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Organo-soluble dendritic zinc phthalocyanine: photoluminescence and fluorescence properties

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ABSTRACT

In this study, the spectroscopic measurements of the second generation dendritic zinc phthalocyanine (phthalocyanine dendrimer with tris) **2** were made and its potential to be used in optoelectronic applications was investigated. To examine the intramolecular energy transfer properties, fluorescence quantum yields were calculated and the contribution of first (phthalocyanine dendrimer with triethyl methanetricarboxylate) **1** and second **2** generation dendrimers to this energy transfer was investigated. The photoluminescence properties and optical band gap of the second generation zinc phthalocyanine **2** were investigated depending on the temperature. In addition, the quantum efficiency of singlet oxygen was calculated to evaluate the usability of this compound in photodynamic therapy. Also, aggregation behavior of compound **2** was examined in different solvents (DMF, DMSO and THF) and different concentrations in THF. To the best of our knowledge, this is the first study to examine the photoluminescence properties and temperature dependent changes of dendritic phthalocyanines.

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KEYWORDS

Phthalocyanine; dendrimer; photoluminescence; fluorescence; singlet oxygen

Introduction

Phthalocyanines (Pc) have attracted great interest among researchers due to their optical, electrical and structural properties.^[1–6] These compounds are composed of heterocyclic conjugated molecules therefore demonstrate high chemical and thermal stability,^[7] and the synthesis of the molecules do not require a large amount of energy consumption and yet complex instrumentation. Besides, chemical properties can be tuned up by designing the substituents.^[8] The most commonly used substituents are alkyl,^[9,10] alkyloxy,^[11,12] alkyloxymethyl^[13] along with carboxy^[14–17] and sulfo groups,^[18] alkylthio,^[19] perfluoroalkyl,^[20] oligo(ethyleneoxy)^[21] and aryloxy substituents,^[22] as well as aromatic^[23] or heteroaromatic groups,^[24] and also bulky substituents.^[25,26] Although relationship between molecular structure and the physical and chemical properties of Pc was investigated, a wide range of experiments on a specific use in various applications are still on-going. Among these applications, organic semiconductors such as organic light-emitting diodes (OLEDs), transistors, photovoltaic (PV) cells, organic solar cells and lasers are the most interesting topics and thus they are widely studied.^[27] It is also possible to develop a new structurally controllable organic macromolecule to be used in optoelectronic applications. It is desirable that organic compounds to be used in optoelectronic applications do not exhibit aggregation behavior, have high fluorescence quantum yield, have

absorption at high wavelengths and have appropriate orbital levels to permit electron transfer. These properties of phthalocyanines were strongly affected by the metal ion in the cavity and by the nature, number and position of substituent.^[28–34] At the same time, the solubility of phthalocyanine is also an important factor determining their potential for use in applications.

Dendrimers are macromolecules which can be used in optical and optoelectronic applications, because of the optical properties of the dendrimers can be controlled by the central or functional groups of the dendrimer can be altered.^[35] Due to the dendritic phthalocyanines have tunable chemical properties such as exhibiting a non-aggregation behavior, having high fluorescence quantum yield, absorption at long wavelengths and appropriate orbital levels to permit electron transfer.^[35–38] In this way, they have the potential to be used actively in many applications.

In the present study, organo-soluble second-generation dendritic zinc phthalocyanine **2** was investigated. In addition, singlet oxygen (¹O₂) measurements were exhibited and suggested that it may be a candidate drug for photodynamic therapy of compound **2**. It can be said that the second generation dendritic phthalocyanine compound **2**, which is soluble in organic solvents, has the potential to be used in optoelectronic and medical applications.

