Synthesis, Characterization and Photophysicochemical Properties of Zinc(II) Phthalocyanine With New Benzenesulfonamide Derivative Substituents

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Abstract

Novel (E)-4-((5-bromo-2-hydroxy-3-methoxybenzylidene)amino)-N-(pyridin-2-yl)benzenesulfonamide 1, (E)-4-((5-bromo-2-(3,4-dicyanophenoxy)-3-methoxybenzylidene)amino)-N-(pyridin-2-yl)benzene sulfonamide 2 and 2(3),9(10),16(17),23(24)-tetra-[(E)-4-((5-bromo-3-methoxy-2-(λ1-oxidanyl)benzyl idene)amino)-N-(pyridine-2-yl)benzenesulfonamide]phthalocyaninato zinc(II) phthalocyanine 3 were synthesized. Their (1-3) structures were illuminated with spectroscopic methods such as FT-IR, 1H NMR, 13C NMR, UV–vis, MALDI-TOF mass spectra and also elemental analysis. The spectroscopic, photophysical and photochemical properties of the zinc(II) phthalocyanine 3 were investigated in dimethyl sulfoxide and its effects on the above mentioned properties were reported as a result of containing new type benzenesulfonamide derivatives as substituents. In addition, its above-mentioned properties were reported by comparing different species with those of their substituted and/or unsubstituted counterparts. The zinc(II) phthalocyanine 3 has photosensitizing abilities suitable and sufficient especially for photocatalytic applications.

Introduction

Schiff base metal complexes are widely used in medicine for treating multiple viral diseases due to their transition metal complexes, which plays a key role in several areas, including antibacterial, antifungal, anticancer, and anti-inflammatory drugs. Moreover, these organometallic materials are used as a catalyst in many reactions. Many Schiff base complexes are used to synthesize medication compounds. This is because of the reactive interaction of the Schiff base ligand with the metal ion which is more effective when compared with the interaction of metal-free Schiff bases [1]. Sulfonamides with other drugs enables the spectrum of activity to be further expanded. Sulfonamide compounds are used in the field of chemistry as polymer, ion carrier, reagent, antiseptic agent and ligand. In the field of pharmacy, they are frequently used as antimicrobial agents [2]. Sulfonamides are cheap and durable, they can be applied easily, and their spectrum of activity is wide, which ensures their widespread use.

Phthalocyanines (Pcs) are synthetic pigments that contain four isoindole units and they have low solubility in common solvents. Substitutions can change the solubility, photophysicochemical properties of phthalocyanines. Substituted Pc derivatives have great technological and commercial interest as dyes and pigments [3]. Numerous properties arise from their electronic delocalization, which makes them valuable in science and technology as photo-conducting agents in photocopying devices, electrocatalysts, data storage systems, liquid crystals, photosensitizers in photodynamic therapy (PDT), gas sensors, solar cell technology, optical read–write discs, Langmuir–Blodgett films and non-linear optics [3–9]. Pcs generate singlet oxygen (1O2) in solutions by excitation at Q band region. 1O2 reacts with organic molecules. This oxidizing process is favourable for many applications such as degradation of pollutants, catalysis of some reactions, anti-microbial studies, DNA degradation and PDT of cancer [10–13].
Metallophthalocyanines (MPcs) have relatively high singlet oxygen quantum yields. Especially zinc phthalocyanines (ZnPcs) are of interest due to their high molar absorption coefficients in red wavelength and its strong activity to produce singlet oxygen [14]. The main restriction of ZnPc utilization is low resolution due to aggregation. PDT is used in the treatment of cancer followed by activation of the chemicals by light [10, 13]. Such applications are based on the relative stability of Pc molecules to air and light, and on the delocalized electronic nature of the Pc ring system [15–17]. Interactions affect aggregation and solubility tendencies in most organic solvents which limit their applications in many fields [18, 19]. The photophysical properties of the phthalocyanine dyes are strongly influenced by the nature of the central metal ion [19–21]. The presence of diamagnetic metal ion such as zinc (II) in the phthalocyanine core results in large triplet state quantum yields, leading to generation of higher concentration of singlet oxygen, hence improved PDT activity [19–21]. ZnPcs have been extensively studied as potential photosensitizers in PDT [19–21].

The pyridine ring is widely used as an important compound in pharmaceutical chemistry due to its potential biological activity. Pyridine structures are found in many natural compounds; it is also frequently used in functional materials [22, 23]. Pyridine and its derivatives have anticarcinogenic, antiviral, antioxidant, antidiabetic, antibacterial properties which exhibit biological and pharmacological activities.

The aim of this study is to synthesize a new photosensitizer for PDT with sufficient and suitable fluorescence properties, photostability and high singlet oxygen generating ability, which combines three different bioactive groups Schiff base, benzenesulfonamide and phthalocyanine in a single structure. The effects of the presence of a new benzenesulfonamide derivative containing electron donor group as methoxy and Schiff base and strongly electron acceptor groups such as Schiff base, bromine, and pyridine on the Pc ring on spectroscopic, photophysicochemical properties were researched in dimethyl sulfoxide (DMSO). In addition, these properties of the new zinc(II) Pc 3 were compared with the properties of different benzenesulfonamide derivative substituted zinc(II) phthalocyanines and unsubstituted zinc(II) phthalocyanine presented in previous studies [24, 25].

