

## Synthesis of chalcone-containing zinc and cobalt metallophthalocyanines; investigation of their photochemical, DPPH radical scavenging and metal chelating characters

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**Abstract:** In this study, two new phthalocyanines (M = Zn and Co) were synthesized using the (*E*)-4-(4-(3-(4-(benzyloxy)phenyl)acryloyl)phenoxy)phthalonitrile (**3**) as ligand prepared from the chemical reaction of 4-nitrophthalonitrile with (*E*)-3-(4-(benzyloxy)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (**2**). All compounds were characterized using by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV-Vis, FT-IR, and MALDI-TOF mass spectra. Singlet oxygen quantum yields of the synthesized compounds, aggregates in different solutions, metal chelating and 2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical scavenging properties were reported.

**Keywords:** Phthalocyanines; photochemical studies; singlet oxygen; quantum yields; metal chelating; DPPH radical scavenging. ©2020 ACG Publication. All right reserved.

### 1. Introduction

Phthalocyanines (Pcs) and Metallophthalocyanines (MPcs) have been studied for a wide range of applications in view of their distinct and unique optical, spectroscopic, electronic, electrochemical, and thermal properties.<sup>1-3</sup> The presence of diamagnetic metals in phthalocyanines (such as zinc, aluminum, silicon) makes them a useful photosensitizers in photodynamic therapy (PDT) with their high quantum yields and long triplet lifetime.<sup>4-7</sup> PDT requires the use of photosensitive molecules known as photosensitizers. Photoactivation causes the formation of singlet oxygen, which produces peroxidative reactions that can cause cell damage and death.<sup>8</sup> In the earlier studies, hematoporphyrin derivatives and porfimer sodium (photofrin) were successfully used in PDT and, many second-generation photosensitizer, porphyrines and derivatives, have been synthesized for this purpose.<sup>9,10</sup>

The ligands prepared via Claisen-Schmidt condensation are known as chalcones which are belonging to the flavonoid family.<sup>11-12</sup> Chalcones are aromatic pigments with antioxidant effect on fruits, vegetables and various wounded plant tissues, which act as chemical messenger, physiological regulator and inhibitors of cell cycle. The role of flavonoids against cancer, aging, atherosclerosis, ischemic injury, inflammation and neurodegenerative diseases (Parkinson, Alzheimer) have been reported<sup>13-14</sup>. Their antioxidant, anti-tumor, anti-inflammatory and antiviral activities were seriously discussed in the literature.<sup>13-19</sup> In addition, dissolution force of chalcone-based ligands in organic solvents increased the interest in chalcone-fused phthalocyanines.

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Regarding to those properties, synthesis of chalcone-containing zinc and cobalt metallophthalocyanines and their photochemical properties, DPPH radical scavenging and metal chelating capacities were reported herein.

## 2. Experimental

### 2.1. General

Benzyl chloride (Sigma-Aldrich, reagent plus(R), 99%), 4-hydroxybenzaldehyde (Sigma-Aldrich, 98%), 4-hydroxyacetophenone (Sigma-Aldrich, 99%), 4-nitrophthalonitrile (Sigma-Aldrich, 99%), thionyl chloride (SOCl<sub>2</sub>) (Sigma-Aldrich, reagent plus(R), ≥99%), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (Alfa Aesar, anhydrous, 99%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Merck, 98%), zinc acetate dihydrate Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (Sigma-Aldrich, reagent grade), cobalt (II) acetate tetrahydrate Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (Sigma-Aldrich, reagent grade), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) (Alfa Aesar, ACS, 99.0% min), 2,2',2'',2'''-(ethane-1,2-diylidinitrilo)tetraacetic acid (EDTA) (Sigma-Aldrich, ≥98.0% (KT)), ferrous chloride (FeCl<sub>2</sub>) (Sigma-Aldrich, reagent plus (R), 98%) were used as supplied without further purification. Reactions under anhydrous conditions were performed in dried solvents (such as, N,N-dimethylformamide (DMF), dichloromethane (DCM), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and ethanol (EtOH)) under argon atmosphere. Silica gel 60 (40–63 μm, Fluka) was used for chromatography. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a VARIAN Infinity Plus 300 MHz NMR spectrometer. Chemical shifts were expressed in ppm relative to CDCl<sub>3</sub> (δ 7.26 and 77.0 for <sup>1</sup>H and <sup>13</sup>C NMR, respectively) and Tetramethylsilane (TMS) was as a internal standard. IR spectra were recorded on an Ati Unicam Mattson 1000 Series FT-IR (ATR system) spectrometer. MALDI-TOF spectra were taken on Bruker Daltonics flex Analysis. Electronic absorption spectra were measured on a Shimadzu UV 2600 UV-Vis spectrophotometer

### 2.2. Chemistry

#### 2.2.1 Synthesis of 4-(benzyloxy)benzaldehyde (1)

4-Hydroxy benzaldehyde (1.0 g, 8.19 mmol) in DMF was added K<sub>2</sub>CO<sub>3</sub> (1.130 g, 8.19 mmol). The mixture was stirred at room temperature for 30 min. Benzyl chloride (1.400 g, 8.19 mmol) was added dropwise, and the mixture was stirred for 3 h, and the reaction mixture was poured dropwise into ice water (250 mL) and stirred. The white solid product was filtered and washed with water, dried and recrystallized in ethanol to afford **1**. Yield: 1.51 g (87%), m. p.: 69-71 °C. IR  $\nu_{\max}/\text{cm}^{-1}$ : 3362 cm<sup>-1</sup> (Ar-H); 2829 cm<sup>-1</sup> (aliphatic C-H); 1685 cm<sup>-1</sup> (C=O); 1598, 1572, 1508 cm<sup>-1</sup> (Ar-C=C); 1018 cm<sup>-1</sup> (C-O-C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ ppm: 9.86 (s, 1H, CHO), 7.82 (quasi d, H<sub>2</sub> and H<sub>6</sub>, 2H, *J* = 9.0Hz), 7.15 (quasi d, H<sub>3</sub> and H<sub>5</sub>, 2H, *J* = 9.0Hz), 7.48 – 7.32 (m, 5H, Ph), 5.12 (s, 2H, PhCH<sub>2</sub>O). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ ppm: 190.77, 163.62, 135.85, 131.93, 129.96, 128.65, 128.26, 127.44, 115.04, 70.13.

