

## Fluoro functionality zinc phthalocyanine: Photophysical properties for photodynamic effects

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### ABSTRACT

Photodynamic therapy is an alternative method to surgical methods used in the treatment of cancer and one of its three basic components is photosensitizer. The high singlet oxygen generating capacity, high solubility in common organic solvents, low aggregation tendency and lightfastness are the characteristics that photosensitizers must have. Phthalocyanines with bulky substituents are candidate molecules that can be used as sensitizers in photodynamic therapy due to prevent aggregation in the solutions and improve solubility. Based on these facts in this study, singlet oxygen quantum yield and photodegradation quantum efficiency were calculated to evaluate the potential of bis(4-fluorophenyl)-methoxy-substituted zinc phthalocyanine, which does not form aggregation and has high solubility in organic solvents commonly used in photodynamic therapy applications. The metallo phthalocyanine generated higher singlet oxygen than unsubstituted zinc phthalocyanine. According to the singlet oxygen quantum yield, the addition of bis(4-fluorophenyl)-methoxy groups to the phthalocyanine ring increases the singlet oxygen production. The results show that this phthalocyanine may be suitable candidates as photosensitizers in photodynamic therapy with the singlet oxygen quantum yield values are 0.76 and 0.70 in DMSO and DMF, respectively.

**Keywords:** Phthalocyanines; Singlet oxygen; Photophysical; Photodynamic therapy

### INTRODUCTION

Considering that cancer is one of the leading causes of mortality in the world, photodynamic therapy (PDT), as opposed to more conventional cancer treatment options like immunotherapy, surgery, chemotherapy, or radiotherapy, has recently attracted more attention. This technique uses sensitizers that produce harmful reactive oxygen species (ROS) when activated at the proper wavelength. Due to their properties that satisfy the prerequisites, such as high intensity absorption ( $>670$  nm,  $>10^5$  mol<sup>-1</sup>cm<sup>-1</sup>) in the visible region for deeper tissue penetration, high singlet oxygen production, and high triplet quantum efficiencies, phthalocyanines (Pcs) are known as photosensitizers used in PDT applications [1-3]. Besides this feature, they have chemical and thermal stability [4]. Due to their interesting and changeable properties, they have applications in many fields such as optical recording material [5], semiconductors [6-8], non-linear optics, sensors, thermal writing displays and sensitizers for solar cells [9-11], and sensitizers for photovoltaics [12, 13].

The substituent group and center metal ion of Pcs change its photophysical properties and are of major importance in making it more suitable for PDT applications [14]. It

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is widely known that heavy atoms affect the photosensitizers' capacity to produce singlet oxygen. Heavy atoms raise spin-orbit coupling (SOC) which promotes intersystem crossover rates and increase the efficiency of PSs' singlet oxygen generation. A larger halogen atom size among halogen atoms leads to a higher SOC value [15].

Metallophthalocyanine complexes containing heavy atom metals such as zinc(II), indium(III) and silicon(IV) have been found to be highly promising photosensitizers for photodynamic therapy due to their photophysical properties such as intense absorption in the phototherapeutic window (650-850 nm) [3,16,17].

Fluorine atoms are strong electron attractors. The addition of strong electron-withdrawing fluorine atoms to the Pc macrocycle further reduces the energy levels of the conduction and valence bands of the molecule [18]. Fluorine-containing phthalocyanines are both well soluble in fluorine-derived common polar and non-polar solvents, which have the highest electronegativity [19], and do not show aggregation tendency. For this reason, they show improvement in PDT processing and Pcs with fluoro are promising photosensitizers for PDT of cancers [19-24].

This study aimed to design a promising photosensitizer with efficient singlet oxygen yields by combining heavy atom and fluoro substituent groups in a phthalocyanine ring, which promotes intersystem transition rates and increases the efficiency of singlet oxygen production of PSs. For this purpose, a bulky group containing an electron-withdrawing (-F) substituted phthalonitrile derivative and zinc as the centre atom were used for the synthesis of the phthalocyanine complex. The absorbance, fluorescence, singlet oxygen quantum efficiencies and photodegradation quantum efficiencies of compound **2** in DMSO and DMF solutions were investigated, and it was concluded that this compound is promising as a possible photosensitizer in PDT applications.