Materials And Methods

Experimental Section

The materials, equipment, devices, photophysical and photochemical parameters, formulas and the rest of the figures used in this study are given in Electronic Supplementary Information file.

\[(E)-4-(5-bromo-2-hydroxy-3-methoxybenzylidene)amino]-N-(pyridine-2-yl)benzenesulfonamide (Compound 1)\]

Two solutions were prepared under N₂ by adding sulfapyridine (1.99 g, 0.01 mol) in 100 mL absolute Ethanol (EtOH) and mixing, and also by adding 5-Bromo-3-methoxysalicylaldehyde (1.85 g, 0.01 mol) in
10 mL EtOH and mixing. Under N$_2$, 5-Bromo-3-methoxysalicylaldehyde solution was added dropwise to the Sulfapyridine solution and stirred. Then, a catalytic amount of p-Toluenesulfonic acid monohydrate (p-TsOH) was added to this mixture and it was refluxed under N$_2$ at 78 °C for 6 hours. The resulting orange precipitate was filtered, and the crude product was purified by washing several times with cold EtOH. Yield: 3.55 g (95.55%). Anal. Calc. for C$_{19}$H$_{16}$N$_3$O$_4$S: C, 49.36; H, 3.49; N, 9.09; S, 6.97. Found: C, 49.73; H, 3.16; N, 9.25; S, 6.46%. IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$): 3435 (O-H), 3129, 3017, 2965, 1614 (C=N), 1254 (C-O), 1143 (-SO$_2$ str, sym), 1350 (-SO$_2$ str, asym), 1143, 1134 (C–O std.), 1083, 1027, 958, 873, 837, 762, 662 (C–C str.). $^1$H NMR (DMSO-d$_6$, $\delta$, ppm): 14.24 (s, 1H, O-H), 11.52 (s, 1H, N-H), 9.20 (s, 1H, CH=N), 8.33-6.56 (m, 11H, Ar-H), 4.00 (s, 3H, -OCH$_3$); $^{13}$C NMR (DMSO-d$_6$, $\delta$, ppm): 163.57 (C8), 160.67 (C7), 156.97 (C9), 153.21 (C2), 152.77 (C13), 139.78 (C12), 128.56 (C11), 122.11 (C10), 139.22 (C4), 121.39 (C6), 116.14(C16), 110.69 (C3); UV-vis (DMF, $\lambda_{\text{max}}$(nm) (log)): 360 (2.88), 290 (3.44).

$\text{[(E)-4-((5-bromo-2-(3,4-dicyanophenoxy)-3-methoxybenzylidene)amino)-N-(pyridine-2-yl)benzenesulfonamide} (\text{Compound 2})$

5-Nitrobenzene-1,2-dicarbonitrile (0.166 g, 0.95 mmol) and compound 1 (0.50 g, 1.08 mmol) were added to 12 ml of dried DMSO solvent under N$_2$, and the temperature of the reaction mixture was increased to 55°C and stirred for a period. Finely ground dehydrated K$_2$CO$_3$ (1.60 g, 11.56 mmol) was put in to the reaction mixture in six equal portions at ten-minute intervals, and the resulting reaction mixture was stirred at 55°C for four days. At the end of this period, after determining that the reaction was completed using thin layer chromatography technique, it was poured into ice water, the precipitate formed was washed several times with distilled water and filtered under vacuum, and also dried over P$_2$O$_5$ in vacuum. The crude product was separated using column chromatography technique with silica gel as filler and THF:Hexane (1:1; per vol.) solvent system as eluent to give pure dark brown compound 2 (0.42 g, 73%) using the column chromatography technique. The compound 2 is soluble in THF, Acetone, N,N-dimethylformamide (DMF) and DMSO. Mp: 84°C. Anal. Calc. for C$_{27}$H$_{18}$BrN$_5$O$_4$S: C, 55.11; H, 3.08; N, 11.90; S, 5.45 Found: C, 55.32; H, 3.16; N, 11.84; S, 5.15%. IR (ATR) $\nu_{\text{max}}$/cm$^{-1}$: 3056 (=C–H str.), 2230 (C≡N str.), 1601 (C=C str.), 1531 (C=N), 1486, 1406 (C–H bend.), 1381 (-SO$_2$ str), 1265, 1134(C–O std.), 1083, 1027, 958, 873, 837, 762, 662 (C–C str.). $^1$H NMR (DMSO-d$_6$, $\delta$, ppm): 10.19(s, 1H, -N-H), 8.88(s, 1H, CH=N), 8.52-6.48(m, 11H, Ar-CH), 3.81(s, 3H, -OCH$_3$). $^{13}$C-NMR (DMSO-d$_6$) (δ: ppm): 164.09, 161.29, 156.11, 153.27, 151.54, 150.77, 150.38, 149.79, 147.43, 142.21, 139.22, 136.55, 135.69, 130.77, 129.42, 129.06, 128.55, 125.27, 124.10, 123.62, 122.34, 121.86, 120.17, 118.86, 112.95,108.87, 57.10.