#### 2.2.2 Synthesis of (E)-3-(4-(benzyloxy)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (2)

Compound **2** was prepared according to the method reported in the literature.<sup>20</sup> 4-(Benzyloxy)benzaldehyde (0.500 g, 2.36 mmol) and 4-hydroxyacetophenone (0.321 g, 2.36 mmol) were mixed in ethanol, and then thionyl chloride (0.5 mL) was added After stirring for 14 h, the mixture was added to water. The product was filtered and washed with cold ethanol to afford compound **2** as yellow crystal. Yield: 0.69 g (89%), m. p.: 187-189 °C. IR  $\nu_{\max}/\text{cm}^{-1}$ : 3059 cm<sup>-1</sup> (OH); 3049 cm<sup>-1</sup> (Ar-H); 2849 cm<sup>-1</sup> (aliphatic C-H); 1641 cm<sup>-1</sup> (C=O); 1597, 1586 cm<sup>-1</sup> (Ar-C=C); 1037 (C-O-C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> / CD<sub>3</sub>OD: 5/1) δ ppm: 7.97 (quasi d, 2H, H<sub>2</sub>' and H<sub>6</sub>', *J* = 9.0 Hz), 7.76 (d, CH=CH-CHO, 1H, *J*=15 Hz), 7.62 (quasi d, 2H, H<sub>2</sub>" and H<sub>6</sub>" *J* = 9.0 Hz), 7.10 (d, 2H, H<sub>3</sub>' and H<sub>5</sub>', *J* = 9.0 Hz), 6.92 (d, 2H, H<sub>3</sub>" and H<sub>5</sub>" *J* = 9.0 Hz), 5.12 (s, 2H, PhCH<sub>2</sub>O). <sup>13</sup>C NMR (75

MHz, CDCl<sub>3</sub> / CD<sub>3</sub>OD: 5/1)  $\delta$  ppm: 189.48, 161.57, 160.68, 143.96, 136.38, 131.10, 130.20, 128.69, 128.20, 127.96, 127.54, 119.63, 115.44(2C), 115.24, 70.11.

### 2.2.3 Synthesis of (*E*)-4-(4-(3-(4-(benzyloxy)phenyl)acryloyl)phenoxy)phthalonitrile (**3**)

A mixture of 4-nitrophthalonitrile (0.6 g, 3.45 mmol) and (*E*)-3-(4-(benzyloxy)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (**2**) (1.14 g, 3.45 mmol) in 25 mL of dry DMF was stirred at 50 °C under N<sub>2</sub>. Anhydrous K<sub>2</sub>CO<sub>3</sub> (0.57 g, 4.14 mmol) was added to the mixture for over a period of 1.5 h. After stirring the reaction mixture for a further 24 h, the undissolved salt was removed by filtration. The reaction mixture was added dropwise into ice water (250 mL). The organic phase was extracted with DCM (250 mL) and dried on Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solution under reduced pressure gave yellow residue. The residue was purified by silica gel column chromatography to afford **3**. Yield: 1.20 g (76%), m. p.: 198 °C. IR  $\nu_{\max}/\text{cm}^{-1}$ : 3073 cm<sup>-1</sup> (Ar-H); 2949 cm<sup>-1</sup> (aliphatic C-H); 2230 cm<sup>-1</sup> (C≡N); 1655 cm<sup>-1</sup> (C=O); 1588, 1575, 1508 cm<sup>-1</sup> (C=C); 1025 cm<sup>-1</sup> (C-O-C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 8.19 (quasi d, 2H, H<sub>3'</sub> and H<sub>5'</sub>,  $J = 9.0\text{Hz}$ ), 7.84 (d, 1H, H<sub>3''</sub>,  $J = 15\text{Hz}$ ), 7.78 (overlapped 2 H), 7.51 – 7.23 (m, 9 ArH), 7.20 (d, 2H, H<sub>2''</sub> and H<sub>6''</sub>,  $J = 9.0\text{Hz}$ ), 7.03 (d, 2H, H<sub>3''</sub> and H<sub>5''</sub>,  $J = 9.0\text{Hz}$ ), 5.13 (s, 2H, PhOCH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 188.97, 161.29, 160.86, 157.35, 145.58, 136.50, 135.85, 131.46, 130.67, 128.95, 128.48, 127.77, 122.59, 122.41, 120.38, 119.26, 118.11, 115.58, 115.06, 110.06, 70.36.

### 2.2.4 General Procedure for Preparation of the Synthesis of zinc (II) phthalocyanine (**4a**)

A mixture of **3** (0.1 g, 0.22 mmol), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.058 g, 0.26 mmol) and 2-3 drops 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) were stirred at 130 °C in dry DMF under N<sub>2</sub> for 24 h. The reaction mixture was cooled to rt and undissolved salt was removed by filtration. The dark green solution was poured into ice-water (100 mL) and stirred for 1 h and filtered. The filtrates were washed with a plenty of water then hot ethanol and removed of the unreacted organic materials. The product was dried in the oven to give a crude **4a** which is soluble DCM, THF, DMF and DMSO. Then the it was purified using column chromatography on silica gel. The chromatography was repeated and various solution ratios (DCM / THF, DCM / EtOH, THF / EtOH) were used. All purified fractions were collected to give compound **4a** as green solid. Yield: 0.05 g (43%), m. p.: >350 °C. IR  $\nu_{\max}/\text{cm}^{-1}$ : 3063 cm<sup>-1</sup> (Ar-H); 2958 cm<sup>-1</sup> (aliphatic C-H); 1657 cm<sup>-1</sup> (C=O); 1594, 1574, 1505 cm<sup>-1</sup> (C=N, C=C); 1025 cm<sup>-1</sup> (C-O-C). UV-Vis (DMF),  $\lambda_{\max}$ , nm: 679.5, 618, 354.5. MALDI-TOF MS:  $m/z$  [M]<sup>+</sup> calcd. for C<sub>120</sub>H<sub>80</sub>N<sub>8</sub>O<sub>12</sub>Zn: 1891.38; found [M + H]<sup>+</sup> 1891.17. Elemental analysis for [C<sub>120</sub>H<sub>80</sub>N<sub>8</sub>O<sub>12</sub>Zn]: C, 76.20; H, 4.26; N, 5.92. Found: C, 76.28; H, 4.32; N, 5.99%.