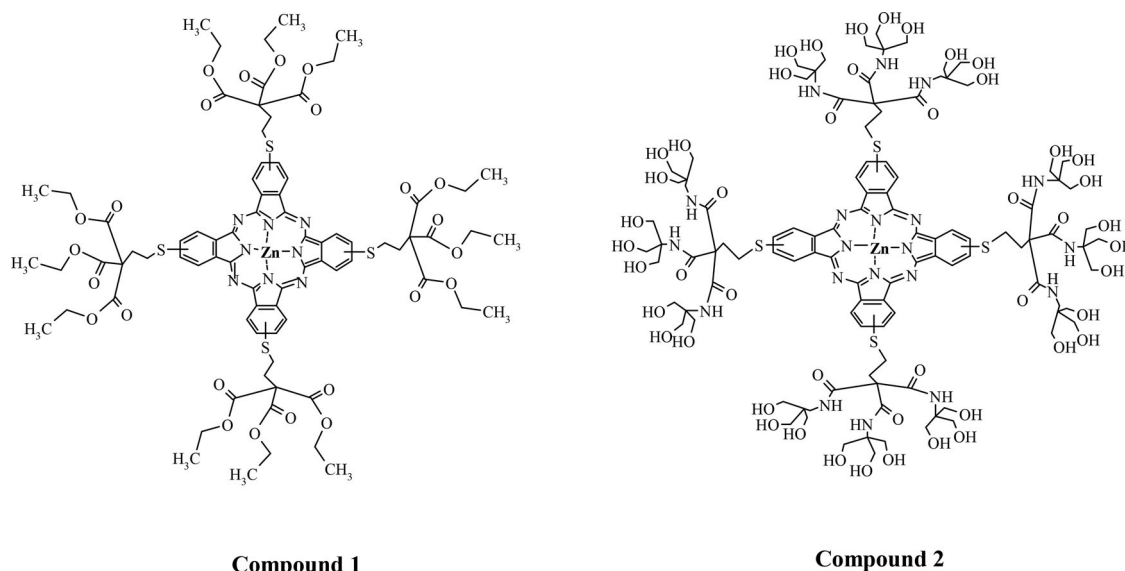


Figure 1. First 1 and second 2 generation dendritic zinc phthalocyanine compounds.

Experimental

General

All solvents were dried by molecular sieves or proper methods.^[39] The dendritic phthalocyanines were synthesized^[40] on the basis of Newkome's divergent-growth approach according to the literature.^[41] UV-vis spectrum was recorded on a Shimadzu UV-1800 UV-vis spectrophotometer. Fluorescence spectra of compounds were conducted with Shimadzu RF 5301 fluorescence spectrophotometer. Photoluminescence (PL) measurements were recorded with Andor-Solis Photoluminescence Spectrometer. Samples are loaded in a closed-circuit cooler so that measurements can be taken in the 20–280 K temperature range for PL measurements. Laser used to stimulate the sample in photoluminescence measurements is a Single Mode diode laser with a wavelength of 732 nm.

Preparation of organic thin films

Thin films of second generation dendritic phthalocyanine compound 2 were prepared by the drop-casting method. For the preparation of thin film, solution of the phthalocyanine compound in tetrahydrofuran (THF) was initially prepared. Then the organic solution was dropped on the glass surface and left to dry at room temperature.

PL measurements

Thin film of the compound was prepared on the glass surface by drop-casting method. Samples are loaded in a closed-circuit cooler so that measurements can be taken in the 10–300 K temperature range. Laser used to stimulate the samples in photoluminescence measurements within a Single Mode diode laser with a wavelength of 732 nm. PL measurements were evaluated in the temperature range of 50 to 300 K. Low temperature photoluminescence measurements

were performed by a 785 nm single-mode diode laser with 100 mW optical output power.