## EXPERIMENTAL

### Materials and equipments

The used chemicals, equipments, materials, photochemical, and photophysical procedures are given as supplementary material file.

### Synthesis

The synthesis and characterization of phthalonitrile derivative (**1**) and Tetrakis [bis(4-fluorophenyl)-methoxy] phthalocyaninato zinc(II) (**2**) was done and reported in our previous study [25].

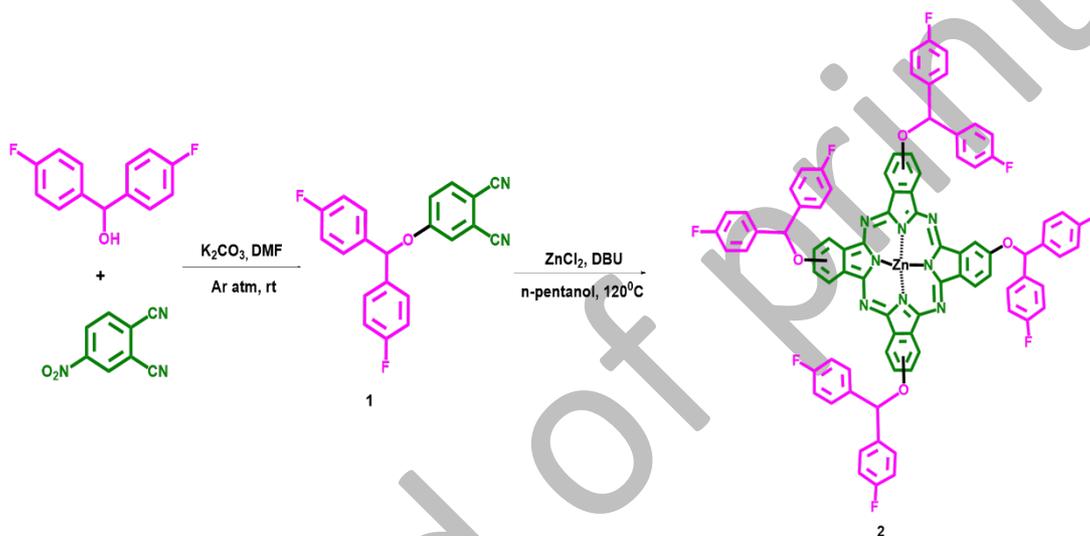
### Photophysical and photochemical studies

The fluorescence quantum yield as photophysical property and the singlet oxygen quantum yield and photodegradation quantum yield as photochemical properties were performed by using the methods described in the supplementary material file.

## RESULTS AND DISCUSSION

## Synthesis and Characterization

The synthetic route to compounds **1** and **2** gives in Scheme 1. Phthalonitrile derivative (**1**) and metallo Pc (**2**) were obtained by applying the synthesis route specified in our previous study [25]. The starting compound **1** was formed by the nucleophilic aromatic nitro displacement reaction of 4-nitrophthalonitrile with bis(4-fluorophenyl)-methanol in dry DMF in the presence of the basic catalyst  $K_2CO_3$ . Peripherally tetra-substituted zinc phthalocyanine (**2**) is prepared by template cyclotetramerization of bis(4-fluorophenyl)-methoxy phthalonitrile (**1**). Complex **2** was synthesized by treatment of compound **1** with anhydrous  $ZnCl_2$  in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base in dry 1-pentanol at reflux temperature under argon atmosphere.



