



Preparation and investigation of aggregation, fluorescence and singlet oxygen generation properties of gallium and metal-free phthalocyanines

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Abstract: The synthesis, characterization, aggregation, optical, fluorescence and singlet oxygen generation properties of 2-furylmethoxy substituted gallium and metal-free phthalocyanines (**2** and **3**, respectively) are reported for the first time. Characterization of the novel synthesized compounds was performed with elemental analysis, ultraviolet-visible spectrophotometry, fourier transform infrared spectrometry, $^1\text{H-NMR}$ spectroscopy and mass spectrometry. When the concentration behavior of the synthesized complexes is examined in a certain concentration range in THF, it has been shown that the phthalocyanines predominantly consist of monomeric species. Furyl-containing new phthalocyanines are quite soluble in common organic solvents and this makes them possible to be used in several important applications. Fluorescence behavior of these phthalocyanines were investigated. In this study, the metal ion's effect on the UV-Vis and photophysical features of the MPcs is also cited. These results show that the metal in the core of the phthalocyanine is an important factor in the fluorescence behavior and quantum yield (Φ_f) of the complexes. In singlet oxygen generation studies showed that the phthalocyanines containing the 2-furylmethoxy group indicated a high level of photosensitization and singlet oxygen generation capacity. Consequently, these gallium and metal-free complexes are promising photosensitizer for photodynamic therapy applications.

Keywords: Gallium, metal-free, phthalocyanine, fluorescence, singlet oxygen

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INTRODUCTION

Furan groups and their derivatives, which have important properties such as low viscosity, high reactivity and excellent solvent properties, are used as chemical building blocks for drug synthesis, as well as polymer-based resin construction as an intermediate for the synthesis of natural products and their analogues (1,2).

Phthalocyanines (Pcs) which are an important family of macrocyclic compounds class, have many uses such as gas sensors (3), catalysts (4), solar cells (5), electrochromic devices (6),

Langmuir Blodgett films (7), liquid crystals (8) and photosensitizers (9,10) in photodynamic cancer therapy (PDT). Photodynamic therapy (PDT) is a treatment modality that is widely used today against some types of cancer without surgical intervention (11). Therapy involves three components: light, molecular oxygen and a photosensitizer that absorbs light in the wavelength range of 600-800 nm. With these three important components, molecular oxygen ($^3\text{O}_2$) converts to singlet oxygen ($^1\text{O}_2$). Tetrapyrrolic macrocyclics include porphyrins, and especially phthalocyanines are among the most studied photosensitizers (10). To have an

effective photodynamic therapeutic effect, a phthalocyanine must absorb light in the 600-800 nm region, thereby providing penetration into human tissues. Up to this time, many photosensitizer have been tested *in vitro* and *in vivo* in PDT experiments, but very few of them have shown ideal properties. This has led to a focus on the development of new photosensitizer and the enhancement of their effectiveness in studies conducted. The features that a photosensitizer should have for a successful PDT operation; chemical purity, being selective for cancer cells, accumulating in the tissue shortly after application, rapid cleaning from the body. In the treatment of PDT, ensuring that sufficient quantities of light reach the entire tumor tissue is one of the most important steps in the success of treatment. To understand this, it is necessary to examine the passage of light from tissues, absorption and scattering. In addition, distribution, absorption, or scattering of light in tumorous tissue depends both on the type of tissue applied and on the wavelength of the light (12).

By introduction of different substituents, the photophysical and photochemical characteristics of Pcs can be fine-tuned. It is also accepted that the metal atom coordinating to the phthalocyanine ring can significantly change the physical, chemical and biological properties of the complex (13–21). Phthalocyanines' solubility in common organic solvents and water is low, which is a major disadvantage. These low solubilities of the phthalocyanines limit the number of applications in which soluble derivatives are used. This problem can be solved by increasing the solubility of the bulky groups or long alkyl, alkoxy groups in the nonpolar solvent by attaching to the peripheral/non-peripheral positions of the phthalocyanines (17).

Chemical derivatives containing furan group, which is substituted at the peripheral and non-peripheral positions of the phthalocyanines ring to eliminate the solubility problems of the phthalocyanines, can also play an important role in altering the solubility and absorption properties of the complexes. Therefore, in this study, peripherally tetrakis(2-furylmethoxy)-substituted gallium and metal free phthalocyanines have been prepared for the first time. The synthesized phthalocyanines were characterized in a spectroscopic manner. The optical, fluorescence and singlet oxygen generation properties of these Pcs were determined and compared.