Fluorescence measurement

Fluorescence measurements were taken in solution phase. The spectroscopic grade dimethylsulfoxide (DMSO) was used in the measurements. Fluorescence quantum yield was calculated according to equation 1 given below:

$$\Phi_F = \Phi_F(\text{Std}) \frac{F A_{\text{Std}} \eta^2}{F_{\text{Std}} A \eta_{\text{Std}}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the compound and the ZnPc standard, respectively. A and A_{Std} are the absorbance of the samples and ZnPc standard at the excitation wavelength, respectively. η and η_{Std} are the refractive indexes of solvents used for compound and ZnPc standard, respectively. Fluorescence quantum yield for unsubstituted ZnPc is 0.18 in DMSO.^[42–44]

Singlet oxygen measurement

Singlet oxygen measurements 1,3-diphenylisobenzofuran (DPBF) was used as a singlet oxygen trap in dimethylsulfoxide (DMSO) and was purchased from Sigma-Aldrich. Methylene blue (MB) ($\Phi_{\Delta} = 0.49$ in DMSO)^[45] was employed as a reference compound for singlet oxygen quantum yield calculation. In a typical procedure for the detection of singlet oxygen generation by using trap molecules, compound 2 (2 μM) and DPBF were mixed in O_2 bubbled DMSO. Initially several dark measurements were taken followed by irradiation of the mixture using LED light (680 nm, 10 mW/cm²) repeatedly from 10 cm distance for 5 seconds. Absorbance decrease of DPBF was monitored suggesting singlet oxygen generation in the presence of light and compound 2. Slope of absorbance maxima of DPBF at 414 nm versus time graph were drawn. Finally, singlet

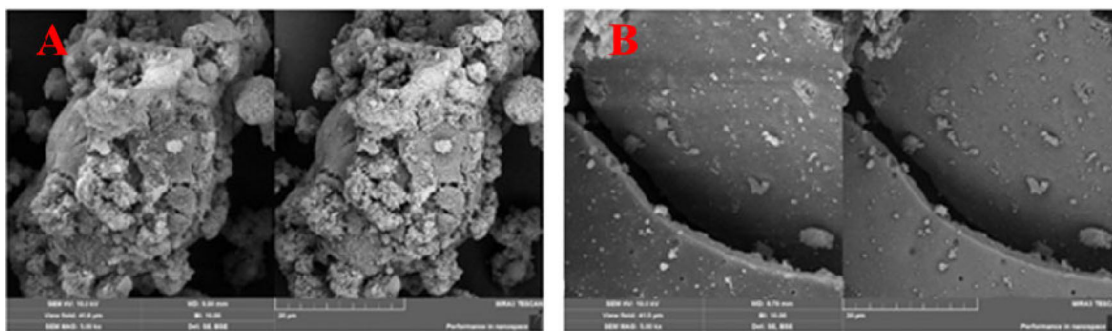


Figure 2. SEM images of first generation 1 (A) and second generation 2 (B) dendritic zinc phthalocyanines solids.^[46]

oxygen quantum yields were calculated according to the equation 2 given below:

$$\Phi\Delta(\text{PS}) = \Phi\Delta(\text{ref}) \times \frac{m(\text{PS})}{m(\text{ref})} \times \frac{F(\text{ref})}{F(\text{PS})} \times \frac{PF(\text{ref})}{PF(\text{PS})} \quad (2)$$

where PS and ref represent compound 2 and methylene blue, respectively. m is the slope of absorbance maxima of DPBF at 414 nm versus time graph, F is the correction factor, which is given by $F = 1 - 10^{-\text{OD}}$ (OD at the irradiation wavelength, which is 680 nm), and PF is absorbed photonic flux in $\mu\text{Einstein dm}^{-3} \text{ s}^{-1}$. PF was ignored in the calculations as both compound 2 and MB were irradiated with the same light source (680 nm LED).

Result and discussion

A dendrimer is defined as structures formed with the repeating units surrounded to the center. Furthermore, the number of repeating units belonging to groups that are substituted for phthalocyanine means whether the compound is in the first or second generation. The chemical structures of the first and second generation zinc phthalocyanine compounds 1 and 2, which were synthesized according to the literature,^[40] are shown in Figure 1. The solubility of these materials in organic solvents increases their usability in applications and it easily be coated on surfaces. In addition, as the generation increases, the molecule forms a more regular structure and provides controllable properties in applications.