### 2.2.5 General Procedure for Preparation of the Synthesis of Cobalt (II) phthalocyanine (**4b**)

A mixture of **3** (0.1 g, 0.22 mmol), Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.065 g, 0.26 mmol) and 2-3 drops 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) were stirred at 130 °C of dry DMF under N<sub>2</sub> for 24 h. The reaction mixture was cooled down to room temperature. The undissolved salt was removed by filtration. After the dark green product was poured into ice-water (100 mL) and stirred. It was filtered and washed with water, hot ethanol, remove the unreacted organic materials. The resulting dark green product was dried in an oven. This compound is readily soluble DCM, THF, DMF and DMSO. Then the dark green residue was purified using column chromatography on silica gel. The chromatography were repeated with various solution ratios (DCM / THF, DCM / EtOH, THF / EtOH). All purified fractions were collected to afford **4b** as green solid. Yield: 0.06 g (53%), m. p.: >350 °C. IR  $\nu_{\max}/\text{cm}^{-1}$ : 3066 cm<sup>-1</sup> (Ar-H); 2930 cm<sup>-1</sup> (aliphatic C-H); 1656 cm<sup>-1</sup> (C=O); 1592, 1556, 1507 cm<sup>-1</sup> (C=N, C=C); 1025 cm<sup>-1</sup> (C-O-C). UV-Vis (DMF),  $\lambda_{\max}$ , nm: 667.5, 602.5, 345.5. MALDI-TOF MS:  $m/z$  [M]<sup>+</sup> calcd. for C<sub>120</sub>H<sub>80</sub>N<sub>8</sub>O<sub>12</sub>Co: 1884.94; found [M + H]<sup>+</sup> 1884.78. Elemental analysis for [C<sub>120</sub>H<sub>80</sub>N<sub>8</sub>O<sub>12</sub>Co]: C, 76.47; H, 4.28; N, 5.94. Found: C, 76.55; H, 4.25; N, 5.92%.

### 2.3. Metal Ions Chelating Effects Assay

Metal chelating activities of the phthalocyanines were examined using ferrous ion–ferrozine complex method. Results were compared to EDTA, which was used as a reference compound. 500  $\mu\text{L}$  of varying concentrations (25–100  $\mu\text{M}$ ) of phthalocyanine was prepared and added to 2 mM, 50  $\mu\text{L}$   $\text{FeCl}_2$  and 5 mM, 100  $\mu\text{L}$  ferrozine. After 10 minute incubation at room temperature, optical density of the samples was measured at 562 nm. A control assay mixture without phthalocyanine was also studied. All experiments were repeated three times and the results were stated as the mean  $\pm$  standard deviation (S.D.). Metal chelating effect was calculated using the equation below.<sup>21-28</sup>

$$\text{Metal chelating effect (\%)}: \left[ \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \right] \times 100 \quad (\text{Eq. 1})$$

The reduction of DPPH induces the radical to change color (violet to yellow) and this change is quantifiable at 517 nm.

### 2.4. DPPH Radical Scavenging Activity Assay

DPPH radical scavenging activities of Pcs were measured to predict their in vitro antioxidant activities.<sup>29-30</sup> Briefly, 0.5 mL of Pcs **4a** and **4b** at different concentrations in DMSO were added to a freshly prepared 1 mL of 0.1 mM DPPH in methanol. The assay mixtures were incubated in dark for 50 minutes, at room temperature. Their optical density of the assay mixtures was measured at 517 nm. A control without Pcs and a gallic acid standard was studied at the same conditions. All experiments were repeated three times and the results were stated as the mean  $\pm$  standard deviation (S.D.). Free radical scavenging effect of Pcs was calculated using the equation (3).

### 2.5. Singlet Oxygen Measurements

The compound with singlet oxygen quencher was irradiated in the Q band region using photo-irradiation apparatus.<sup>31</sup> Quantum yields  $\Phi_{\Delta}$  for singlet oxygen were performed according to relative method ZnPc in DMSO. DPBF (1,3-diphenylisobenzofuran) was used as a chemical quencher. The experimental part was performed in DMSO. To a solution of **4a** was added a singlet oxygen quencher ( $3 \times 10^{-5}$  mol/dm<sup>3</sup>) and the intensity of light was applied as  $8.15 \times 10^{15}$  photon s<sup>-1</sup> cm<sup>-2</sup> Eq. (2).<sup>32</sup>

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{R \cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot I_{\text{abs}}} \quad (2)$$

Where,

$\Phi_{\Delta}^{\text{Std}}$  defines the singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) for the standard Zn-Pc ( $\Phi_{\Delta}^{\text{Std}} = 0.67$  in DMSO).

$R$  and  $R^{\text{Std}}$  are DPBF photo-bleaching properties in the presence of **4a**.

$I_{\text{abs}}$  and  $I_{\text{abs}}^{\text{Std}}$  are the rate of light used for samples and standard.<sup>33,34</sup>

### 2.6. Photodegradation Measurements

Photodegradation quantum yield ( $\Phi_{\Delta}$ ) was measured by using Eq. (3), to examine the changes in fluorescence in the course of degradation of the compound exposed to light. During the photodegradation of phthalocyanine compounds, the decrease in Q band was determined and the trends of the calibration graphs were calculated in specific time intervals.<sup>35-36</sup> Photodegradation quantum yield ( $\Phi_{\Delta}$ ) determination was described in the literature.<sup>24</sup>

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{abs} \cdot S \cdot t} \quad (3)$$

Where,

$C_0$  and  $C_t$  are MPc concentrations before and after illumination, respectively,