$2,9(10),16(17),23(24)$-teta-$\text{[(E)-4-((5-bromo-3-methoxy-2(\lambda^1$-oxidanyl)benzylidene)amino-N-(pyridine-2-yl)benzenesulfonamide)]zinc(II) phthalocyanine} (\text{ZnPc 3})$

In a glass sealed tube, a mixture of the compound 2 (0.20 g, 0.406 mmol) and Zinc(II) acetate dihydrate [Zn(OAc)$_2$.2H$_2$O] (0.149 g, 0.812 mmol) was added into dried N,N-dimethylformamide (DMF) (2 mL) under N$_2$. The reaction mixture was heated to 85°C for a time under N$_2$. Then, 3 drops of 1,8-
diazabicyclo[5.4.0]undec-7-ene (DBU) were added to the reaction mixture as a basic catalyst under N₂ and stirred by heating at 158°C for 7 hours. As a result of this time, a certain amount of crude product 3 with a dirty grass green color was formed. It was precipitated with the solvent system of acetic acid: water (70:30; per vol.) and collected by filtration. The precipitate was purified by washing several times with hot acetic acid, water, methanol, ethanol, acetone, and diethyl ether sequentially, using the Soxhlet apparatus. In addition, the crude product obtained after the above extraction step was separated with the aid of column chromatography as an advanced purification technique, using silica gel as filler and Chloroform:Methanol (10:3; per vol.) solvent system as eluent to give pure grass green phthalocyanine complex 3 (0.06 g, 22%). The ZnPc 3 is soluble in THF, Acetone, DMF and DMSO. M.p. > 300°C. Anal. Calc. for C₁₀₈H₇₂Br₄N₂₀O₁₆S₄Zn: C, 53.58; H, 3.08; N, 11.57; S, 5.30 Found: C, 53.72; H, 3.11; N, 11.35; S, 5.76%. IR (ATR) υ_max/cm⁻¹: 3049(=C‒H str.), 1524 (C=N), 1489 (C‒H bend.), 1230 (C−O std.), 1341 (O=S=O)sym. 1H-NMR (400MHz, DMSO-d₆, ppm): 10.06 (s, 4H, -N‒H); 8.60 (s, 4H, C=H=N); 8.23-6.48 (m, 44H, Ar-C); 3.31 (s,12H, -OC₃H₃). 13C-NMR (DMSO-d₆), (δ; ppm): 188.54, 161.02, 160.85, 156.06, 154.12, 153.77, 153.26, 152.86 143.69, 140.87, 139.46, 136.98, 136.78, 133.11, 131.46, 129.87, 128.52, 124.41, 123.70, 123.59, 121.85, 118.88, 117.23, 116.50, 116.35, 115.84, 114.40, 112.95, 109.50, 107.84. UV–vis (DMSO): λ_max(nm) (logɛ): 698 (2.92), 627 (1.25), 322 (1.81). MALDI-TOF-MS (m/z): Calculated: 2419.12; Found: 2420.14 [M+H]+.

Results And Discussion

The newly compound 1 was synthesized by the condensation reaction of 5-bromo-3-methoxysalicylaldehyde, a derivative of salicylaldehyde, and sulfapyridine, the antibiotic agent and main metabolite of Sulfasalazine, under an inert atmosphere of nitrogen (N₂), in anhydrous ethanol and presence of p-toluene sulfonic acid (p-TsOH) as a catalyst. The newly compound 2, on the other hand, was synthesized by the nucleophilic aromatic substitution reaction of compound 1 and 4-Nitrophthalonitrile under an inert atmosphere in dried DMSO and in the presence of K₂CO₃ as a mild base catalyst. Finally, in this study, the newly ZnPc complex 3 was synthesized through the cyclotetramerization reaction of the compound 2 with zinc acetate dihydrate in dried N, N-dimethylformamide (DMF) under an inert N₂ atmosphere (Scheme 1). Each of the synthesized new compounds (1 and 2) and newly ZnPc complex 3 were purified using different purification techniques. The structures of each of these (1-3) were characterized by the spectroscopic techniques. In the IR spectrum of the compound 1, its absorption bands, broad O-H stretching vibration attributed to its phenolic group, as well as a sharp C=N stretching vibration attributed to its azomethine group, were observed at 3435 cm⁻¹ and 1614 cm⁻¹, respectively (Fig. S1 in ESI). Also, the absorption bands of stretching vibrations attributed to its aromatic CH, aliphatic CH, C=C, phenolic C-O, observed at 3017-3129 cm⁻¹, 2745-2965 cm⁻¹ and 1254 cm⁻¹, respectively (Fig. S1 in ESI). Absorption bands of its vibrations attributed to SO₂ (asymmetric) and SO₂ (symmetrical) groups were also observed at 1350 cm⁻¹ and 1143 cm⁻¹, respectively (Fig. S1 in ESI). The absence of strong absorption bands in the FT-IR spectrum of the compound 2 in the ranges of 1500-1570 cm⁻¹ and 1300-1370 cm⁻¹ is attributed to the fact that it does not
contain –NO₂ group. Also, no absorption bands were observed in it, attributable to a strong or moderate and broad O-H stretching vibration at frequencies of 3600-3300 cm⁻¹ and attributable to O-H bending vibration at frequencies of 1450-1200 cm⁻¹. In its FT-IR spectrum, the weak intensity sharp bond stretching vibration observed at 2230 cm⁻¹ is attributed to the nitrile group, and the severe bond stretching vibration observed at 1265 cm⁻¹ is attributed to the Ar–O–Ar group (Fig. S2 in ESI). The absence of sharp bond stretching vibration with weak or moderate intensity in the FTIR spectrum of the ZnPc 3 in the range 2210 cm⁻¹ to 2280 cm⁻¹ was attributed to the absence of the nitrile group and indicated its conversion to the ZnPc 3 [24-27] (Fig. S3 in ESI). Therein, moderate absorption bands attributed to aromatic and –C=C– stretch vibrations were observed at 3049 cm⁻¹ and 1633 cm⁻¹ and 1588 cm⁻¹, respectively (Fig. S3 in ESI).