The surface properties of first 1 and second 2 generation dendritic phthalocyanines in powder form were investigated in detail by SEM in our previous study^[46] and it is observed that as the structure grows, a more regular and plaque dust growth is achieved (Figure 2). Dendritic phthalocyanine 1 powder containing substituted ester groups, although there are plate formations in the structure, is generally porous and nucleation and growth morphology is dominant. It has been observed that certain surface cracks due to drying and nano-precipitation due to nucleation enlarge the structure toward a spherical form. According to this information, it can be said from the SEM photographs that with the increase of generation, there is a more regular structural growth and that the molecules can show controllable properties.

On the other hand, it is preferred that organic compounds used in optoelectronic applications have properties such as showing non-aggregation behavior, having high fluorescent quantum efficiency, high wavelength absorption and suitable orbital levels that allow electron transfer.^[47–49] Therefore, in this study, we investigated the fluorescence, photoluminescence properties and aggregation behavior of the compound 2 in order to determine their usability potential in optoelectronic applications.

Phthalocyanine aggregation generally defines as a coplanar association of structures from monomer to dimer and toward more phthalocyanine molecules by no bonded attractive interaction.^[50] UV-Vis spectroscopy can be used to characterize the aggregation of the phthalocyanine molecules. Aggregation is dependent on the concentration of solution, species of metal ions, nature of the solvent, nature of substituents and temperature. In many cases, the spectra in the Q-band region show the effects of aggregation, typically by a blue shift and broadening of the maximum absorbance. Aggregation of phthalocyanines is not wanted as it reduces energy efficiency in applications.^[51–53] In this study, the aggregation behavior of compound 2 was investigated in solution (Figure 3). Compound 2 did not show an aggregation in THF, DMF and DMSO. The aggregation behavior of compound 2 was also investigated at different concentrations (from $10 \cdot 10^{-5}$ to $10 \cdot 10^{-6} \text{ mol dm}^{-3}$) in THF. No aggregation observed for compound 2.

PL spectra have an important role since the optical properties are determined by providing information about energy gap (E_g), exciton, traps and levels of energy. The relaxation process of the excited states in the PL materials has been discussed by the exciton migration and the following capture of the exciton at the radiative and the non-radiative sites. Also, the band gap, which is defined as the minimum energy change required for the electron to participate in the transmission, is a parameter that determines how much energy is needed from the sun for transmission and how much energy is produced. From this perspective, band gap is an important parameter for photovoltaic applications, and when the band gap of semiconductor materials coincides with the visible region in the solar spectrum, it can be said that these materials can be used for photovoltaic applications. At the same time, the band gap tells us how much incoming solar radiation can be absorbed.^[54–57]

Phthalocyanines, which are organic semiconductors, have the potential to be used in many optoelectronic applications