$V$  is the reaction volume,

$N_A$  is Avogadro constant,

$S$  is the irradiated cell,

$t$  is the irradiation time.<sup>37</sup>

### 3. Result and Discussion

#### 3.1. Chemistry

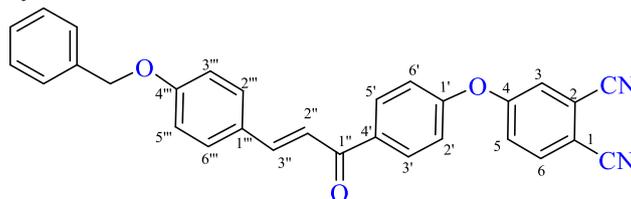
A metal ion in the core of a metallophthalocyanine could be active as a catalyst/photocatalyst. For photocatalytic activities of MPcs, it should contain metal ions, such as Mg (II), Al (III), Si (IV) and Zn (II), with a closed p or d electron configuration, resulting in a highly excited state life time. However, metal phthalocyanines with redox active metal ions, like Co (II) and Fe (II), having an open shell structure, show catalytic and electrocatalytic properties.<sup>38, 39</sup>

Pcs containing four chalcone groups at peripherals were prepared using zinc (II) and cobalt (II) acetate salts (Scheme 1). The synthesis was initiated by reacting 4-hydroxybenzaldehyde with benzyl chloride in DMF in the presence of potassium carbonate as a base, which yielded 4-(benzyloxy)benzaldehyde **1** as a sole product in 87%.<sup>40</sup> Condensation of **1** and 4-hydroxyacetophenone in a mixture of EtOH and SOCl<sub>2</sub> gave the conjugated system, (*E*)-3-(4-(benzyloxy)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one **2**.<sup>20, 38-41</sup> Nucleophilic substitution reaction between **2** and 4-nitrophthalonitrile was performed in DMF, using potassium carbonate as a base at 50 °C for 24 hours under nitrogen atmosphere to afford the donor compound **3** in 76% yield.<sup>42</sup> Syntheses of phthalocyanine derivatives **4a** and **4b** (Scheme 2) were performed at 130 °C, using Zn and Co metal salts under nitrogen atmosphere in DMF in the presence of DBU as a catalyst.<sup>43</sup> and achieved in good yields (43 and 53%).

The selection of metal atoms, i.e. Zn and Co, was made considering intramolecular donor-acceptor interaction between the soluble ligand and the terminal metal valence shells in phthalocyanine complexes. Thus, the final Pcs had good solubility properties obtained through the presence of conjugated systems at the peripherals. They were characterized by using UV-Vis, FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MALDI-TOF mass spectra.

Details of the structure elucidation of compounds **1-2** was discussed in supporting information file to avoid repetition of the literature.

IR spectra of compound **3** (Figure 1, (Figure S13).) demonstrated an aromatic C-H band at 3073 cm<sup>-1</sup> and an aliphatic C-H vibration band at 2931 cm<sup>-1</sup>. A characteristic C≡N-vibration band of phthalonitrile appeared at 2232 cm<sup>-1</sup>. While a C=O band was observed at 1655 cm<sup>-1</sup>, aromatic C=C bands appeared at 1599 cm<sup>-1</sup> and 1588 cm<sup>-1</sup>. Moreover, a band between 1140-1242 cm<sup>-1</sup> was attributed to C-O-C moiety.

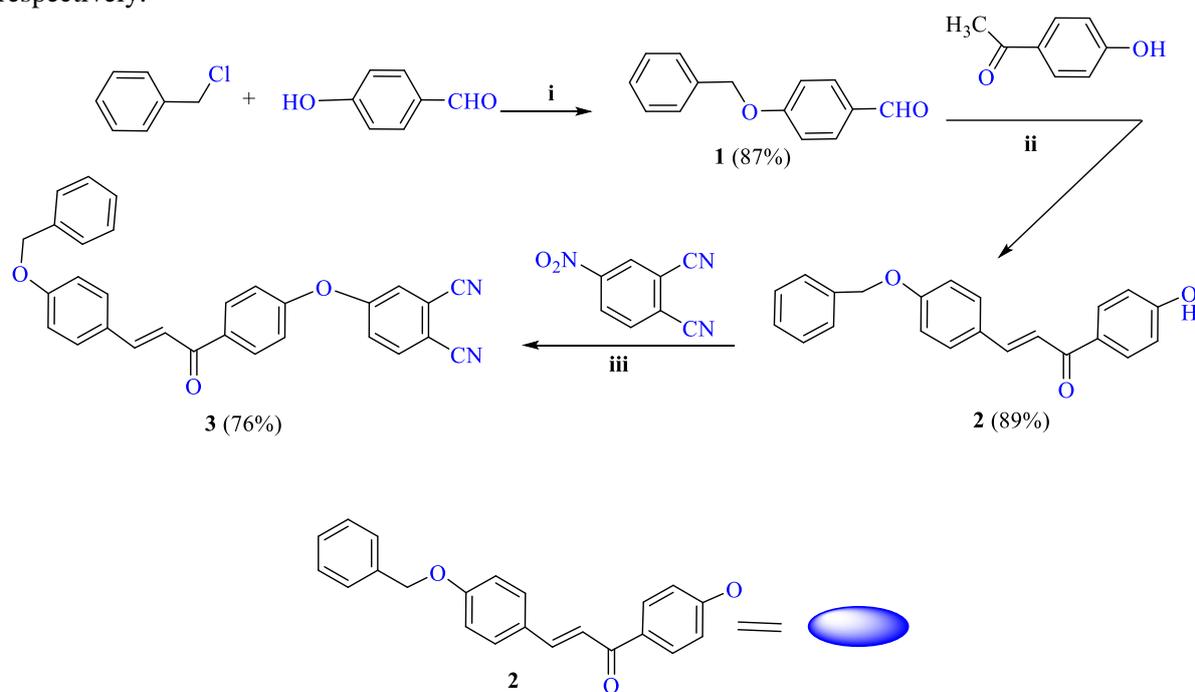


**Figure 1.** (*E*)-4-(4-(3-(4-(benzyloxy)phenyl)acryloyl)phenoxy)phthalonitrile **3**

Regarding the <sup>1</sup>H NMR of the compound **3**, while H<sub>3</sub>/H<sub>5</sub>' resonated as an AA' part of AA' BB' system giving quasi doublet at 8.19 ppm, H<sub>3</sub>'' resonated by giving doublet ( $J=15.0$  Hz) at 7.84 ppm

