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The New Ball-Type Zinc Phthalocyanine with S-S Bridge; Synthesis, Computational and Photophysicochemical Properties

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Graphical abstract



Research Highlight

- Synthesis and characterization of 4,4'-disulfanediyldiphthalonitrile as ligand and their ball-type zinc phthalocyanine
- The single crystal X-ray diffraction experiment and the Hirshfeld surface analysis.
- Quantum chemical calculations of 4,4'-disulfanediyldiphthalonitrile and their ball-type zinc phthalocyanine.
- The ball-type zinc phthalocyanine with high singlet oxygen quantum yield as 0,89.

Abstract

In this study, the starting compound 4,4'-disulfanediyldiphthalonitrile (1) and its ball-type zinc phthalocyanine (2) were synthesized and characterized by standard spectroscopic methods. The molecular structure and supramolecular dynamics of the compound (1) have been investigated by the analysis of the single crystal X-ray diffraction data. To further understand the intermolecular interactions of compound (1), the Hirshfeld surface analysis has been carried out. The compound (1) and (2) were investigated by quantum chemical calculations. Their quantum chemical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), chemical hardness were performed by B3lyp, HF, M062x method. The ΔG values of the compound (1) and (2) were calculated by using the obtained results. The calculated Infrared spectroscopy, Nuclear Magnetic Resonance, and UV-Vis spectra of the compounds were investigated. In addition, photophysical (fluorescence quantum yields) and photochemical (singlet oxygen generation and photodegradation under light irradiation) properties of newly synthesized ball-type zinc phthalocyanine (2) were investigated in dimethyl sulfoxide (DMSO) solutions. We obtained very high singlet oxygen quantum yields as 0.89, suggesting its potential as photosensitizer in PDT treatment.

Keywords: Ball-type phthalocyanine, single crystal, Quantum Chemical Calculation, Photochemical and Photophysical

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1. Introduction

Phthalocyanines have been extensively investigated as functional materials in scientific research due to their important chemical, biological and physical properties in recent years [1]. The extraordinary chemical and physical features of phthalocyanines are due to the delocalized $18-\pi$ electron system [2, 3]. Thanks to the delocalized $18-\pi$ electron systems, phthalocyanines are interesting for many application areas such as gas sensors [4], chemical sensor [5], liquid crystals [6], optical disks [7], catalysts [8], optoelectronics [9], electrochromic devices [10], photovoltaic cell [11], and photodynamic therapy [12].

The cancer is one of the most dangerous diseases of our day. Chemotherapy, radiotherapy, surgery and photodynamic therapy (PDT) are common technics used in the treatment of cancer. Compared to the surgery, chemotherapy and radiotherapy methods, photodynamic therapy has got some advantages and has been thought as a more promising method in the treatment of cancer. Photodynamic therapy is based on the transformation of light energy into chemical energy through a photosensitizer and singlet oxygen generation to kill cancer cells **[13, 14]**.

Ball-type phthalocyanines are one of the macrocyclic compounds which have increasing importance in recent years. In these kinds of compounds, the two phthalocyanine monomers are generally bridged to each other with benzene derivatives from the peripheral positions of the benzene rings. In this study, the two phthalocyanine monomers are linked by S-S bridges instead of benzene derivatives unlike others. The spectroscopic, electrochemical, photochemical and photopysical properties of ball-type phthalocyanines are different from phthalocyanine monomers [15-17]. Some studies on ball-type phthalocyanines have been published after being synthesized in 2002 for the first time [18]. But, photophysical and photochemical properties of ball-type phthalocyanines are still limited [19-21].

In this present work, 4,4'-disulfanediyldiphthalonitrile (1) as ligand and their ball-type zinc phthalocyanine (2) were prepared. In order to reveal the molecular structure and the bonding dynamics of the supramolecular structure for the compound (1), the single crystal X-ray diffraction experiment and the Hirshfeld surface analysis have been done. The spectral,

structural and computational properties of compound (1) and (2) were performed. Then, we have investigated the photochemical (singlet oxygen quantum yields and photodegradation quantum yields) and photophysical properties (fluorescence quantum yields) of ball-type zinc phthalocyanine (2). We expect that ball-type zinc phthalocyanine (2) was a mixture of isomers of the dimers with the thio groups in different positions. The separation of possible structural isomers of phthalocyanines is very difficult by column chromatography. Hence, no attempt was made to separate the isomers of the ball-type zinc phthalocyanine (2). The obtained photochemical and photophysical results were a mixture of isomers.