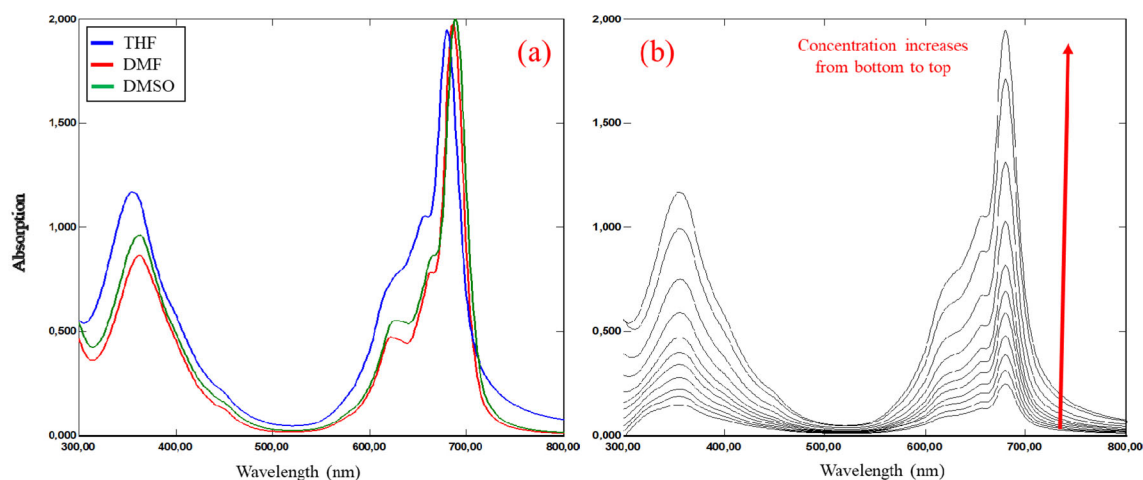


Figure 3. UV-Vis spectra of compound **2** in (a) different solvents (THF, DMF, DMSO) and (b) different concentrations ($10 \cdot 10^{-5} \text{ mol dm}^{-3}$; $9 \cdot 10^{-5} \text{ mol dm}^{-3}$; $8 \cdot 10^{-5} \text{ mol dm}^{-3}$; $7 \cdot 10^{-5} \text{ mol dm}^{-3}$; $6 \cdot 10^{-5} \text{ mol dm}^{-3}$; $5 \cdot 10^{-5} \text{ mol dm}^{-3}$; $4 \cdot 10^{-5} \text{ mol dm}^{-3}$; $3 \cdot 10^{-5} \text{ mol dm}^{-3}$; $2 \cdot 10^{-5} \text{ mol dm}^{-3}$; $1.5 \cdot 10^{-5} \text{ mol dm}^{-3}$; $10 \cdot 10^{-6} \text{ mol dm}^{-3}$) in THF.

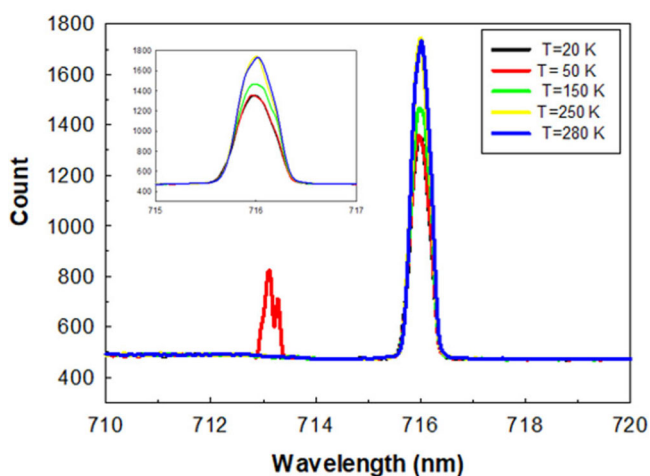


Figure 4. PL spectra for compound **2** thin film at 20 K and 280 K using excitation wavelength 732 nm.

due to their interesting electronic properties.^[1] In the literature, it is observed that phthalocyanine and its derivatives with a band gap of approximately 1.5–2.0 eV show effective properties in photovoltaic applications.^[54–57] In this study, we measured the PL of the second generation dendritic zinc phthalocyanine **2** compound. PL measurements were taken in the temperature range of 20 to 280 K. Compound **2** displayed significantly sharper peaks on thin film as shown in Figure 4.

The wavelength of compound **2** observed at 716 nm and also the peak density decreases steadily with increasing temperature (Figure 4). The energy gap for compound **2** was calculated as 1.73 eV which is appropriate for optical applications. The temperature dependences reveal mechanisms of energy transfer between different excited states and changes in molecular symmetry. As seen in Figure 4, it was observed that as the temperature decreased, the peak wavelength did not change, only the intensity decreased. This shows that the molecular symmetry in the molecular ring has changed, and the planarity has not deteriorated against temperature. It can also be seen from the graph that there is a peak

around 713 nm (1.74 eV) at low temperature (50 K). This peak was not observed at temperatures higher than 50 K. On the other hand, the absorption edges of the thin film of the dendritic phthalocyanine compound **2** are largely red-shifted from the monomer bands, suggesting that the lowest-lying exciton is allowed. At low temperatures, the emission bands moved slightly to red, corresponding to the red movement of the absorption edge due to the thermochromism. From these observed features, we can also conclude that the luminescence is emitted from the lowest-lying allowed exciton state.^[58] When compared with the values given in the literature, we can say that compound **2** has the potential to be used especially in photovoltaic applications, according to its band gap value.^[59]