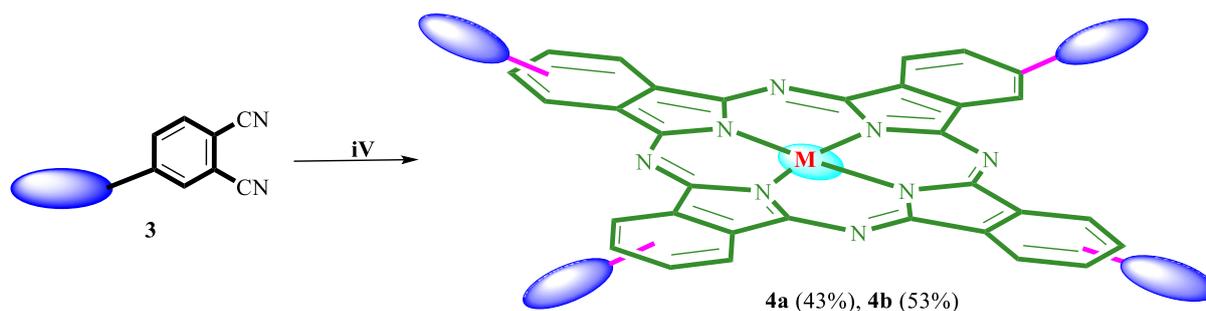
overlapping with H<sub>6</sub> at 7.80 ppm. H<sub>2</sub>'/H<sub>6</sub>' were seen as AA' part of AA' BB' system at 7.63 ppm. 5 ArH of phenyl ring, H<sub>3</sub>, H<sub>5</sub>, H<sub>2</sub>'', resonated as multiplets at 7.55-7.25 ppm (PhCH<sub>2</sub>O protons resonated as singlet at 5.19 ppm (Figure S7 and Figure S11). The <sup>13</sup>C-NMR resonance signals were in agreement with structure (Figure S8-S10).

Although zinc phthalocyanine **4a** looked soluble in common organic solvents, its NMR measurements could not be performed due to aggregation, leading to broadening of the proton signals. Also, the NMR measurements of the cobalt phthalocyanine **4b** was precluded owing to its paramagnetic nature.<sup>20,41</sup> In the electronic absorption spectrum, two absorption bands were observed for the phthalocyanine compounds, which are B and Q bands at about 300-450 and 600-700 nm, respectively.



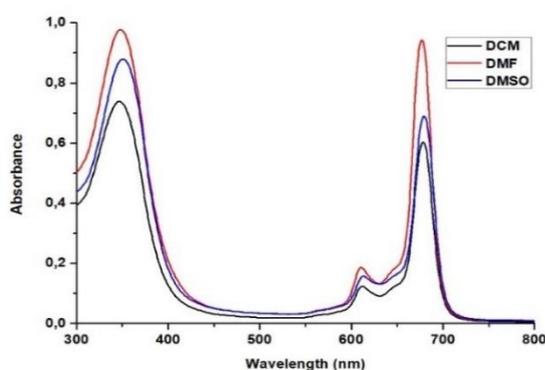
**Scheme 1.** Synthetic route of compounds **1**, **2**, **3**. (i) K<sub>2</sub>CO<sub>3</sub>, DMF, rt; (ii) SOCl<sub>2</sub>, EtOH, r.t., 12 h; (iii) K<sub>2</sub>CO<sub>3</sub>, DMF, 50 °C.

The phthalocyanines developed herein are well soluble in different solvents such as dichloromethane (DCM), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). Moreover, they have low aggregation in these solvents and demonstrate characteristic absorption bands, i.e. a B-band between 360-385 nm and a Q-band band between 580-700 nm (Figure 4 and Figure 5). The UV-Vis spectra of the phthalocyanine derivatives **4a** and **4b** are good indication for their structures. Regarding the IR peaks of **4a** and **4b** (Figure S16 and Figure S19, respectively), while the characteristic functional group vibration of -CN (2232 cm<sup>-1</sup>) were disappeared, appearance of the stretching vibration bands of C=O groups at 1594 cm<sup>-1</sup> (for Pc **4a**), and 1593 cm<sup>-1</sup> (for Pc **4b**) confirmed both phthalocyanines. The characteristic C-O-C bands at 1162 cm<sup>-1</sup> for **4a**, and 1213 cm<sup>-1</sup> for **4b** are also good indications for the structures. The other weak absorption bands between 3064-2865 cm<sup>-1</sup> for **4a**, and between 3068 - 2930 cm<sup>-1</sup> for **4b** are the aromatic =C-H stretching bands for the substituted phthalocyanines. The mass spectra of phthalocyanine derivatives **4a** and **4b** supported the proposed molecular formula. Molecular ion peaks identified *m/z* [M]<sup>+</sup> calcd. for C<sub>120</sub>H<sub>80</sub>N<sub>8</sub>O<sub>12</sub>Zn: 1891.38; found [M + H]<sup>+</sup> 1891.17 for **4a** (Figure S15) and *m/z* [M]<sup>+</sup> calcd. for C<sub>120</sub>H<sub>80</sub>N<sub>8</sub>O<sub>12</sub>Co: 1884.94; found [M + H]<sup>+</sup> 1884.78 for **4b** (Figure S18).



**Scheme 2.** Synthetic route of compounds **4a** and **4b**. **4a**  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , DMF, 130 °C, 24 h; **4b**  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , DMF, 130 °C, 24 h

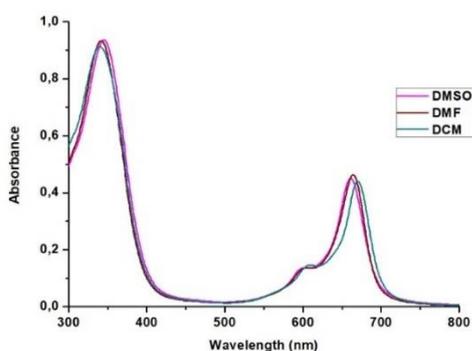
UV-Vis spectra of the compounds **4a** and **4b** were recorded in DMSO, DCM and DMF (Figures 2 and 3, respectively). The  $\lambda_{\text{max}}$  values for B and Q bands performed in these solutions are given in the Tables 1 and 2.