**Scheme 1.** The synthesis routes of compound **1** and its zinc phthalocyanine derivative **2**

The characterization of the compounds **1** and **2** was performed by various analysis methods such as elemental analysis, UV-Vis, FT-IR, NMR and MALDI-TOF MS techniques. The obtained results are compatible with the previously published literature [25]. The characteristic vibrations corresponding to aromatic C-H, aliphatic C-H and  $C\equiv N$  groups were observed at  $3078\text{ cm}^{-1}$ ,  $2961\text{--}2834\text{ cm}^{-1}$  and  $2230\text{ cm}^{-1}$  for **1**, respectively. The distinctive sharp  $C\equiv N$  stretch at  $2230\text{ cm}^{-1}$  for **1** disappeared after conversion into metallo phthalocyanine **2**. Compound **2** displayed distinctive vibrations of aromatic and aliphatic CH stretching at about  $3070\text{ cm}^{-1}$  and  $2960\text{--}2895\text{ cm}^{-1}$ , respectively, and ether groups (C-O-C) at about  $1250\text{ cm}^{-1}$ . At around  $\sim 1095\text{ cm}^{-1}$ , the aromatic fluorur (Ar-F) peak for **2** was seen. By using  $^1H$  NMR, it was determined that phthalocyanine **2** was pure since all of its substituents and ring protons could be seen in the appropriate places.

The phthalocyanine ring protons of compound **2** were observed in the range 7.35 to 7.24 ppm integrated for 12 protons, the bulky fluoro functional groups of the substituent on the phthalocyanine ring were observed in the range 7.15 to 7.05 ppm integrated for 32 protons, the O-CH protons were observed at 6.30 ppm integrated for 4 protons as expected.

In addition to these demonstrating results for the structures, the mass spectra of compound **2** gave the characteristic molecular ion peaks at  $m/z$ : 1448.36 [ $M^{2+}$ ] (Fig. S1) [25].

### Studies on aggregation behavior and UV-Vis spectroscopy

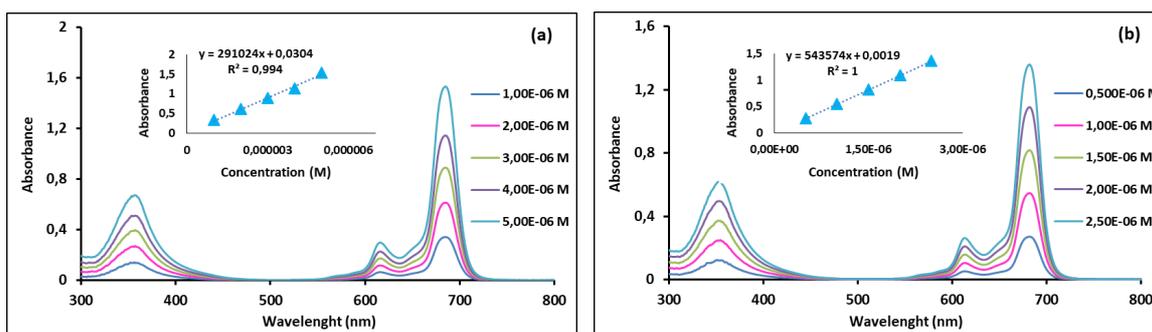
The electronic ground state spectra are particularly helpful for determining the phthalocyanines' structural makeup. Phthalocyanines often exhibit typical electronic UV-Vis spectra with the two powerful absorption bands known as the Q band in the visible region (600-750 nm) and B band in the UV region (300-400 nm) [26]. The solvent, substitution position, central metal, axial ligation and aggregation affect the position and strength of the Pcs absorption bands. The solubility of compound **2** was examined in a series of organic solvents of different polarity. In our previous study [25], the UV-Vis absorbance spectra of **2** carrying (bis(4-fluorophenyl)-methoxy) moieties in the mentioned solvents were examined and the absorption spectra of **2** carrying (bis(4-fluorophenyl)-methoxy) moieties in the said solvents were examined. It has been reported to exhibit monomeric behavior as evidenced by a single Q band (Figure S2a). The Q bands of **2** in DMSO, CHCl<sub>3</sub>, THF, CH<sub>2</sub>Cl<sub>2</sub> and DMF were observed at 685, 684, 682, 685 and 689 nm, respectively (Table 1). In general, it demonstrates that the red-shift of the Q band rises as the solvent's refractive index does [27]. Small discrepancies between the Q band locations were found as a result of the influence of solvents. The red-shift values of the compound was compared with respect to the solvents that were used. ZnPc **2** displayed a high red-shift in DMSO and a low red-shift in THF in this situation.