The ¹H-NMR spectra of the compounds 1 and 2 and the ZnPc 3 were documented in DMSO-d₆ at 25°C. The characteristic ¹H-NMR peaks of the compound 1 are at 14.24 δ(OH), 11.52 δ(NH), 9.20 δ(CH=N), and 8.33-6.56 ppm δ(Ar-H) (Fig. S4 in ESI). Also, in the ¹³C-NMR spectrum of the compound 1, carbons (C8), (C7) and (C9) were watched at 163.57, 160.67, 156.97 ppm, respectively, and its other aromatic ring carbons between 153.21-110.69 ppm (Fig. S5 in ESI). No proton attributed to -O-H was observed in the ¹H NMR spectrum of the compound 2. In its NMR spectrum, protons attributed to new aromatic protons were observed, unlike those of the compound 1 (Fig. S6 in ESI). In it, signals attributed to methoxy (–OCH₃) protons were observed individually at δ3.81 ppm (Fig. S6 in ESI). Therein, attributed to 1,2-Benzenedicarbonitrile, as well as [(E)-4-((5-bromo-2-(3,4-dicyanophenoxy)-3-methoxybenzylidene)amino]) N-(pyridin-2-yl) signals of aromatic protons attributed to the benzenesulfonamide derivative were observed in the ranges of δ 7.40-8.08 ppm and δ 8.52-6.48 ppm, respectively (Fig. S6 in ESI). Therein, chemical shifts at δ 10.19 ppm and δ 8.88 ppm, respectively, attributed to -NH attached to the -SO₂ group and which are broad, and also attributed to (-CH= N) and integrated as a proton for each, were observed (Fig. S6 in ESI). In the ¹³C-NMR spectrum of the compound 2, the signals in the range of δ118-125 ppm attributed to the nitrile carbon were monitored (Fig. S7 in ESI). In the ¹³C-NMR spectrum of the compound 2, signals in the range of δ118-125 ppm attributed to nitrile carbons were monitored. Other signals attributed to its aliphatic and aromatic carbons for the compound 2 were monitored, in harmonious with the structure proposed (Fig. S7 in ESI). In the ¹H-NMR spectrum of the ZnPc 3, the signals of the protons attributed to the -N-H units containing hydrogen bonds, as well as to the HC=N- units, were monitored at δ 10.06 ppm and δ 8.60 ppm, respectively, as 4 protons for each (Fig. S8 in ESI). Therein, signals attributed to its aromatic protons, multiplet and integrated as 44 protons, were monitored in the range of δ 8.23-6.48 ppm (Fig. S8 in ESI). The signals attributed to aliphatic protons of its –OCH₃ groups, integrated as singlet and 12 protons, were monitored at δ3.31 ppm (Fig. S8 in ESI).

In the ZnPc 3’s ¹³C-NMR spectrum, no minimum intensity signals were observed, typically in the range of 115-125 ppm, attributed to the C≡N unit, as characteristic of hydrogen-free carbons and deshielding due to nitrogen (Fig. S9 in ESI). In the ¹³C-NMR spectrum of the ZnPc 3, signals characteristically attributable to its aliphatic and aromatic carbons were observed in the respective chemical shift regions, consistent with the proposed structure (Fig. S9 in ESI). These results obtained in its ¹³C NMR spectrum indicate that
the cyclotetramerization reaction has taken place successfully and is converted into a proposed newly benzenesulfonamide-derived zinc(II) phthalocyanine 3.