**Table 1.** The  $\lambda_{\text{max}}$  values of B and Q bands for **4a** performed in different solvents

Solvent	$\lambda_{\text{max}}$ , (nm) for B	$\lambda_{\text{max}}$ , (nm) for Q <sub>1</sub>	$\lambda_{\text{max}}$ , (nm) for Q <sub>2</sub>
DMSO	354	619	682.5
DCM	352.5	617.5	682
DMF	354.5	618	679.5

**Figure 2.** UV-Vis absorption spectra of: **4a** in different solvents (concentration =  $1 \times 10^{-5}$  M)

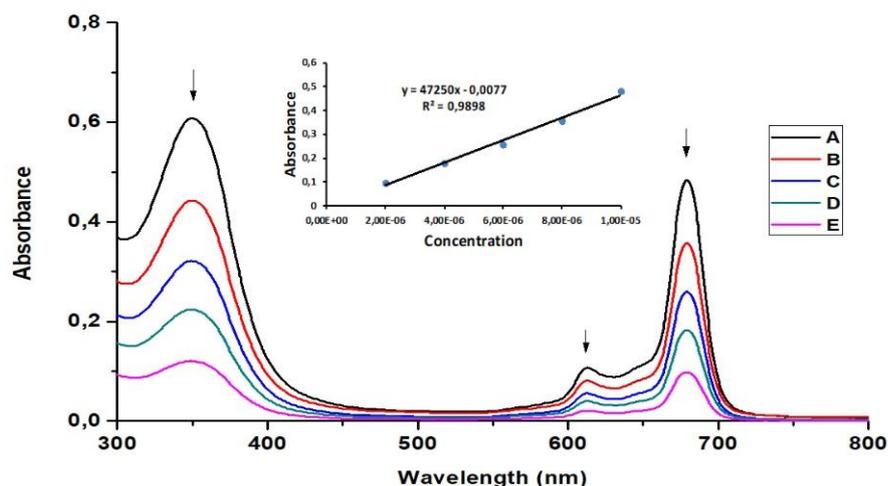


**Table 2.** The  $\lambda_{\text{max}}$  values of B and Q bands for **4b**

Solvent	$\lambda_{\text{max}}$ , (nm) for B	$\lambda_{\text{max}}$ , (nm) for Q <sub>1</sub>	$\lambda_{\text{max}}$ , (nm) for Q <sub>2</sub>
DMSO	359	601.5	664.5
DCM	345	610	674.5
DMF	345.5	602.5	667.5

**Figure 3.** UV-Vis absorptionspectra of: **4b** in different solvents (concentration =  $1 \times 10^{-5}$  M)

In different concentrations, the compound **4a** exhibited a low aggregation. Aggregation behavior of phthalocyanine **4a** in different concentrations depends on its skeleton and the solubility of chalcone groups in the peripheral position attached to this skeleton. Aggregation, which is usually exhibited as a coplanar association, varies according to peripheral or non-peripheral groups, solutions, concentrations and behaviours of the complexed metal ions.<sup>43-46</sup>



**Figure 4.** UV-Vis spectra of ZnPc **4a** in DMSO at different concentrations:  $10 \times 10^{-6}$  (A),  $8 \times 10^{-6}$  (B),  $6 \times 10^{-6}$  (C),  $4 \times 10^{-6}$  (D),  $8 \times 10^{-6}$  mol dm<sup>-3</sup> (E). (inset: plot of absorbance versus concentration)

UV spectra of ZnPc **4a** in DMSO at different concentrations were examined for its aggregation behaviours (Figure 4). At lower concentrations (from  $5 \times 10^{-6}$  to  $1 \times 10^{-6}$ ), the intensity of the Q-band absorption were decreased, and a new band did not form due to aggregation.<sup>44</sup>

### 3.2. Metal Chelating Effects

Fe<sup>2+</sup> has the ability to remove an electron from a peroxide resulting in the formation of a radical.<sup>21-22</sup> In order to avoid radicals in metabolism, Fe<sup>2+</sup> chelation might be a practicable therapeutic approach.<sup>23</sup> Divalent iron can quantitatively *chelates* ferrozine iron yielding a colored complex. The presence of another chelator can block the complex formation. In that case the color is diminished. Measurement of color changes allows the estimation of the chelating capacity of the chelator candidates.<sup>23</sup> Metal chelating activity of the phthalocyanines were determined at 25, 50, 75 and 100  $\mu$ M concentrations using their 1 mM stock solutions in DMSO.

**Table 3.** Ferrous ions chelating activity (%) of the phthalocyanines

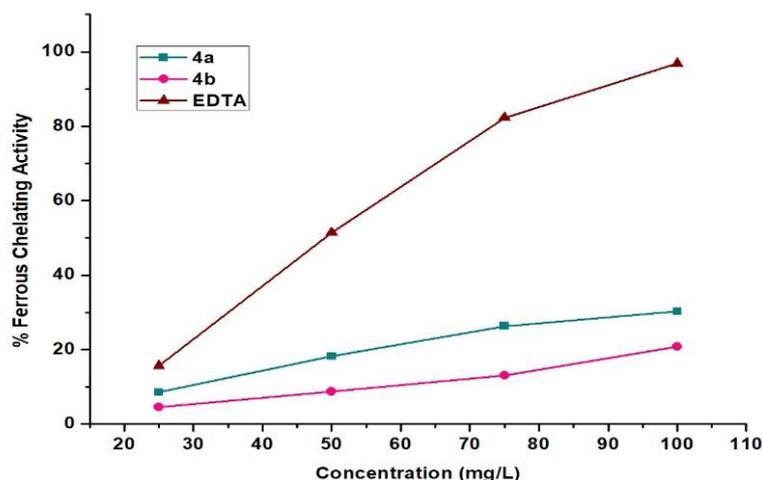
$\mu$ M <sup>a</sup>	<b>4a</b>	<b>4b</b>	EDTA <sup>c</sup>
25	$8.52 \pm 0.18^b$	$4.58 \pm 0.31^b$	$15.65 \pm 0.15^b$
50	$18.27 \pm 0.22^b$	$8.66 \pm 0.28^b$	$51.42 \pm 0.18^b$
75	$26.32 \pm 0.17^b$	$13.12 \pm 0.42^b$	$82.31 \pm 0.08^b$
100	$30.31 \pm 0.31^b$	$20.74 \pm 0.24^b$	$96.85 \pm 0.21^b$

<sup>a</sup> Four experiments were performed for all compounds in each experiment triplicated.