**Table 1** Absorption, excitation, emission spectral and fluorescence quantum yield ( $\Phi_F$ ) results for **2** in studied solvents [25].

Solvent	Q band $\lambda_{\max}$ , (nm)	$\log \epsilon$	Excitation $\lambda_{\text{Ex}}$ , (nm)	Emission $\lambda_{\text{Em}}$ ,(nm)	Stokes Shift $\Delta_{\text{Stokes}}$ , (nm)	$\Phi_F$
CHCl <sub>3</sub>	685	5.13	686	700	15	0.0830
CH <sub>2</sub> Cl <sub>2</sub>	684	5.08	685	696	12	0.0847
THF	682	5.15	684	694	12	0.0949
DMF	685	5.09	686	698	13	0.0775
DMSO	689	5.12	690	702	13	0.0780

The interactions between the 18  $\pi$ -electron systems leading to aggregation of phthalocyanine compounds depend on concentration, the nature of the solvent and substituents, complex metal ions and temperature. The spectroscopic, photophysical and photochemical properties of Pcs are strongly affected by aggregation in solution [28, 29].

The aggregation behavior of **2** in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF, THF and DMSO was presented in our previous publication [25]. Figure 1 presented the absorption spectra of solutions of **2** prepared with DMSO and DMF at increasing concentrations. The solutions prepared with these solvents showed that **2** has high solubility and does not exhibit aggregation.



**Figure 1.** UV–Vis absorption spectra of **2** for aggregation studies in (a) DMSO and (b) DMF at different concentrations. (Inset: Plot of absorbances versus concentrations).

### Photophysicochemical studies

The fluorescence behaviour of complex **2** in various organic solvents was investigated and reported in our previous study [25]. In this study, to demonstrate its suitability for PDT studies, the photochemical (singlet oxygen quantum yields ( $\Phi_{\Delta}$ ) and photodegradation quantum yields ( $\Phi_d$ ) properties of complex **2** in DMF and DMSO were investigated.

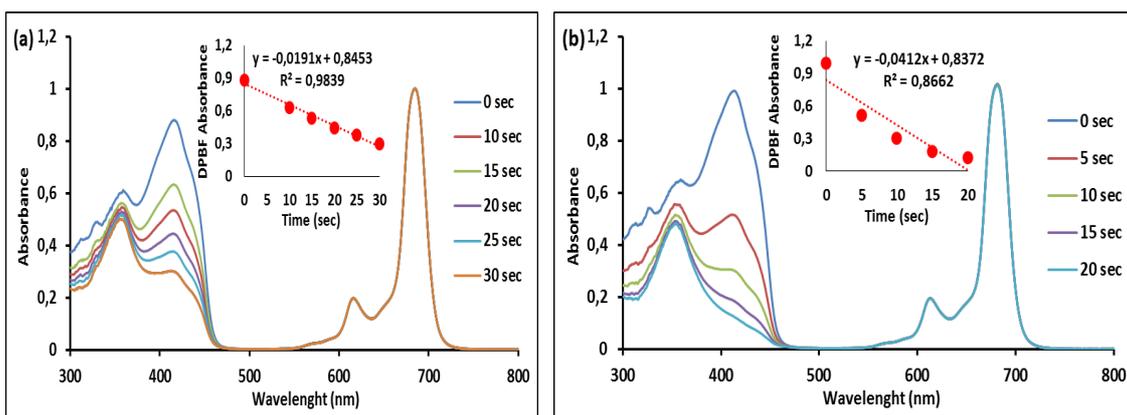
### Fluorescence spectra studies and Fluorescence quantum yields

In our previous study, the fluorescence behaviour of complex **2** was investigated in various solvents including  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , DMF, THF and DMSO. The standard and the studied Pc **2** were excited at the same appropriate wavelength. Table 1 and Figure S2(b) give the resulting fluorescence data and quantum yields, respectively. Fluorescence properties of **2** were observed to be the lowest in DMF. Considering the fluorescence property of compound **2**, it has been determined that it has the potential to be used as a photosensitizer in PDT.

