorption spectra

Fig. 4. The absorption spectra of compounds NiPc (5) and ZnPc (6) in THF at  $1\times10^{-5}$  mol dm $^{-3}$  concentration.

for the studied tetra-substituted phthalocyanine compounds (**4**, **6** and **8**) in THF suggesting that the nuclear configurations of the ground and excited states are similar and not affected



**Fig. 5.** (a) Absorption spectra of compound **6** in THF at different concentrations: A;  $2 \times 10^{-5}$ , B;  $3 \times 10^{-5}$ , C;  $4.0 \times 10^{-5}$ , D;  $5 \times 10^{-5}$ , E;  $6 \times 10^{-5}$ , F;  $7 \times 10^{-5}$  mol dm<sup>-3</sup>. (b) Absorption spectra of compound **6** in different solvents. Concentration:  $4 \times 10^{-5}$  mol dm<sup>-3</sup>.

by excitation. The fluorescence emission of the substituted Ti(IV)Pc compound (8) is less intense than the other studied metal-free (4) and Zn(II) (6) phthalocyanine compounds in THF, suggesting that there is more quenching of the substituted Ti(IV)Pc compound (8).

## 3.6. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields ( $\Phi_F$ ) of the studied phthalocyanine compounds **4**, **6** and **8** are given in Table 2. The  $\Phi_F$  values of these compounds are slightly lower than that of the unsubstituted zinc phthalocyanine, which was used as a standard for the fluorescence quantum yield determinations in THF. For a comparison among the studied phthalocyanine compounds, the  $\Phi_F$  value of the Zn(II)Pc compound (**6**) is the lowest among the studied phthalocyanine compounds.

Fluorescence lifetime ( $\tau_F$ ) values of the studied tetra-substituted phthalocyanine compounds (**4**, **6** and **8**) are higher compared to the unsubstituted zinc phthalocyanine compound in THF, except for the substituted Zn(II)Pc compound (**6**). However, the  $\tau_F$  values are typical for phthalocyanine compounds [63–65].

The natural radiative lifetime ( $\tau_0$ ) and the rate constants for fluorescence ( $k_F$ ) values are also given in Table 2. The  $\tau_0$  values of the studied tetra-substituted phthalocyanine compounds (**4**, **6** and **8**) are higher than for the unsubstituted Zn(II)Pc compound,

except for the tetra-substituted Zn(II)Pc compound in THF. The rate constants for fluorescence ( $k_F$ ) of studied tetra-substituted phthalocyanine compounds (**4**, **6** and **8**) are lower than for the unsubstituted Zn(II)Pc compound, except for the tetra-substituted Zn(II)Pc compound in THF. The  $k_F$  value of compound **6** is the highest among the studied zinc Pc compounds.

#### 3.7. Singlet oxygen quantum yields

The quantity of the singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) is a sign of the capability of the compounds as photosensitizers in photocatalytic applications, for instance PDT. The  $\Phi_{\Delta}$  values of the studied tetra-substituted phthalocyanine compounds (**4**, 6 and **8**) were determined in THF using a chemical method and DPBF used as a scavenger. A reduction of the DPBF absorbance at 417 nm was monitored using a UV–Vis spectrophotometer for all the studied phthalocyanine compounds.

Many factors can be responsible for the magnitude of the singlet oxygen generation by a phthalocyanine, such as the 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 of the phthalocyanine and the ground state of oxygen. It is believed that during photosensitization, the photosensitizer molecule is first excited to its singlet state and through intersystem crossing forms the triplet



**Fig. 6.** (a) Absorption spectra of compound **7** in THF at different concentrations: A;  $1.2 \times 10^{-5}$ , B;  $1.6 \times 10^{-5}$ , C;  $2.0 \times 10^{-5}$ , D;  $2.4 \times 10^{-5}$ , E;  $2.8 \times 10^{-5}$ , F;  $3.2 \times 10^{-5}$  mol dm<sup>-3</sup>. (b) Absorption spectra of compound **7** in different solvents. Concentration:  $2.4 \times 10^{-5}$  mol dm<sup>-3</sup>.

state, and then transfers its energy to ground state oxygen,  $O_2(^3\sum_g)$ , generating excited singlet state oxygen,  $O_2(^{1\Delta}g)$ . This process is known as the Type II mechanism. The formed singlet oxygen is the main cytotoxic species and subsequently degradates the substrate.