The $^1$H- and $^{13}$C- NMR spectral results of the newly compounds 1, 2 and ZnPc 3 are in concordance with those of their counterparts in the literature [24,25]. The ZnPc 3 was also characterized by MALDI-TOF mass spectrometry using 2,5-dihydroxybenzoic acid as a MALDI matrix (Fig. S10 in ESI). Its molecular ion peak, [M+H]$^+$, was watched at 2420.14 Da (Fig. S10 in ESI). In Figure S11 in the electronic supplementary information file (ESI), electronic transitions in the range of 300-400 nm were observed in the UV-vis spectrum of the new benzenesulfonamide derivative 1 in DMF. These electronic transitions are band transitions originating from aromatic rings and unpaired electrons. The band observed at 340 nm is the $n\to\pi^*$ transition belonging to the CH=N (azomethine) group [30]. Figure 2 and Table 1 show the ZnPc 3 in DMSO has monomeric demeanor demonstrated by a single and narrow Q band, distinctive feature of metallo-phthalocyanines [24-29]. Its Soret band, characteristic for phthalocyanines, was also watched at about 340 nm (Figure 2). Since the ZnPc 3 has (E)-4-((5-bromo-3-methoxy-2-($\overset{1}{\lambda}$-oxidanyl)benzylidene)amino)-N-(pyridine-2-yl) as substituents on its ring, its Q band was observed that shifted to red region about 18 nm compared to Std-ZnPc. These properties allow the use of light with longer wavelengths that can penetrate more into the tissue, enabling more effective treatment of deeply located lesions [31]. It was determined that its Q band in DMSO was shorter and less red shifted than ZnPcs containing different types of benzenesulfonamide-derived substituents in the literature [24,25]. This may be related to the binding of the novel benzenesulfonamide derivative, which contains strong electron acceptor groups that deactivate the ring, such as pyridine and bromine, at the peripheral positions of the phthalocyanine ring, resulting in less redshift of absorption in the NIR region [32] than its counterparts [24,25].

The ZnPc 3 in DMSO has a higher molar extinction coefficient ($\varepsilon$) than its counterparts in the literature [24, 25] (Table 1). This result is related to the effect of increasing the monomerization of Pc [33]. It was also found that this effect was reduced when the Pc ring was replaced by a benzenesulfonamide derivative containing 2-methyl-1,3,4-thiadiazole and methoxy units or containing only 2-methyl-1,3,4-thiadiazole unit [24, 25].

**Photophysical properties**

**Aggregation studies**

The ZnPc 3, practically soluble in polar aprotic solvents dichloromethane (DCM) and dimethylsulfoxide (DMSO), as well as in chloroform (CHCl$_3$), one of the apolar solvents, without aggregation (Figure 1). The ZnPc 3 is soluble with very little aggregation in DMF, THF, acetonitrile, which are polar aprotic solvents, and in toluene, another apolar solvent (Figure 1). In addition, the ZnPc 3 in methanol (MeOH) and ethanol (EtOH), which are polar protic solvents, is very slightly soluble (Figure 1). The tendency for the ZnPc 3 to form aggregates in different types of solvents increases in the following order: DMSO < CHCl$_3$ < DCM < DMF < THF < toluene < acetonitrile < EtOH < MeOH. This result indicates that aggregation can increase
with solvent polarity. DMSO is an organic dipolar aprotic solvent with an amphipathic structure that can dissolve a wide variety of poorly soluble polar and apolar molecules. It is used in biological studies, drug therapy, and in vivo administration of water-insoluble substances. The photophysicsochemical properties of the ZnPc 3 have been investigated in DMSO both because of the above-mentioned properties of DMSO and because it shows a very good solubility in DMSO without aggregation.

The Q and B bands of a Pc are affected by different concentrations of Pc in the solvent during its aggregation study, the observation of a new band formation indicates that the Pc contains aggregate species [19,34]. The aggregation behavior of the ZnPc 3 was investigated at ten different concentrations, starting from $1.00 \times 10^{-5}$ M in DMSO, up to $2.00 \times 10^{-6}$ M (Figure 2). It was determined that the Q and B bands of the ZnPc 3 were not affected in this solvent and at above-stated concentration ranges, and Lambert-Beer law was obeyed, and no new band formation was observed. It was observed that the intensities of the Q and B band absorptions decreased together with the decrease of the concentration of the ZnPc 3 in this solvent. Also, no new band formation of H- or J-type aggregation was observed due to the concentration change of the ZnPc 3 in this solvent. The ZnPc 3 has monomeric species in this solvent.

**Fluorescence spectra**

The fluorescence emission and excitation spectra of the phthalonitrile compound 2 containing the novel benzenesulfonamide derivative in DMSO are given in Figure S12 in ESI. Its excitation wavelengths ($\lambda_{\text{Ex}}$) resulting from electronic transitions were observed with maximum intensity at 300 and 353 nm. Its emission wavelength was observed with maximum intensity at 421 nm. The ZnPc 3 and Std-ZnPc's $I_{\text{Ex}}$ and $I_{\text{Em}}$ peaks with maximum intensity, as well as Stokes shifts ($\Delta_{\text{Stokes}}$), are listed in Table 1. The ZnPc 3’s $\Delta_{\text{Stokes}}$ in DMSO is both typical and similar for MPcs [19,34-37]. Its $\Delta_{\text{Stokes}}$ in DMSO was shorter than that of its counterparts in the literature [24,25]. The fluorescent excitation spectrum of the ZnPc 3 in DMSO is like its fluorescent emission spectrum (Figure 3). Also, in the same solvent, the fluorescence excitation spectrum of the ZnPc 3 and its absorption spectrum are mirror images of each other. Thus, it was determined that the nuclear configurations of the ground and excited states for the ZnPc 3 in DMSO were similar and it was not affected by excitation [19,34-37]. The ZnPc 3 was exhibited similar fluorescent behavior with its counterparts in the previous studies [24,25].