2. Experimental

2.1. Materials and Methods

The used all solvents and chemical compounds such as 4-nitrophthalonitrile, SnCl₂, zinc(II) acetate. chloroform(CHCl₃), dichloromethane $(CH_2Cl_2),$ dimethylformamide(DMF), ethanol(EtOH), methanol(MeOH), dimethyl sulfoxide(DMSO), tetrahydrofuran(THF), hydrochloric acid (HCl), sodium nitrite (Na₂S₂), 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) were purchased from commercial suppliers such as Merck, Fluka, Aldrich and Alfa Aesar. All reactions were carried out under a dry N₂ atmosphere. The structure of the compounds was analyzed with common spectroscopic technics such as fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (¹H-NMR), carbon nuclear magnetic resonance (¹³C-NMR), ultraviolet and visible light (UV-Vis) spectral data, and matrix-assisted laser desorption/ionization-time of flight mass spectrometer (MALDI-TOF MS). FT-IR spectra of the compounds were taken by Perkin Elmer Spectrum Two FT-IR Spectrometer. UV-Vis spectra of the compounds were recorded by Agilent Model 8453 diode array ultraviolet-visible spectrophotometer. Fluorescence properties were performed by Hitachi S-7000 fluorescence spectrophotometer. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300 spectrometer instruments.

2.2. Synthesis of 4,4'-disulfanediyldiphthalonitrile (1)

4-nitrophthalonitrile was converted to 4-aminophthalonitrile in the presence of hydrochloric acid and Tin (II) chloride according to literature [22]. The diazonium salt of obtained product was prepared with addition of sodium nitrite solution in hydrochloric acid and then 4,4'-

disulfanediyldiphthalonitrile (1) was obtained in the presence of sodium sulfide according to literature (Scheme 1) [23]. $C_{16}H_6N_4S_2$ (318,38 g.mol⁻¹) elemental analysis: calculated (C, 60.36; H, 1.90; N, 17.60) found (C, 60.41; H, 1.98; N, 17.11). ¹H NMR (300 MHz, in DMSO) δ ppm: 8.01 (dd, 1H (H-4 and H-14), Jo= 8.20 Hz, Jm= 1.5 Hz), 8.09 (d, 1H (H-3 and H-13)), 8.33 (d, 1H (H-6 and H-10)). ¹³C NMR (75 MHz, in DMSO) δ ppm: 113.7 (C-2, C-12), 116.0 (C-1, C-11), 116.3 (C-15, C-19, C-21, C-23), 131.6 (C-6, C-10), 131,8 (C-3, C-13), 135.0 (C-4, C-14), 143.5 (C-5, C-9). UV-Vis (in DMSO) λ_{max} : 233nm and 277 nm.

2.3. Synthesis of ball-type zinc phthalocyanine (2)

4,4'-disulfanediyldiphthalonitrile (150 mg, 0.47 mmol) in 2-dimethylamino-ethanol (DMAE) (5 mL) and DBU (0.05 cm³) was heated at 160 °C for 30 minutes under N₂ atmosphere. The anhydrous zinc (II) acetate (0.030 g, 0.22 mmol) was added to the reaction. The reaction mixture was stirred for 12h (**Scheme 2**). After the reaction was completed, reaction mixture was cooled to room temperature. First of all, the reaction mixture was precipitated with hexane and then the solid product was washed with water, acetonitrile and MeOH in order to remove impurities, respectively. Further purification was made by column chromatography with CHCl₃-MeOH (20/2 v/v) as eluent. After the purification, ball-type zinc phthalocyanine (**2**) was obtained with % 13 yields (20 mg). The novel ball-type zinc phthalocyanine (**2**) is well soluble in DMF and DMSO and is partially soluble in THF, CHCl₃ and CH₂Cl₂. The chemical formula of (**2**): C₆₄H₂₄N₁₆S₈Zn₂, calculated molecular weight: 1404.32 g.mol⁻¹ (**Table S1**). Elemental analysis: calculated (C, 54.74; H, 1.72; N, 15.96), found (C, 55.01; H, 1.68; N, 16.13), ¹H-NMR (300 MHz, in DMSO) δ ppm: 7.96–8.15 (16H, Pc–H), 8.30–8.38 (8H, Ar–H). UV-Vis (in DMSO): λ_{max} , (log ε); 687 nm (4.81) (Q-Band) and 355 nm (4.85) (B-Band). MALDI-TOF-MS, (Dithranol): m/z: 1404.89 [M+H]⁺.