On the other hand, fluorescence quantum yield is a measure of the efficiency of converting absorbed light into emitted light and is a parameter that can be used to explain energy transfer within the molecule.^[60] The fluorescence properties of **1** and **2** in solution phase were examined and Figure 5 shows the emission and excitation spectra for **1** and **2**. The excitation and the absorption spectra of **1** and **2** are similar in DMSO, and these spectra are mirror images in the emission spectra.^[61] Fluorescence quantum yields were calculated from measured emission spectra of compounds. Fluorescence quantum yields for compound **1** and **2** were found to be 0.26 (26%) and 0.33 (33%) respectively (Table 1). The fluorescence quantum yields of compounds **1** and **2** are higher than the fluorescence quantum yields of unsubstituted ZnPc. At the same time, it was observed that fluorescence quantum yield increased with increasing generation in dendritic phthalocyanines. As a result, the substituents attached to the phthalocyanine ring have a significant effect on the fluorescence quantum yield.^[62] The energy transfers between the phthalocyanine ring and the substituted groups may have resulted in an increase in fluorescent quantum efficiency.^[60]

On the other hand, photodynamic therapy (PDT), which uses photosensitizing drug and visible or near-infrared light (wavelength range of about 630–800 nm is used to achieve

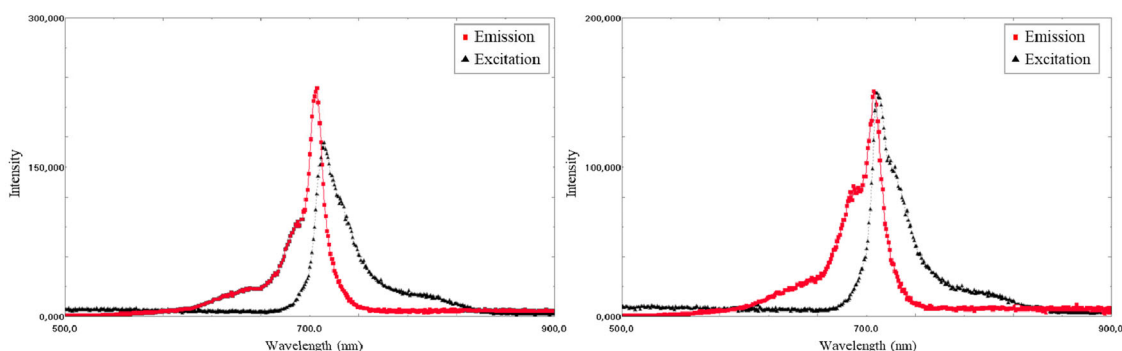


Figure 5. Excitation and emission spectra of compounds 1 (left) and 2 (right) in DMSO.

Table 1. Photophysical results of compounds 1 and 2.

Compound	λ_{abs} [nm] ^a	λ_{ems} [nm] ^a	Φ_{F} [%] ^{a, b}	Φ_{Δ} [%] ^{a, c}
1	688	690	26	n.d. ^d
2	690	695	33	62

^aMeasured in DMSO

^bZnPc was used as a reference in DMSO ($\Phi_{\text{F}} = 0.18$)

^cMethylene blue was used as a reference in DMSO ($\Phi_{\Delta} = 0.49$)

^dNot determined.