**Fluorescence quantum yields and lifetimes**

The fluorescence quantum yield ($\Phi_F$) and fluorescence lifetime ($\tau_F$) of a fluorophore are significant parameters for fluorophores in single-molecule fluorescence spectroscopy. $\Phi_F$ is the primary parameter characterizing the emission properties around a chromophore. $\Phi_F$ gives the possibility that the excited state is disabled by fluorescence rather than some other non-radiative mechanism [38,39]. The values of the photophysical parameters of the ZnPc 3 and Std-ZnPc in DMSO are presented in Table 2. Among the photophysical parameters of the ZnPc 3 in DMSO, $\Phi_F$, $\tau_F$, fluorescence rate constant ($k_F$), natural radiation lifetime ($\tau_0$) values are characteristic for MPcs [19,34-37] (Table 2). Except for the $k_F$ value, all
its above-mentioned values are lower than both its counterparts in the literature [24,25] and those of Std-ZnPc (Table 2). The reduction in \( \Phi_F \) from a fluorophore induced by various molecular interactions with the quencher molecule is related to the quenching of fluorescent intensity due to the nature of the substituent on the Pc ring.

The ZnPc 3's \( t_F \) in DMSO was determined by use of the time-correlated single photon counting (TCSPC) technique and by fitting the fluorescence decay data to a mono-exponential in DMSO (Fig. 4). The reason why its \( t_F \) is shorter than its counterparts in the literature [24,25] and Std-ZnPc [36,37] may be related to the fact that it contains different kinds of benzenesulfonamide derivatives from peripheral positions as tetrakis (Table 2). Thus, the shorter lifetime may result from an increase in non-radiative processes as relaxation becomes important with a higher state density.

In its fluorescence decay process, \( k_F \)’s value, a first-order rate constant [39,40], may be higher than that of Std-ZnPc [36,37] and its counterparts in the literature [24,25] (Table 2). This may be due to the presence of a new benzenesulfonamide derivative containing both electron donor and strongly electron acceptor groups on the Pc skeleton. If the emission is the only decay process, the time the molecule will have been called the natural radiation lifetime (\( \tau_0 \)). The fact that it's \( \tau_0 \) has a shorter duration than both its counterparts in the literature [24,25] and Std-ZnPc [36,37]. It may be related to the presence of different types of benzenesulfonamide derivative substituents containing electron donor and strongly electron acceptor units, as mentioned above. The rate constant of the ZnPc 3 for intersystem crossing (\( k_{ST} \))' value in DMSO is higher than that of tetra-(15-crown-5)-Pc and its lutetium Pcs in the literature [41] and Std-ZnPc (Table 2). The type of substituent containing different groups on its skeleton and the metal in its cavity may have increased its \( k_{ST} \) value by significantly altering it [42]. The rate constant for non-radiative depopulation of S1 (\( k_{nr} \)) contains the rate constants of all non-radiative processes [40]. The \( knr \) value of the ZnPc 3 in DMSO is lower than that of the MPcs containing different types of substituents and metal in the literature [43-45] but higher than that of Std-ZnPc (Table 2). \( k_{nr} \) is about six times its radiation rate constant; therefore, further reduction of the radiation-free rate will affect the emission lifetime. The observed rate constant (\( k_{obs} \)) is the sum of all rate constants depopulating the first excited singlet state (S1) [44,46]. The \( k_{obs} \) value of the ZnPc 3 in DMSO is lower than that of Pc containing 2,6-dimethoxyphenoxy substituted strontium(II) (SrPc) in the literature [44] but higher than that of Std-ZnPc. The nonradiative relaxation processes in the medium, on the order of a few milliseconds, are related to the triple state lifetime [47]. The nonradiative lifetime (\( \tau_{nr} \)) of the ZnPc 3 in DMSO was found longer than that of the SrPc [44] in the literature, but shorter than that of different kinds of ZnPcs [44,48,49] and Std-ZnPc. The presence of benzenesulfonamide-derived substituents containing donor and strong acceptor units on the phthalocyanine ring distinctively changes its photophysical parameters.