2.4. X-ray data collection and refinement for the 4,4'-disulfanediyldiphthalonitrile (1)

The HKL data of the 4,4'-disulfanediyldiphthalonitrile (1) has been collected by a Bruker APEX II Quazar three-circle diffractometer with mono-chromated Mo-K_{α} radiation (λ = 0.71073 Å). In the experiment done at 172 K, a colorless crystal with a size of 0.494 × 0.177 × 0.086 mm has been chosen. Totally 10375 reflections have been observed. Among them, 1339 reflections were independent and 1318 reflections were I > 2 σ (I). The molecular structure of compound 4,4'-disulfanediyldiphthalonitrile (1) has been solved by using the intrinsic phasing in SHELXT and then refined by full-matrix least-squares refinements on F^2 using SHELXL in Olex2 program. The **table 1** presents the crystallographic information, data collection and the summary of the final refinement results for the 4,4'-disulfanediyldiphthalonitrile (1).

2.5. Photophysical and Photochemical Parameters

2.5.1. Fluorescence quantum yields

Fluorescence quantum yield (Φ_F) of the novel ball-type zinc phthalocyanine (2) was determined with the comparative method using by the following equation (1) in DMSO at room temperature [24, 25].

$$\Phi_{\rm F} = \Phi_{\rm F} \left({\rm Std} \right) \quad \frac{{\rm F.A_{\rm Std}.n^2}}{{\rm F_{\rm Std}.a.}{\rm n_{\rm Std}^2}} \tag{1}$$

In this equation, $\Phi_{\rm F}$ is the quantum yield of the compound (1), $\Phi_{\rm F}$ (Std) is the quantum yield of the reference compound, F and F_{Std} are the areas under the fluorescence emission curves of the novel ball-type zinc phthalocyanine (2) and unsubstituted zinc phthalocyanine as a standard, respectively. Absorbance of the reference and sample compounds are A_{Std} and A, respectively. n^2 and n_{Std}^2 are the refractive indices of solvents used for the sample and standard, respectively. The quantum yield of the reference compound (unsubstituted zinc phthalocyanine) was used as $\Phi_{\rm F} = 0.20$ according to literature [26].

2.5.2. Singlet oxygen quantum yields

The singlet oxygen quantum yield of novel ball-type zinc phthalocyanine (2) was determined in air by using the following equation in DMSO at room temperature; in the equation (2), zinc phthalocyanine as a reference and DPBF as chemical quencher were used.

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{\mathbf{R} \cdot \mathbf{I}_{\text{abs}}^{\text{Std}}}{\mathbf{R}^{\text{Std}} \cdot \mathbf{I}_{\text{abs}}}$$
(2)

In this equation, $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield of reference sample. The singlet oxygen quantum yield of the reference compound (unsubstituted zinc phthalocyanine) was used as $\Phi_{\Delta}^{\text{Std}} = 0.67$ in DMSO according to literature) [26]. R and R_{Std} are the photobleaching rates of DPBF in the presence of the novel ball-type zinc phthalocyanine and unsubstituted zinc phthalocyanine as a reference. I_{abs} and I_{abs}^{Std} are absorption rates of light in the presence of the novel ball-type zinc phthalocyanine as a reference. The solutions containing DPBF prepared in dark environment and the degradation of DPBF at 417 nm was monitored after each 5s irradiation [27, 28]. The absorption band of DPBF at 417 nm reduced after the light irradiation [28].

2.5.3. Photodegradation quantum yields

The photo degradation quantum yield of novel ball-type zinc phthalocyanine was determined by using the following equation (3);

$$\Phi_{\rm d} = \frac{(C_0 - C_t) \cdot V \cdot N_{\rm A}}{I_{\rm abs.} S \cdot t}$$
(3)

In this equation, C_0 is the concentration of novel ball-type zinc phthalocyanine before the irradiation and C_t is the concentration after the irradiation. V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area, "t" is the irradiation time, I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples **[28]**.

3. Results and discussion

3.1. Synthesis and characterization

The structure of synthesized compounds was verified by using some spectroscopic methods such as UV-Vis, FT-IR, ¹H-NMR, ¹³C-NMR, elemental analysis and MALDI-MS. The theoretically calculated IR, NMR, and UV-Vis spectra of the starting compound (1) and their ball-type zinc phthalocyanine (2) were investigated and the obtained parameters were compared with experimental values. All the obtained results are compatible with the expected compound structures.

4,4'-disulfanediyldiphthalonitrile (1) was synthesized from 4-nitrophthalonitrile as shown in **Scheme 1**. 4-nitrophthalonitrile was converted to 4-aminophthalonitrile and then 4,4'- disulfanediyldiphthalonitrile was obtained. FT-IR and ¹H-NMR results supported the expected compound structures.