<sup>b</sup> Mean values  $\pm$  SD are shown for triplicate experiments.

<sup>c</sup> Reference compound.

Table 3 presents ferrous ions chelating activity (%) of **4a** and **4b**. For all studied samples, the chelation activity increased with the increase of their concentrations. **4a** was a good chelator and its chelation capacity increased from  $8.52 \pm 0.18\%$  to  $30.31 \pm 0.31\%$ . **4a** and **4b** showed more or less ferrous ion chelation properties when compared with EDTA. Phthalocyanines with similar and higher metal chelating properties were reported in the literature<sup>21-22, 24</sup> (Figure 5)



**Figure 5.** Ferrous chelating activity of **4a** and **4b** complex. The compounds were tested with concentrations ranging from 25  $\mu$ M to 100  $\mu$ M. EDTA was used as reference compound

### 3.3. DPPH Radical Scavenging Activity

This method is mainly based on reduction of 1,1-diphenyl-2-picrylhydrazyl (DPPH), which produces an easily identifiable strong violet color. The reduction of DPPH induces the radical to change color (violet to yellow) and this change is 517 nm.<sup>25</sup> DPPH radical scavenging assay is frequently used to detect the antioxidant capacity of synthesized compounds or plant extracts.<sup>21-22, 25-28</sup> The ability of Pcs to scavenge DPPH radical were studied using above method. Pcs stock solutions in DMSO were treated with DPPH in methanol. Samples were used at different concentrations ranging from 25 to 100  $\mu$ M. DMSO was used as a control. DPPH radical scavenging capacity of Pcs are presented in Table 4. **4a** and **4b** exhibited DPPH radical scavenging capacity at studied concentrations (**4a**: 16.85  $\pm$  0.32%, 23.88  $\pm$  0.16%, 29.74  $\pm$  0.38%, 39.65  $\pm$  0.34% and **4b**: 8.62  $\pm$  0.27%, 14.41  $\pm$  0.37%, 29.45  $\pm$  0.52%, 34.99  $\pm$  0.36%). The highest antioxidant activity was observed with **4a** complex 25  $\mu$ M, 50  $\mu$ M, 75  $\mu$ M and 100  $\mu$ M. **4b** complex was not as effective as gallic acid<sup>24</sup> (Figure 6).

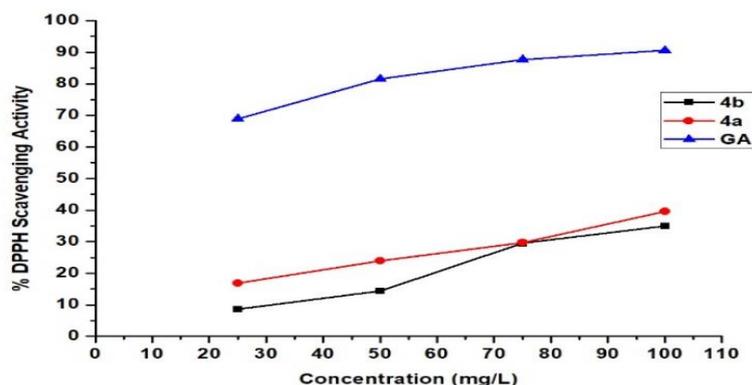
**Table 4.** Radical-scavenging activity on DPPH radicals (%) of the phthalocyanines.

$\mu$ M <sup>a</sup>	<b>4a</b>	<b>4b</b>	Gallic Acid <sup>c</sup>
25	16.85 $\pm$ 0.32 <sup>b</sup>	8.62 $\pm$ 0.27 <sup>b</sup>	68.88 $\pm$ 0.40 <sup>b</sup>
50	23.88 $\pm$ 0.16 <sup>b</sup>	14.41 $\pm$ 0.37 <sup>b</sup>	81.53 $\pm$ 0.42 <sup>b</sup>
75	29.74 $\pm$ 0.38 <sup>b</sup>	29.45 $\pm$ 0.52 <sup>b</sup>	87.71 $\pm$ 0.38 <sup>b</sup>
100	39.65 $\pm$ 0.34 <sup>b</sup>	34.99 $\pm$ 0.36 <sup>b</sup>	90.58 $\pm$ 0.50 <sup>b</sup>

<sup>a</sup> Four experiments were performed for all compounds in each experiment triplicated.

<sup>b</sup> Mean values  $\pm$  SD are shown for triplicate experiments.

<sup>c</sup> Reference compound.

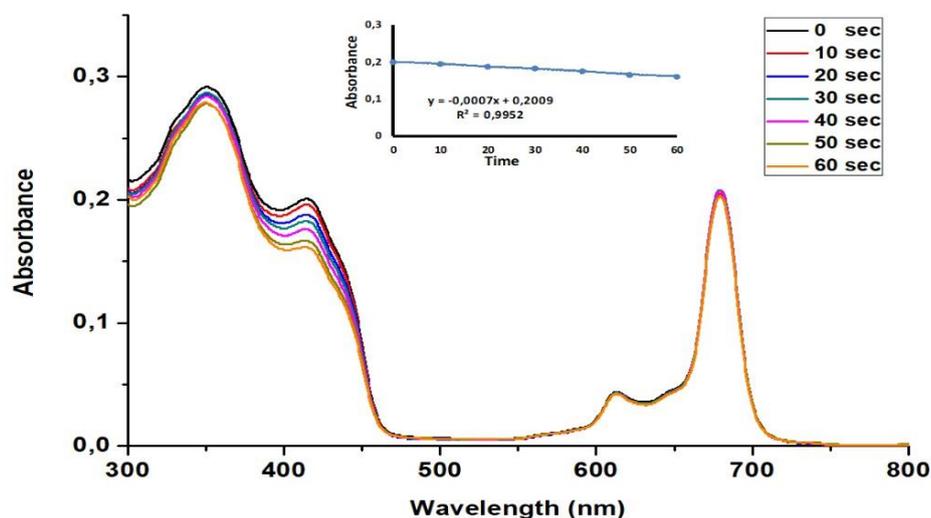


**Figure 6.** Radical-scavenging activity on DPPH radicals (%) of **4a** and **4b** complex. The compounds were tested with concentrations ranging from 25  $\mu\text{M}$  to 100  $\mu\text{M}$ . Gallic acid (GA) was used as standard mixtures