There were not any changes in the Q band intensities of the studied tetra-substituted phthalocyanine compounds during the  $\Phi_{\Delta}$  determinations (see Fig. 8 as an example for compound **4**), confirming that the compounds were not degraded during the singlet oxygen studies. The  $arPsi_\Delta$  values of the studied tetra-substituted phthalocyanine compounds (4, 6 and 8) are given in Table 2. While the  $\Phi_{\Lambda}$  value of the metal-free phthalocyanine compound **4** is lower, the  $\Phi_{\Delta}$  values of the Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanine compounds are higher than the unsubstituted Zn(II)Pc compound in THF. The studied tetra-substituted Zn(II)Pc compound (6) showed the highest  $\Phi_{\Delta}$  value among the studied phthalocyanine compounds (Table 2). Generally, Zn(II)Pc compounds possess high triplet yields and they can generate singlet oxygen due to the d<sup>10</sup> configuration of the central Zn<sup>2+</sup> ion, which make them appropriate photosensitizers for PDT applications. The metal-free phthalocyanine compound (4) showed the lowest  $\Phi_{\Delta}$  value among the studied tetra-substituted Pc compounds (Table 2). It is suggest that the presence of a metal ion in the phthalocyanine cavity could enhance intersystem crossing between excited singlet and triplet states.

#### 3.8. Photodegradation studies

Degradation of the molecules under light irradiation gave the idea to study their stability and this is especially important for those molecules intended for use in photocatalytic applications. The collapse of the absorption spectra without any distortion of the shape confirms photodegradation not associated with photo-transformation into different forms of MPc absorbing in the visible region. The spectral changes observed for the studied tetra-substituted phthalocyanine compounds **4**, **6** and **8** during light irradiation are as shown in Fig. 9 (using compound **9** as an example in THF), and these confirm photodegradation occurred without phototransformation.

Table 2 shows that the  $\Phi_d$  values of the studied tetra-substituted metal-free (**4**) and Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanine compounds are higher than the unsubstituted Zn(II)Pc compound and that these studied compounds are less stable to degradation under light irradiation compared to the unsubstituted Zn(II)Pc



Fig. 7. Absorption, excitation and emission spectra of the compounds: (A) for complex 4, (B) for complex 6 and (C) for complex 8 in THF. Excitation wavelength = 640 nm for 4, 645 nm for 6 and 635 nm for 8.

Compound	Q band $\lambda_{max}$ (nm)	$\log \varepsilon$	Excitation $\lambda_{Ex}$ (nm)	Emission $\lambda_{Em}$ (nm)	Stokes shift $\varDelta_{Stokes}$ (nm)
4	697, 663	4.88, 4.87	698, 665	703	5
5	680	4.79	-	-	-
6	675	5.27	675	681	6
7	680	4.29	-	_	_
8	698	4.91	699	703	4
ZnPc <sup>a</sup>	666	5.19	666	673	7

<sup>a</sup> Data from Ref. [64].

Table 1

compound in THF. Especially, the  $\Phi_d$  value of Ti(IV) phthalocyanine compound **8** is very sensitive to light irradiation.

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

Phthalocyanine compounds 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 phthalocyanine-quinone systems have proved to be the favored candidates for understanding the energy transfer process [34,66].

The fluorescence quenching behavior of the studied tetrasubstituted phthalocyanine compounds **4**, 6 and **8** by BQ in THF was found to obey Stern–Volmer kinetics, which is consistent with

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Compound	$arPhi_{ m F}$	$\tau_{\rm F}({\rm ns})$	$\tau_0$ (ns)	$k_{\rm F}^{\rm a}~({ m s}^{-1})~( imes~10^7)$	$arPsi_{ m d}~( imes 10^{-4})$	$arPhi_\Delta$
4	0.24	2.85	11.87	8.42	0.19	0.08
6	0.20	1.65	8.25	12.1	3.49	0.73
8	0.23	3.23	14.05	7.11	0.001	0.63
ZnPc	0.25 <sup>b</sup>	2.72 <sup>b</sup>	10.90 <sup>b</sup>	9.17 <sup>b</sup>	0.02 <sup>b</sup>	0.53 <sup>c</sup>

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<sup>a</sup>  $k_{\rm F}$  is the rate constant for fluorescence. Values calculated using  $k_{\rm F} = \Phi_{\rm F} / \tau_{\rm F}$ .