FT-IR spectra of 4-nitrophthalonitrile and 4-aminophthalonitrile were given in **Fig. S1**. The characteristic -C=N stretching peaks belong to the dinitriles shifted from 2243 cm⁻¹ to 2214 cm⁻¹ after the conversion reaction of 4-nitrophthalonitrile to 4-aminophthalonitrile. The characteristic peaks at 1532 cm⁻¹ and 1350 cm⁻¹ related to nitro groups were disappeared and stretching vibrations corresponding to primary amino groups at about 3488 cm⁻¹ and 3358 cm⁻¹ were appeared. The characteristic -C=N stretching peaks shifted from 2214 cm⁻¹ to 2233 cm⁻¹ and aromatic CH stretching peaks were observed at 3094 cm⁻¹, 3060 cm⁻¹ and 3019 cm⁻¹ (**Fig. S2**). The novel ball-type zinc phthalocyanine (**2**) was synthesized with cyclotetramerization reaction of 4,4'-disulfanediyldiphthalonitrile (**1**). After the reaction, characteristic -C=N stretching peak at 2233 cm⁻¹ disappeared. This supported the formation of the phthalocyanine (**2**) (**Fig. S2**).

UV-Vis spectroscopy is a very useful technique for the characterization of phthalocyanines. Because phthalocyanines have some characteristic peaks in electronic absorption spectra. This characteristic peaks are that 650-700 nm regions (Q-band) arising from the π - π *transition and 300-400 nm regions (B-band) arising from deeper π - π *transitions. Especially, Q band regions provides information about whether metallophthalocyanines or metal-free phthalocyanines. The electronic absorption spectra of novel ball-type zinc phthalocyanine (2) were recorded in DMSO and DMF. The Q-band absorption arising from the π - π *transition of compound (2) was appeared as a single band with high intensity at 688 nm in DMSO and 689 nm in DMF. The B-band absorption arising from the deeper π - π *transition of compound (2) was appeared at 352 nm in DMSO and 351 nm in DMF.

One of the common spectroscopic techniques used for characterization is mass spectroscopy.

Thus, mass spectroscopy was used for characterization. The molecular ion peak of ball-type zinc phthalocyanine (2) was observed at m/z: 1404.898 [M]⁺ in the MALDI-TOF-MS (Dithranol as matrix) (Fig. S3).

In the ¹H-NMR spectrum of 4,4'-disulfanediyldiphthalonitrile (1), the aromatic protons appeared at between δ :7.997 and 8.331 ppm. H-4 shows a doublet of doublets at 8.01 ppm. The interaction constants were calculated as 8.20 Hz for ortho (with H-3) and 1.5 Hz for meta (with H-6). H-3 shifted as a doublet at 8.09 ppm, and H-6 shifted as a doublet at 8.33 ppm (**Fig. S4**). In the ¹³C-NMR spectrum of 4,4'-disulfanediyldiphthalonitrile, the related carbon

peaks appeared at δ : 113.7 (C-2, C-12)4, 116.0 (C-1, C-11)4, 116.3 (C-15, C-19, C-21, C-23)4, 131,.6 (C-6, C-10)1, 131,8 (C-3, C-13)77, 135.20 (C-4, C-14), 143.5 (C-5, C-9)49 ppm (**Fig. S5**). In the ¹H-NMR spectrum of the novel ball-type zinc phthalocyanine (**2**), the aromatic protons were obtained in a higher area and broader compared to compound (**1**) due to the face to face interaction of two monomers in ball-type zinc phthalocyanine (**2**).

3.2. Results of X-ray diffraction experiment for the 4,4'-disulfanediyldiphthalonitrile (1)

The XRD experiment proved that an orthorhombic (P2₁2₁2) single crystal has formed with the unitcell parameters of a = 12.3002 Å, b = 12.9658 Å, c = 4.7080 Å. There are two molecules in the unitcell. The **Fig. 1(a)** presents the asymmetric unit of the compound (1), which is the half of a molecule. In the **Fig. 1(b)**, a completed arrangement is given with the atomic labels and gravity centres for five/six-membered rings. For clarity, the hydrogen atoms were not labelled in the figure, but they have been labelled as the same number with carbon atom labels which they are bonded (like C6—H6).

In the completed fragment of the molecule, a strong intra-molecular S1a···H6 (or/and S1···H6a) interaction has been observed with an interaction distance of 2.72 Å which is ~%10 shortened compared to their Van der Waals radii (1.80 Å and 1.20 Å, respectively). Thus, two five-membered rings (S1a—S1—C1—C6—H6 and S1—S1a—C1a—C6a—H6a) have formed as a planar conformation with an RMS deviation of 0.0948 Å. The dihedral angle between these two planes is 75.1° and the Cg2···Cg2a distance is 2.30 Å. Also, the six-membered rings exhibit a perfect planar conformation with an RMS deviation of 0.0034 Å. The dihedral angle between the six-membered ring planes is 86.5° and the Cg1···Cg1a distance is 5.681 Å. The selected bond geometries for the 4,4'-disulfanediyldiphthalonitrile (1) have been presented in **table S2**.