### Singlet oxygen quantum yields ( $\Phi_{\Delta}$ )

PDT is based on the selective destruction of target tissue by  $^1\text{O}_2$  produced as a result of the dynamic interaction between a Ps, light of a wavelength suitable for the excitation of Ps, and molecular oxygen. Singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) is a measure of the singlet oxygen generation capacity of a molecule and is one of the most important parameters in studying molecule potential to be used as a Ps for PDT applications [29,30].

For this reason, the search for suitable photosensitizers is a continuing investigation issue among researchers. In present study, the photochemical properties of fluoro-functional Zn(II) phthalocyanine **2** were investigated in DMSO and DMF due to lack of standard in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ . 1,3-diphenylisobenzofuran (DPBF) was used as the chemical extinguisher of singlet oxygen. In this study, singlet oxygen generation potentials of fluoro-functional Zn(II) phthalocyanine, which was synthesized to shift the absorption to the Vis region and whose photophysical properties were investigated in DMSO and DMF due to lack of standard in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ . Singlet oxygen quantum yields were calculated. Information about the singlet oxygen measurements conditions were given in the supplementary file. DPBF degradation at 417 nm (in DMSO) and 415 nm (in DMF) [3] was recorded by UV-Vis spectrophotometer (Fig. 2). The absence of any changes in Q band intensities during singlet oxygen generation indicated that the complex was not degraded during  $\Phi_{\Delta}$  determinations.



**Figure 2.** Absorption changes during the determination of singlet oxygen quantum yield in (a) DMSO and (b) DMF using DPBF as a singlet oxygen quencher.

The  $\Phi_{\Delta}$  values of the peripherally tetra [bis(4-fluorophenyl)-methoxy]-substituted Pc was calculated and this values are presented in Table 2. The  $\Phi_{\Delta}$  values are 0.76 and 0.70 in DMSO and DMF, respectively. The heavy atom effect of halogen atoms is weak because they are not very close to the Pc ring [31]. When the effect of halogen atom was examined, the Pc ring carrying F showed higher singlet oxygen activity in DMSO ( $\Phi_{\Delta}=0.76$ ) and DMF ( $\Phi_{\Delta}=0.70$ ) compared to unsubstituted zinc phthalocyanine ( $\Phi_{\Delta \text{ DMSO}}=0.67$  and  $\Phi_{\Delta \text{ DMF}}=0.56$  [3]). Another factor affecting the photochemical properties is the polarity and coordination strength of the solvents [27]. This may be due to the attempt of the amine group in DMF to quench singlet oxygen. In general, the singlet oxygen quantum yield values of phthalocyanines are higher in DMSO than in DMF [3, 27], and results in complex **2** are in line with this trend. The data obtained determined that **2** has the potential to provide favorable singlet oxygen production in PDT, in agreement with the literature [16, 20-22]. Singlet oxygen quantum yields were calculate only in DMSO and DMF due to luck of standart in in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ . Normally, water solubility is important properties of phthalocyanine compounds for PDT applications. But many Pcs are soluble in organic solvents such as DMSO, DMF etc. Our samples are not soluble in water but they have good singlet oxygen quantum yield in DMSO. DMSO is not toxic solvent for biological cell studies required concentration for PDT application. For many phthalocyanine complexes which is insoluble in water, biocompatible solvent DMSO is used as medium in in vivo or in vitro studies. Fluorinated phthalocyanines have been also reported to show improved photosensitizer activity for PDT compared to nonfluorinated derivatives [32-35] as given in Table 2.

**Table 2** Comparison of Photophysical and photochemical parameters of similar fluorinated phthalocyanines in the literature.