**Photochemical properties**

**Singlet oxygen quantum yields (\( \Phi_\Delta \))**
Fluorescent emission into the triplet manifold of a photosensitizer and cross-system transition are the two main photophysical processes that take place after photosensitizers have formed their singlet excited states. Thanks to this factor, the fluorescent emission competes with the intersystem crossing (ISC) and follows the singlet oxygen production processes. However, these results are not mutually exclusive. Thus, a photosensitizer can participate in high ISC efficiency and singlet oxygen generation as well as have a $\Phi_F$ [50]. Singlet oxygen quantum yield ($\Phi_\Delta$) is a quantitative amount of efficiency at which it can use energy in the form of light to convert ground-state oxygen to reactive-type $^1$O$_2$ to determine the use of photosensitizers in PDT. 1,3-Diphenylisobenzofuran (DPBF) can react with $^1$O$_2$ and changes in its concentrations are reflected in its singlet oxygen production [51]. DPBF is more accurate and has a better absorption spectrum, higher speed reaction with $^1$O$_2$ and greater sensitivity and responsiveness to $^1$O$_2$ [52]. $\Phi_\Delta$ of the ZnPc 3 in DMSO was determined by using DPBF as a quencher. There was no change in the Q band intensities of the ZnPc 3 during the $\Phi_\Delta$ determination and the disappearance of DPBF absorbance at 417 nm confirmed that the ZnPc 3 was not degraded during singlet oxygen study (Fig. 5). The $\Phi_\Delta$ value of the ZnPc 3 in DMSO was found less than its counterparts in the literature [24,25] and Std-ZnPc, and it was characteristic for MPcs [19,38] (Table 2). The presence of the substituent containing electron donor and strongly acceptor units in the phthalocyanine skeleton may promote less ISC between the single and triplet states of the molecules, resulting in less efficient $^1$O$_2$ generation [53-58].

**Photodegradation studies**

For use as a photosensitizer in PDT, a drug must also have appropriate stability under applied light [59]. That is, it must be neither strongly determined to be eliminated from the body for a long time nor unstable to decay before it kills the cancer cells. This stability is necessary to maintain the photosensitizing molecule’s efficiency for $^1$O$_2$ production and to keep the unchanged drug concentration. Pcs commonly display optimum stability against decomposition caused by light irradiation. Photodegradation is oxidative degradation of a compound to determine its stability under applied light irradiation, and is a process in which Pc, as photosensitizer, decays under light irradiation due to $^1$O$_2$ attack, which also express for photocatalytic studies PDT [59]. The $\Phi_d$ was determined by monitoring the degradation behavior of the ZnPc 3 by the light using UV-vis spectrophotometer after photo-irradiation for every 20 minutes (Fig. 6). It was determined that the spectrum band shapes of the ZnPc 3 were not distorted under the light irradiation and only intensities of both the B and Q bands decreased (Fig. 6). This indicates that during its photodegradation studies, degradation under light irradiation takes place without any photo-transformation. The ZnPc 3 $\Phi_d$ value is characteristic for MPcs [19] (Table 2) and the ZnPc 3 has similar stability for MPcs [19]. It was determined that the ZnPc 3 had the desired stability for photochemical degradation and was more stable than its counterparts containing different types of benzenesulfonamide in literature [24,25]. The stability of the ZnPc 3 is considerably less than that of Std-ZnPc [19,36,37]. This is due to the presence of new types of benzenesulfonamide-derived substituents containing electron donor and strong electron acceptor groups in its skeleton. This may make it suitable for use in photocatalytic reactions, particularly as a photosensitizer for PDT [60-62].
Conclusion

In this study, the synthesis of three different new compounds, benzenesulfonamide derivative 1 and its phthalonitrile derivative compound 2 and zinc(II) phthalocyanine 3 (ZnPc 3), containing Schiff base, pyridine, 4-bromo-2-methoxyphenol groups together, were carried out. Also, their structures were characterized by widely known spectroscopic techniques. The ZnPc 3’s aggregation behavior in different solvents and concentrations as well as its photophysicochemical properties in DMSO were investigated and the results obtained for these properties were compared with those of its other counterparts in the literature [24,25], as well as with that of unsubstituted zinc(II) phthalocyanine (Std-ZnPc). The ZnPc 3 is practically soluble without aggregation in dichloromethane and chloroform, as well as in dimethylsulfoxide (DMSO) which is biocompatible and non-toxic to cells. It exhibited little aggregation in N, N-dimethylformamide, Tetrahydrofuran, acetonitrile, and toluene, therefore it has slightly soluble in these solvents. It aggregates significantly in methanol and ethanol, and very slightly soluble. With these solubility and aggregation properties in the specified solvents, it can be used for photocatalytic applications, especially as photosensitizer for photodynamic therapy (PDT) and for other technological applications. Its Q band in DMSO was reported to be less redshifted than those of Pc containing different types of benzenesulfonamide derivatives in the literature [24,25]. It was determined that the shape of its emission spectrum is approximately mirror image of the shape of the absorption spectrum, so that the ground and excited state have similar vibrational properties, and the emitting molecule is the same as the absorbing molecule. The presence of benzenesulfonamide-derived substituents containing donor and strong acceptor units on the Pc ring was reported to significantly alter its photophysical parameters compared to its counterparts in the literature [24,25]. Its ability to produce singlet oxygen has been reported to be lower than that of benzenesulfonamide-derived counterparts containing different types of groups in the literature [24,25], but as a photosensitizer for PDT applications, it has the potential to produce sufficient singlet oxygen. The presence of a substituent containing an electron withdrawing group in Pc skeleton can distinctively change the ability to produce singlet oxygen by affecting intersystem crossing between the singlet state and triplet state of the molecules. The photostability of the newly benzenesulfonamide-derived ZnPc 3 containing both electron donor and electron acceptor units from peripheral positions as tetra on its skeleton has been reported to be suitable for a photosensitizer. In conclusion, these data obtained both for the ZnPc 3 new benzenesulfonamide derivative in this study and for ZnPcs containing different types of benzenesulfonamide derivatives from the literature [24,25] suggest that they are more clinically useful agents for cancer PDT. Therefore, these phthalocyanines need to be investigated further in tumour models both in vivo and in vitro.