The supramolecular structure of the 4,4'-disulfanediyldiphthalonitrile has been stabilized by the domination of Cg...Cg, Cg...N, Cg...S, one strong D—H...A (C6—H6...N1= 2.54 Å) and one week D—H...A (C3—H3...N2=2.72 Å) interactions. As shown in **Figure S6**, the C—H...N interactions provide the stability along the ab plane while the other interactions provide the stability along the c-axis. These interactions have been listed in **table S3** and **table S4**. The unitcell presentation through the view for (100), (001), (010), (011) and (101) of the compound (1) were given in (**Fig S7- Fig S11**), respectively.

3.3. Results of Hirshfeld surface analysis for the 4,4'-disulfanediyldiphthalonitrile (1)

To further understand the intermolecular interactions of the 4,4'-disulfanediyldiphthalonitrile (1), the Hirshfeld surface analysis has been done. This is a method that can show intermolecular interactions in a powerful way and also it supplies visual results. The **figure S12** presents the Hirshfeld surfaces of the 4,4'-disulfanediyldiphthalonitrile in three different angles of view with d-norm, shape index and curvedness modes. The red zones in d-norm and shape index, which are shown by black arrows in the figure, indicate the strongest D—H···A and Cg···X (X: S1, N1) interactions, respectively.

The D—H···A bonds have already been presented in **figure S6**. The Cg···X bonds have been presented in **figure 2** (along c-axis). The sulfur atoms of the top molecule conform almost top of the midpoint of the six-membered rings of the bottom molecule. Similarly, the half of the nitrogen atoms of bottom molecule conforms to midpoint of six membered rings of top molecule.

According to Hirshfeld surface analysis, the percentages of intermolecular interactions are given as follows: $C \cdots C = \% 8.6$, $C \cdots H = \% 11.5$, $C \cdots N = \% 11.2$, $C \cdots S = \% 11.5$, $N \cdots H = \% 46$, $N \cdots N = \% 1.6$, $N \cdots S = \% 3.8$, $S \cdots H = \% 1.2$, $H \cdots H = \% 4.6$. All of these interactions have been presented in fingerprint plots (*di:* internal distance, *de:* external distance) in **Figure S13**.

3.4. Calculation Results

It is well known that theoretical studies are used to investigate the activity of molecules and chemical reactions. The chemical parameters obtained by quantum chemical calculations are used to describe them. In this present work, the results obtained from the quantum chemical parameters are interpreted by comparing the activities of the molecules in **table S5 and S6**. HOMO and LUMO values of the studied molecules should be known for interpret these results. The most important parameter used to compare the activity of molecules is HOMO energy value, which is demonstrates the electron-donating ability of the organic and inorganic molecules **[29-31]**.

HOMO and LUMO energy values are the most widely used parameters to compare the chemical activity of organic and inorganic molecules [32, 33]. In **figure 3**, the optimized state of the 4,4'-disulfanediyldiphthalonitrile (1) is shown in the first picture; the second picture has a HOMO representation of the 4,4'-disulfanediyldiphthalonitrile (1). In this illustration, it is seen that HOMO orbitals are formed on which atoms. In the third picture, the 4,4'-disulfanediyldiphthalonitrile (1) have LUMO representation. In this picture, it is seen on

which atoms LUMO orbitals are formed. In the last picture, the electron distribution of the 4,4'-disulfanediyldiphthalonitrile (1) is shown [29].

Quantum chemical parameters of molecules are calculated by using HOMO and LUMO energy values of molecules [33, 34]. These quantum chemical parameters are electronegativity (χ), chemical hardness (η) and global softness (σ), which is related to HOMO and LUMO energy values. These parameters are used to compare chemical activities of molecules and measure interactions across metal atoms.

In figure S14, the structure optimized for the metal complex consisting of a combination of ligand molecule and Zn metal is shown from different angles. In figure 4, The HOMO, LUMO and electrostatic potentials of the metal complex obtained as a result of the optimization are shown. 4 different isomers were formed by the combination of ligands. The structural forms of these formed isomers are shown in figure 4. The energy values of each isomer were calculated. Looking at the energy values, the isomer (2^c) was found to be more stable than the others (Table S7).

The Gibbs free energy (ΔG) was calculated by using the equation below:

$$\Delta G = E_{M-L_{complexe}} - (E_{M^{2+}} + 4\sum E_{Ligand})$$
(4)

where $E_{M-L_{complexe}}$ is the sum of the electronic and thermal free energies of the metalcomplex, E_{Ligand} is the sum of the electronic and thermal free energies of the ligand and $E_{M^{2+}}$ is the sum of the electronic and thermal free energies of the metal ion. The Gibbs free energy (ΔG) value of the studied complex is given in **table S8**. This value was negative in the calculations. A negative value indicates that the reaction is spontaneous.