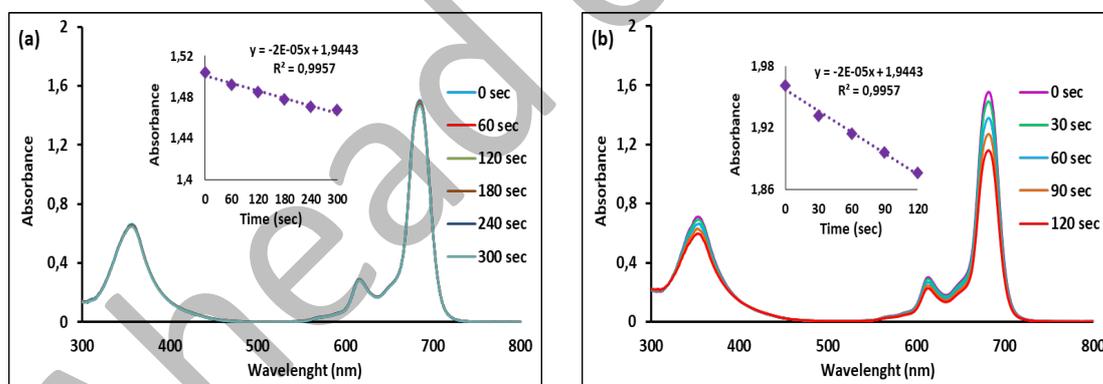
Reference	Solvent	$\Phi_F$	$\Phi_d$	$\Phi_{\Delta}$
This study	DMSO	0.0780	$4.01 \times 10^{-4}$	0.76
	DMF	0.0775	$6.03 \times 10^{-3}$	0.70
Std-ZnPc <sup>a</sup>	DMSO	0.20	$0.26 \times 10^{-4}$	0.67
	DMF	0.17	$0.23 \times 10^{-4}$	0.56

[22]	DMSO	0.167	$2.4 \times 10^{-4}$	0.71
[33]	DMF (for <b>3c</b> [31])	0.19	-	0.04
[34]	THF (for <b>2</b> [32])	0.20	-	0.72
[35]	Toluene (for <b>6</b> [33])	0.035	$1.39 \times 10^{-6}$	0.60

<sup>a</sup> Ref. [3]

### 3.3.3 Photodegradation quantum yields ( $\Phi_d$ )

In PDT applications, PSs that provide the formation of " $^1O_2$ " molecule must be stable under the applied light. Because this stability is necessary to maintain its effectiveness and to keep the drug concentration unchanged. The  $\Phi_d$  value is an indication that the molecule can be used in PDT as a photosensitizer. In this study, the photodegradation tendency of **2** in DMSO and DMF solutions was followed by exposure to visible light for certain periods of time, followed by changes in the maximum Q-band in the absorption spectra of this compound (Fig. 3). Table 2 presents the  $\Phi_d$  values of **2** in studied solvent. The  $\Phi_d$  value of **2** was higher than the  $\Phi_d$  value of standard zinc phthalocyanine in DMSO, but lower than that in DMF. The stable zinc Pcs compounds have  $\Phi_d$  values as low as  $10^{-6}$  however unstable derivatives have  $\Phi_d$  values of the order  $10^{-3}$  [3]. For this reason, it was determined that the Fluoro-substituent attached to the phthalocyanine ring increases the resistance of the molecule to visible wavelength light in DMSO while destabilizing it in DMF.



**Figure 3.** UV–Vis absorption changes for a) **2** in DMSO and b) **2** in DMF during the determination of photodegradation quantum yield.

## CONCLUSION

In summary, the effect of solvent on the singlet oxygen generating capacity and light stability of **2**, whose synthesis, characterization and photophysical properties were examined in detail in our previous publication, was investigated and its photosensitizer candidacy for PDT was investigated. This complex exhibited good solubility and non-aggregated species in the previously mentioned solvents. The  $\Phi_F$ , singlet oxygen production ability and photostability of **2** was also examined in DMSO and DMF. The effects of bulky fluoro functional of the substituent on the Pc ring and the type of solvent on this properties were also evaluated. The complex **2**

exhibited lower  $\Phi_F$  compared to unsubstituted ZnPc. The  $\Phi_\Delta$  value of compound **2** was found higher than unsubstituted ZnPc in DMSO and DMF. The studied Pc showed a high stability in DMSO and this stability is suitable for PDT applications. Although these Pcs have high  $\Phi_a$  in DMF, this has reasonable singlet oxygen production as photosensitizers for PDT. The results showed that the substitution [bis(4-fluorophenyl)-methoxy] group on the Pc ring effected on photophysical properties of the studied Pcs. This study indicates that the photophysical properties of the studied Pcs are satisfactory to be used as photosensitizer in PDT.

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