Declarations

Authors’ Contributions

ÖFÖ and MP edited the draft for general write up and performed the experiments, GAÖ performed the experiments and characterization studies. ÖFÖ and MP took part in writing the text of the manuscript. All authors took part in the discussion of the results.
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Data Availability

All data generated or analyzed during this study are included in this published article and its supplementary information

Ethics Approval

not applicable

Consent to Participate

not applicable

Consent for Publication

not applicable

Conflicts of Interest/Competing Interests

the authors declare no conflicts of interest or competing interests.

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Tables

Table 1 Absorption data (Q \(\lambda_{\text{max}}\)), excitation (\(\lambda_{\text{Ex}}\)), emission (\(\lambda_{\text{Em}}\)) and Stokes shift (\(\Delta_{\text{Stokes}}\)) spectral data in DMSO for the ZnPc 3 and Std-ZnPc.

| Sample   | \(Q_{\lambda_{\text{max}}}\) (nm); loge | \(\lambda_{\text{Ex}}\) (nm) | \(\lambda_{\text{Em}}\) (nm) | \(\Delta_{\text{Stokes}}\) (nm) |
|----------|----------------------------------------|-----------------------------|-----------------------------|-------------------------------|
| ZnPc 3   | 690; 5.06                              | 700                         | 708                         | 8                             |
| Std-ZnPc | 672; 5.14                              | 672                         | 682                         | 10                            |

\(^a\) Data from Ref. [19].

Table 2 Photophysical and photochemical parameters for the ZnPc 3, and Std-ZnPc in DMSO.

| Sample      | \(\Phi_F\) | \(\tau_F\) (ns) | \(a_k_F\) \(\times10^7\) | \(b_k_{nr}\) \(\times10^7\) | \(c_k_{ST}\) \(\times10^7\) | \(d_k_{obs}\) \(\times10^7\) | \(e_{\tau_o}\) (ns) | \(f_{\tau_{nr}}\) (ns) | \(\Phi_d\) | \(\Phi_\Delta\) | \(\Phi_F + \Phi_\Delta\) |
|-------------|------------|-----------------|--------------------------|--------------------------|--------------------------|--------------------------|----------------|----------------|------------|----------------|-------------------------|
| ZnPc 3      | 0.14       | 2.71            | 5.17                     | 31.73                    | 31.76                    | 36.90                    | 19.36          | 3.15           | 88.51      | 0.50          | 0.64                    |
| Std-ZnPc \(^g\) | 0.20       | 3.99            | 5.01                     | 20.04                    | 25.06                    | 25.05                    | 19.95          | 4.99           | 2.61       | 0.67          | 0.87                    |

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

\(^b\)\(k_{nr}\) is the non-radiative rate constant. Values calculated using \(k_{nr} = (1-\Phi_F) / \tau_F\)
c $k_{ST}$ is the rate constant for intersystem crossing. Values calculated using $k_{ST} = k_F \times (1-\Phi_F) / \Phi_F$

d $k_{obs}$ is the decay constant observed in time-resolved fluorescence experiments. Values calculated using $k_{obs} = k_F + k_{nr}$

e $\tau_o$ is the natural radiative lifetime. Values calculated using $\tau_o = \tau_F / \Phi_F$

f $\tau_{nr}$ is the nonradiative lifetime. Values calculated using $\tau_{nr} = 1 / k_{nr}$

g Data from Ref. [36]

h Data from Ref. [38]

**Scheme**

The Scheme is available in the Supplementary Files section.

**Figures**

![Absorbance vs Wavelength](image.png)
Figure 1

UV-vis spectra of the ZnPc 3 in the studied polar and apolar solvents.

Figure 2

UV-vis spectra of the ZnPc 3 in DMSO at certain concentrations. Inset: Plots of absorbance versus concentration.

Figure 3

Fluorescence absorption, emission, and excitation spectra of the ZnPc 3 in DMSO. Excitation wavelength: 655 nm.
Figure 4

TCSPC technique for the ZnPc 3 in DMSO. Excitation wavelength: 655 nm. Bottom: Fitting residues for the ZnPc 3.
Figure 5

A typical spectrum for the determination of singlet oxygen quantum yield of the ZnPc 3, in DMSO at 1 × 10\(^{-5}\) M. Inset: Plots of DPBF absorbance versus time.

Figure 6

The absorption spectral changes of the ZnPc 3 in DMSO under light irradiation showing the disappearance of the Q-band at twenty minutes intervals. Inset: Plot of absorbance versus time.

Supplementary Files

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- GraphicalAbstract.jpg
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