### 3.4. Photochemical Studies

#### 3.4.1. Singlet Oxygen Quantum Yield ( $\Phi_A$ )

To a  $1 \times 10^{-5}$  M zinc complex of **4a** in DMSO was added 1,3-Diphenylisobenzofuran (DPBF) for singlet oxygen quantum yield measurement as an extinguisher in dark. An  $8.15 \times 10^{15}$  photon  $\text{s}^{-1}\text{cm}^{-2}$  was sent to the mixture every 10 seconds. The changes in absorption at 417 nm were then observed (Figure 7). A decrease of B band was observed. The calculated  $\Phi_A$  was found to be high compare with the literature<sup>30</sup> (Table 5). These results indicated that **4a** could be used as a photosensitizer in PDT applications.



**Figure 7.** A typical spectrum for the determination of singlet oxygen quantum yield of **4a** in DMSO using DPBF as the singlet oxygen quencher. Concentration =  $1 \times 10^{-5}$  mol  $\text{dm}^{-3}$ . (Inset: plots of DPBF absorbance vs. time)

#### 3.4.2. Photodegradation and Quantum Yield ( $\Phi_d$ )

Production of singlet oxygen begins with absorption of a photon at 290-700 nm. Energy of this photon is then transmitted to the electrons in the molecule by converting it to a singlet oxygen, a

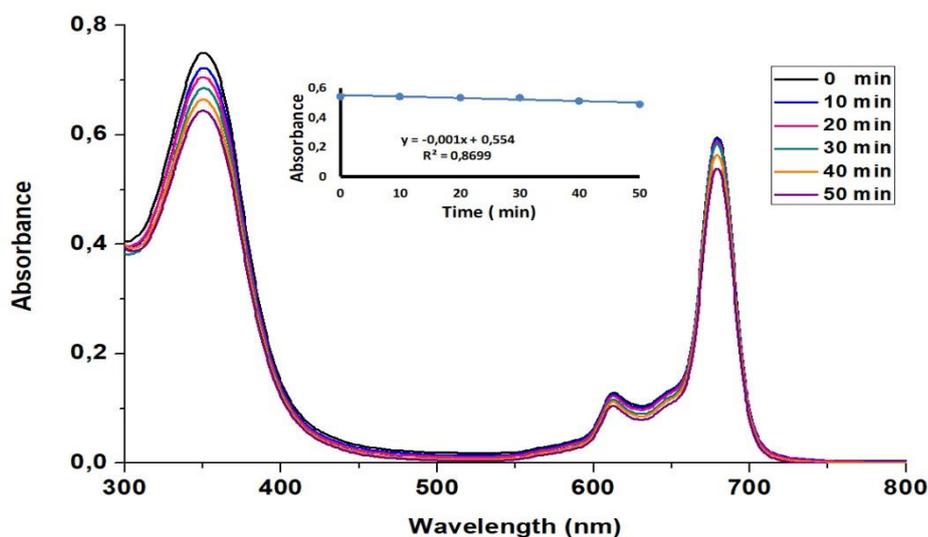
highly reactive form of triplet oxygen. While the molecule is transformed from its basic state into an excited state, it causes formation of functional groups (carbonyl, carboxyl, peroxide, etc.) and new conjugated bonds as well as configuration changes (dehydrogenation, demethylation, dehydromethylation) in the molecule. Moreover, when phthalocyanines are exposed to photons, different reactions may form. If a phthalocyanine contains an acceptor group, it is hardly oxidized, thus, photodegradation reaction slows down.

The compound **4a**, in DMSO, was exposed to UV-Vis light at 682.5 nm for photodegradation. Then, quantum yield in a specific time interval of  $3.26 \times 10^{16}$  photon  $s^{-1}cm^{-2}$ , and the changes in the Q band were examined (Figure. 8). During the photodegradation measurements Q band was observed to decrease over time, i.e. measured every 5 minutes. In line with the literature reports, both photodegradation and quantum yield values of **4a** increased (Table 5).<sup>33</sup> The compounds having photodegradation values in the range of  $10^{-3}$  to  $10^{-6}$  are not considered to be stable, according to the literature.

**Table 5.** Photochemical parameters of **4a** in DMSO

Compound	$\Phi_A$	$\Phi_d$
<b>4a</b>	0.80	$5.7 \times 10^{-4}$
ZnPc <sup>a</sup>	0.67	$2.6 \times 10^{-5}$

<sup>a</sup>Data from Ref.<sup>39</sup>



**Figure 8.** The photodegradation of **4a** in DMSO showing the disappearance of the Q band and the appearance of the reduction band from 0 min to 50 min (Inset: plot of Q band absorbance versus time)

#### 4. Conclusions

In this study, two new phthalocyanines, substituted with chalcone bearing conjugated phenyloxy group, designed, synthesized and characterized. The starting material, 4-(benzyloxy)benzaldehyde **1**, was prepared from 4-hydroxy benzaldehyde and benzyl chloride in the presence of  $K_2CO_3$  in DMF. In the second step, 4-(benzyloxy)benzaldehyde and 4-hydroxyacetophenone were reacted using  $SOCl_2$  in absolute ethanol to give (*E*)-3-(4-(benzyloxy)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one **2**. The nucleophilic substitution reaction between compound **2** and 4-nitrophthalonitrile were afforded compound **3** in DMF using potassium carbonate as the third step. Then ZnPc **4a** and CoPc **4b** were obtained as soluble compounds in good yields. Their photophysical and photochemical properties were investigated along with their biological and metal chelating effects and DPPH radical scavenging assays.

### Conflict of interest

The authors confirm that this article content has no conflict of interest.

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