Table 2

<sup>c</sup> Ref. [35].

diffusion-controlled bimolecular reactions. Fig. 10 shows the quenching of compound **4** by BQ in THF as an example. The slope of the plots shown in Fig. 11 gave the  $K_{SV}$  values and these are listed in Table 3. The  $K_{SV}$  values of the studied tetra-substituted phthalocyanine compounds **4**, 6 and **8** are lower than that of the

unsubstituted Zn(II)Pc compound in THF. The substituted metalfree phthalocyanine compound **4** has the highest  $K_{SV}$  value, the substituted Ti(IV)Pc compound **8** has the lowest  $K_{SV}$  in THF. The bimolecular quenching constant ( $k_q$ ) values of the studied tetrasubstituted phthalocyanine compounds (**4**, 6 and **8**) are also lower



**Fig. 8.** The absorption spectral changes during the determination of singlet oxygen quantum yields. This determination was for compound **4** in DMF at a concentration of  $1 \times 10^{-5}$  M. (Inset: plot of DPBF absorbance vs. time.)



Fig. 9. The absorption spectral changes of compound 8 in THF under light irradiation showing the disappearance of the Q-band at five seconds intervals. (Inset: plot of absorbance vs. time.)

<sup>&</sup>lt;sup>b</sup> Ref. [64].



Fig. 10. Fluorescence emission spectral changes of 4  $(1.00 \times 10^{-5} \text{ M})$  on addition of different concentrations of BQ in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M.



**Fig. 11.** Stern–Volmer plots for BQ quenching of substituted metal-free (**4**), zinc (II) (**6**) and oxotitanium(IV) (**8**) phthalocyanines. [MPc]  $\sim 1.00 \times 10^{-5}$  M in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M.

#### Table 3

Fluorescence quenching data for unsubstituted and tetrakis-4-(1,3-benzothiazol-2yl)phenoxy substituted phthalocyanine compounds in THF.

Compound	$K_{\rm SV} ({ m M}^{-1})$	$k_{\rm q}/10^{10}~({\rm dm^3~mol^{-1}~s^{-1}})$
4	32.69	1.14
6	28.62	1.73
8	26.87	0.83
ZnPc <sup>a</sup>	48.48	1.78
<b>8</b> ZnPc <sup>a</sup>	26.87 48.48	0.83 1.78

<sup>a</sup> Data from Ref. [64].

than that of the unsubstituted Zn(II)Pc compound in THF. The order of  $k_q$  values among the substituted compounds also follows the order 6 > 4 > 8 in THF.

# 4. Conclusions

The novel peripherally tetra 4-(1,3-benzothiazol-2-yl)phenoxy substituted metal free (**4**), Ni(II) (**5**), Zn(II) (**6**), Cu(II) (**7**) and Ti(IV) (**8**) phthalocyanines were synthesized and characterized by elemental analysis, IR, UV–Vis, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy. The aggregation behaviors of Zn(II)Pc and Cu(II)Pc were investigated. Zn(II)Pc and Cu(II)Pc showed monomeric behaviors in THF in the  $2 \times 10^{-5}$ – $7 \times 10^{-5}$  mol dm<sup>-3</sup> and  $1.2 \times 10^{-5}$ – $3.2 \times 10^{-5}$  mol dm<sup>-3</sup> concentration ranges, respectively. The aggregation behaviors of Zn(II)Pc and Cu(II)Pc in different solvents were also investigated. All the studied phthalocyanine compounds (**4**, **6** and **8**) showed similar fluorescence behavior in THF, but the

intensity of the emission spectrum of the substituted Ti(IV)Pc compound (**8**) is less intense than the other studied phthalocyanine compounds. The studied tetra substitute Zn(II) (**6**) and Ti(IV) (**8**) phthalocyanine complexes produced singlet oxygen in THF and these complexes are good candidates for photocatalytic applications, such as PDT. The studied phthalocyanine compounds (**4**, **6** and **8**) are less stable to degradation under light irradiation compared to the unsubstituted Zn(II)Pc compound in THF. Especially, the Ti(IV)Pc compound (**8**) is very sensitive to light irradiation. The fluorescence quenching behavior of the studied tetrasubstituted phthalocyanine compounds (**4**, **6** and **8**) were also determined by BQ in THF and the results were found to obey Stern-Volmer kinetics, which is consistent with diffusioncontrolled bimolecular reactions.

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