3.4.1. NMR spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most important methods used to analyze the structure of molecules. NMR spectroscopy is used for the illumination of covalent compounds. It is based on the measurement of carbon and hydrogen atoms in the molecule that are stimulated to the rotational energy levels by the absorption of electromagnetic radiation in the radio frequency range. The experimental and theoretical NMR values of the studied molecule were determined. These theoretical calculations of

studied molecules were calculated using the gauge-independent atomic orbital (GIAO) method [35]. The atoms in the studied molecules are labeled as shown in the figure S15. The experimental and theoretical ¹H and ¹³C NMR chemical shift values are given in table S9 of studied molecule. The experimental and theoretical ¹H and ¹³C NMR values of this molecule were calculated by the effect of atomic and atomic groups around the atoms [36, 37]. In this study, the theoretical calculation of carbon and hydrogen atoms in the molecule was carried out by using the basis set of HF / 6-31 ++ g. The values obtained as a result of the theoretical calculations were plotted to compare with the experimental values in figure S16. In the drawn graph, the theoretical values against the experimental values were plotted and R^2 values were obtained. These R² values were 0.9876 in gas phase and 0.9919 in DMSO phase. These R² values are about 1, which is a very good result. The high R values indicate that these values are reliable. Considering the results obtained as a result of theoretical studies, it is seen that the carbon atoms in the aromatic ring when they look at chemical shift values are in the range of 120-144 ppm. However, the chemical shift values of aliphatic carbon atoms are in the range of 108-109 ppm. On the other hand, the chemical shift values of hydrogen atoms in the aromatic ring are observed to be in the range of 8.53-9.00 ppm.

3.4.2. UV-Vis spectroscopy

Ultraviolet and visible light (UV-Vis) absorption spectroscopy is a measure of the reduction of a beam after it has passed through a sample or reflected from a sample surface. UV-Vis spectrum of ligand is calculated at hf/6-31++g level in gas (ε =1), chloroform (ε =4.711), methanol (ε =32.613), dimethyl sulfoxide (ε =46.826), water (ε =78.355), n-methyl formamidemixture (ε =181.56) phase in **figure S17**. Otherwise, UV-Vis spectrum of metal complex are calculated at same level only in gas phase in **figure 5**. In the spectrum of UV-Vis obtained, it is examined how electronic transitions occurring in studied ligands are affected in different solvents. In these investigations it has been seen that as the dielectric constant of the solvent increases, the absorbed wavelength increases [**38**, **39**]. When the UV-Vis spectrum of the ligand and metal complex is examined, it is seen that there are generally two basic peaks. At these basic peaks, it is assumed that n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ are electronic transitions.

3.4.3. IR spectroscopy

Infrared spectroscopy involves the interaction of infrared radiation with studied molecules. It covers a range of techniques and method, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. One of the most important methods used to identify the structures of molecules from the IR spectra of ligand and metal complexes. IR spectra of ligand and metal complexes are calculated hf/6-31g (d, p) level in gaussian. IR spectrum values of the studied ligand and metal complexes were obtained by using VEDA software **[40, 41]**. IR spectrum peaks of the studied ligand and metal complexes are given in **table S10**. The two spectra obtained from theoretical and experimental studies, while the blue spectrum was obtained from experimental studies. When compared the theoretical and experimental spectra, it is seen that there are great similarities in the two spectra. The main reason for differences between the spectra are that the theoretical studies are in the gas phase and do not contain experimental inputs.

3.5. Aggregation Studies

Phthalocyanine complexes are known to exhibit aggregation behavior due to the π -electron system. Aggregation behaviors of phthalocyanines can be differing with solvent, concentration, temperature and bulk functional group. The formation of aggregates decreases the Q-band intensity of phthalocyanines and leads to fluorescence quenching and accordingly, decreased singlet oxygen yield. Thus, the synthesis of phthalocyanines that are not aggregating or showing low aggregation is important for photodynamic therapy applications.

The aggregation behavior of novel ball-type zinc phthalocyanine (2) was investigated by UV-Vis spectroscopy in DMSO (Figure S19). Figure S19a exhibits the UV-Vis spectrum of the ball-type zinc phthalocyanine (2) at different concentrations in DMSO. When the concentration of novel ball-type zinc phthalocyanine (2) was increased, the Q band intensity increased. No new band formation was observed due to the aggregated species. Similarly, the new band formation was not observed in transmittance spectra (Figure S19b). Aggregation behaviors of compound (2) were also investigated by derivative spectra. It is well known that derivative spectrum gives much detail information about the spectrum. First derivative spectrum of absorption band gives cross over point as positive maxima and negative minima (Figure S19c). Second derivative spectrum is characterized by two satellite maxima and an inverted band of which the minimum corresponds to the λ max of the fundamental band (Figure S19d). No new band formation was observed when the concentration was increased in the first and second derivative

spectra of ball-type zinc phthalocyanine (2) as being in the absorbance and transmittance spectra. The obtained all figures supported that novel ball-type zinc phthalocyanine (2) did not aggregate in DMSO.