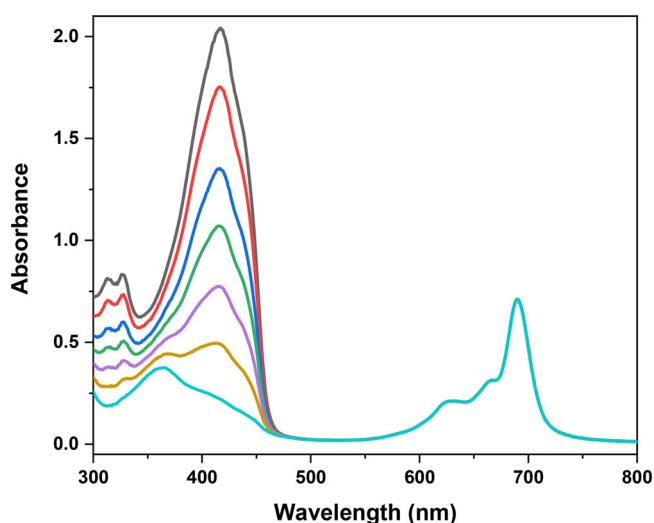


Figure 6. Decrease in the absorbance of DPBF in DMSO upon irradiation of compound 2 (5 μM) with 633 nm LED.

the deepest tissue penetration) to destroy cells by photogeneration of one or more reactive oxygen species, is a treatment method for cancer, infections, and other medical applications. Excited photosensitizing drugs can produce cytotoxic reactive oxygen species via type I and/or type II reactions. In a type II reaction, the excited state of the drug can produce singlet oxygen by transferring energy directly to ground-state molecular oxygen. Singlet oxygen, which is highly reactive, causes fatal damage to cells.^[63,64]

In order to see the experimentally potential of the drug that can be used in PDT, the quantum efficiency of singlet oxygen is calculated. On top of that we finally wanted to check singlet oxygen generation capacity of compound 2 by using DPBF as a trap molecule. In this direction, compound 2 and DPBF were mixed in an oxygen saturated DMSO and irradiated with a LED light source (680 nm, 10 mW/cm²). The absorption signal of DPBF at 414 nm decreased

gradually upon successive irradiations, which clearly suggests photosensitized singlet oxygen generation (Figure 6). ¹O₂ quantum yield of compound 2 was determined by employing methylene blue as a reference photosensitizer and found to be 62% in DMSO (Figure 6), which is slightly lower compared to parent ZnPc core (67% in DMSO) (Table 1).^[65]

Conclusion

Compounds reported in this study are soluble in common organic solvents so they can be easily coated on surfaces. At the same time, their solubility increases their usability in various applications. Thin film of the second generation dendritic phthalocyanine compound 2 was easily prepared on the glass surface by the drop casting method. The photoluminescence properties of the thin film of compound 2 were examined at different temperatures in the range of 20 to 280 K. The optical band gap, which determines the potential of the materials to be used in optoelectronic applications, was found to be 1.73 eV for compound 2. The aggregation behaviors of compound 2 were also examined in different solvents and different concentrations. No significant aggregation was observed. This feature of the molecule provides an advantage in photovoltaic and optical applications. Fluorescence spectra in the solution phase of compounds 1 and 2 were examined and fluorescence quantum yields were calculated. From the obtained results, it was observed that the fluorescent quantum yields of compounds 1 and 2 were higher than the fluorescent quantum yields of unsubstituted ZnPc. On the other hand, the compound 2 was observed to have a high fluorescent quantum yield than the compound 1. It can be said that there is an energy transfer between the phthalocyanine ring and the substituents, and this transfer increases as the generation of dendritic substituents increases. All measurements proved that the organo-soluble dendritic phthalocyanine 2 has high potential for energy, photovoltaic and optical applications. Additionally, it was shown that compound 2 can induce ¹O₂ generation upon light irradiation. This shows that compound 2 could be a candidate for photodynamic therapy (Figure 6). As a result, we can conclude that the growth of phthalocyanine by bulky substituents makes it more organized and implements superior properties.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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