3.6. Fluorescence measurements

3.6.1. Fluorescence spectra and fluorescence quantum yields

Fluorescence properties of novel ball-type zinc phthalocyanine were performed in DMSO at room temperature. Figure 6 exhibits the absorption, excitation and emission spectra of the novel ball-type zinc phthalocyanine (2) in DMSO. The absorption, excitation and emission spectral data of the compound (2) was given in Table 2. The excitation and absorption spectra of the compound (2) are similar and they show the same Q-band maxima. This is indicating that the nuclear configurations of the ground and excited states are similar and not affected by excitation in DMSO [42, 43]. However, the absorption spectrum is slightly broader than the excitation and emission spectrum due to aggregation in the former [19-21]. The fluorescence emission spectra of the compound (2) are mirror images of the excitation spectra. The observed Stokes shift of novel ball-type zinc phthalocyanine (2) is 12 nm. The fluorescence quantum yield (Φ_F) of novel ball-type zinc phthalocyanine (2) was studied in DMSO. The fluorescence quantum yield (Φ_F) value of the compound (2) is 0.09 (table 2). This value is low compared to unsubstituted zinc phthalocyanine or mono type substituted zinc phthalocyanines. It may be suggested that is due to the face to face interaction of two monomer in ball-type phthalocyanines. Energy gap between the triplet state and singlet state may decrease due to face to face interaction of two monomer in ball-type phthalocyanines and reduce the formation of singlet state. This causes a decrease in fluorescence. Thus, the fluorescence quantum yield (Φ_F) of novel ball-type zinc phthalocyanine is low with 0.09 value compared to other zinc phthalocyanines [19-21].

3.6.2. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_{Δ}) of the novel ball-type zinc phthalocyanines (2) was determined by using equation 2 in DMSO at room temperature and listed in **table 2**. 1, 3-

diphenylisobenzofuran (DPBF) was used as singlet oxygen quencher. Figure 7 shows that spectral changes of the novel ball-type zinc phthalocyanine with the disappearance of the peak at 417 nm related to 1,3-diphenylisobenzofuran (DPBF) by using UV-Vis spectroscopy. During the disappearance of peak at 417 nm, no change was observed in the Q band intensity of the novel ball-type zinc phthalocyanines (2). This indicates that the novel ball-type zinc phthalocyanines (2) did not decompose in the presence of DPBF. The Φ_{Δ} value of novel balltype zinc phthalocyanines (2) is 0.89 in DMSO solution. This value is higher than unsubstituted zinc phthalocyanine (Φ_{Δ} = 0.67 from Ref [44]). An ideal photosensitizer must be having high singlet oxygen quantum yield for the use in photodynamic therapy treatment. The novel ball-type zinc phthalocyanine (2) with 0.89 singlet oxygen quantum yield is potential candidate for the photodynamic therapy treatment of cancer.

3.6.3. Photodegradation quantum yields

Photodegradation is a process that shows the stability of photosensitizer compounds under light. It is important to determine the stability of the photosensitizer agent to be used in photodynamic therapy applications. The photodegradation stability of the novel ball-type zinc phthalocyanine was performed in DMSO at room temperature by using UV-Vis spectroscopy.

Figure 8 shows that spectral changes of the novel ball-type zinc phthalocyanine (2) under the light irritation. The change of the Q band intensity of the novel ball-type zinc phthalocyanine with increasing time was recorded. The photodegradation degree of the novel ball-type zinc phthalocyanines (2) under the light irritation was shown to be insignificant. The photodegradation quantum yield (Φ_d) value of the novel ball-type zinc phthalocyanine is 1.9×10^{-5} in DMSO solution. This value is about same with unsubstituted zinc phthalocyanine ($\Phi_d = 2.6 \times 10^{-5}$ in DMSO). An ideal photosensitizer must be having stable for the use in photodynamic therapy treatment. Thus, the novel ball-type zinc phthalocyanine with 1.9×10^{-5} photodegradation quantum yield is potential candidate for the photodynamic therapy treatment of cancer.

4. Conclusions

We have reported the synthesis of 4,4'-disulfanediyldiphthalonitrile (1) as ligand and their ball-type zinc phthalocyanine (2). The single crystal X-ray diffraction experiment of the compound (1) and the Hirshfeld surface analysis has been done in order to reveal the

molecular structure and the bonding dynamics of the supramolecular structure. The structure of 4,4'-disulfanediyldiphthalonitrile (1) and their ball-type zinc phthalocyanine were optimized. IR, UV-Vis and NMR spectra of these structures were obtained. These theoretical spectra were compared with experimental spectra. The data obtained from the theoretical calculations were in great agreement with the experimental data. The photochemical and photophysical properties of ball-type zinc phthalocyanines (2) were investigated. The novel ball type zinc phthalocyanine with 0.89 singlet oxygen quantum yield is potential candidate for the photodynamic therapy treatment of cancer.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Autor statement

Ahmet Turgut BİLGİÇLİ: Investigation, designed, supervised and writing, Hayriye Genç Bilgiçli:, Investigation, synthesis of compounds, Armağan Günsel: the preparation of phthalocyanine compounds and their purification, Hasan Pişkin: The analysis of the single crystal X-ray diffraction data, Burak Tüzün: The performed of quantum chemical parameters such as HOMO, LUMO, chemical hardness by B3lyp, HF, M062x method, M. Nilüfer Yarasir: Investigation and characterization, Mustafa Zengin: Investigation, synthesis and characterization

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Fig. 1 (a) The asymmetric unit. (b) Atomic arrangement, labels and centre of gravities (Cg) for the six membered rings. Cg1 and Cg1a represent the gravity centres for the six-membered rings. Cg2 and Cg2a represent the gravity centres for the five-membered rings.



Fig. 2 The conformation of the molecules through the c-axis. (a) The shape index representation of the Hirshfeld surface. The black dots indicate the $Cg \cdots X$ (X: S1, N1) interactions (b) The Olex 2 representation.



Fig. 3 HOMO, LUMO, ESP and the optimized structure of the 4,4'- disulfanediyldiphthalonitrile (1)



Fig. 4 HOMO, LUMO, ESP and the optimized structure of the studied isomers of the novel ball type zinc phthalocyanine (2)



Fig. 5 Theoretical and experimental UV-Vis spectrum of the novel ball type zinc phthalocyanine (2)



Fig. 6 Absorption, excitation and emission spectra of the novel ball type zinc phthalocyanine (2) in DMSO



Fig. 7 A typical spectrum for the determination of singlet oxygen quantum yield of the novel ball type zinc phthalocyanine (2) in DMSO



Fig. 8 A typical spectrum for the determination of photodegradation oxygen quantum yield of the novel ball type zinc phthalocyanine (2) in DMSO.



Scheme 1 The synthesis of the 4,4'-disulfanediyldiphthalonitrile (1)



Scheme 2 The synthesis of the novel ball type zinc phthalocyanine (2)

CCDC Number	1912759				
Empirical formula	$C_{16}H_6N_4S_2$				
Formula weight (g mol ⁻¹)	318.37				
Temperature (K)	172				
Wavelength (Å)	Mo Kα radiation				
	(0.71073)				
Crystal system	Orthorhombic				
Space group	P21212				
a (Å)	12.3002(17)				
b (Å)	12.9658(17)				
c (Å)	4.7080(6)				
α (°)	90				
β (°)	90				
γ (°)	90				
Volume (Å ³)	750.84 (17)				
Z	2				
Crystal size (mm)	0.494 imes 0.177 imes 0.086				
Crystal description	block, colourless				
ρ_{calcd} (g cm ⁻³)	1.408				
μ (mm ⁻¹)	0.354				
F(000)	324				
θ range for data collection (°)	2.3°–25.1°				
h, k, l	-14/14, -15/15, -5/5				
Reflections collected	10375				
Independent reflections	1339 ($R_{int} = 0.0594$)				
Data/restraints/parameters	1318/0/112				
Goodness of fit on F ²	1.120				
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0236, wR_2 =$				
	0.0642				
Largest diff. Peak and hole	0.18 and - 0.19,				
(e Å- ³)	RMS 0.04				

 Table 1 Data collection, refinement parameters and crystallographic information for the compound (1)

 Table 2 Spectral, photophysical and photochemical properties of the ball-type zinc

 phthalocyanine (2)

Compound	λ _{abs} , (nm)	$\lambda_{Exc} (nm)$	$\lambda_{\text{Ems}}(nm)$	Stokes shift (nm)	Φ_{F}	$\Phi_{\rm d} (10^{-5})$	Φ_Δ
(2)	687	687	699	12	0,09	1.9	0,89
ZnPc	-	-	-	-	0,20 ^a	2.61	0,67 ^b

^a Data from ref. [55], ^b Data from ref. [68],