EXPERIMENTAL SECTION

Materials and methods

All solvents and reagents were obtained from commercial suppliers. The solvents were stored over molecular sieves. The purity of the products was tested in each step by TLC. 4-(2-furylmethoxy)phthalonitrile (**1**) was prepared

according to the reported procedure (22). FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrometer. All absorption and fluorescence excitation, emission spectra were measured by using Shimadzu UV-2600 UV-Vis spectrophotometer and Hitachi F-7000 Fluorescence spectrophotometer, respectively. ¹H-NMR spectra were recorded on Agilent VNMRS 300 MHz. Mass spectra were performed on a Bruker Autoflex III MALDI-TOF spectrometer. Elemental analyses were performed in TÜBİTAK Marmara Research Center. The singlet oxygen generation study carried out under light irradiance of 100 mW cm⁻² (AM1.5) from a 150 W solar simulator (Newport, 96000) with 650 nm cut-on filter.

Preparation

Synthesis of gallium phthalocyanine: A mixture of 4-(2-furylmethoxy)-phthalonitrile (0.100 g, 0.446 mmol), anhydrous GaCl₃ (0.026 g, 0.15 mmol) and DBU (0.2 mmol) as a strong base, in 2 mL of quinoline was refluxed at 160 °C in a sealed glass tube for 12 hours. After cooling to room temperature, the green mixture was precipitated by adding n-hexane and it was filtered. The crude product was washed with methanol in order to remove impurities. The desired product was purified by basic silica gel column chromatography using a gradient of chloroform/ethanol (10/1) as eluents. Finally, it was dried *in vacuo*. Solubility: Highly soluble in THF, CH₂Cl₂, DMF and DMSO. Yield: 0.036 g, (33 %). FT-IR (u_{max}/cm⁻¹): 3010 (Ar-C-H), 2949-2865 (Aliph. -C-H), 1611 (Ar-C=C), 1482, 1288 (Ar-O-R), 1124 (-C-O-C Furan), 996, 932, 748, 595. UV-Vis λ_{max} (nm) THF: 702, 633, 358. ¹H-NMR (300 MHz, DMSO-d₆): δ, ppm 7.68-7.72 (16H, m, 4H, Furan-H and 12H, Pc-Ar-H) 6.80-6.84 (4H, m, Furan-H), 6.64-6.68 (4H, m, Furan-H), 5.20-5.26 (8H, m, methylene -CH₂). Anal. Calc. for C₅₂H₃₂ClGa₁N₈O₈ %: C, 62.33; H, 3.22; Cl, 3.54; Ga, 6.96; N, 11.18; O, 12.77 Found: C, 62.24; H, 3.18; N, 11.36. MS (MALDI-TOF): m/z 1002.48 [M]⁺.

Synthesis of metal-free phthalocyanine: Compound **3** was prepared and purified following the procedure described for complex **2**, starting from 0.100 g of compound **1** (0.33 mmol), 2 mL n-hexanol without metal salt. Solubility: Highly soluble in THF, CH₂Cl₂, DMF and DMSO. Yield: 0.026 g, (26%). FT-IR (u_{max}/cm⁻¹): 3266 (N-H), 3024 (Ar-C-H), 2946-2858 (Aliph.-C-H), 1660 (Ar-C=C), 1466, 1230 (Ar-O-R), 1142 (-C-O-C Furan), 1074 (N-H), 982, 928, 734, 556. UV-vis λ_{max} (nm) THF: 701, 665, 607, 339. ¹H-NMR (300 MHz, DMSO-d₆): δ, ppm 7.15-7.95 (16H, m, 4H, Furan-H and 12H, Pc-Ar-H), 6.50-6.62 (4H, m, Furan-H), 6.35-6.45 (4H, m, Furan-H), 5.02-5.30 (8H, m, methylene -CH₂). Anal. Calc. for C₅₂H₃₄N₈O₈: C, 69.48; H, 3.81; N, 12.47; O, 14.24; found C, 69.52; H, 3.72; N, 12.36. MS (MALDI-TOF): m/z 899.90 [M+H]⁺.

Fluorescence and singlet oxygen generation studies

$$\Phi F = \Phi F(\text{Std}) \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2} \quad (\text{Eq.1})$$

The fluorescence quantum yields (Φ_F) are determined in THF as compared to Equation 1 (23).

where **F** and **F_{Std}** are the areas under the fluorescence emission curves of the samples (**2** and **3**) and the standard, respectively. **A** and **A_{Std}** show the absorbance values of the excitation wave lengths of the samples and standards. n^2

and n_{Std}^2 represent the values of the refractive indices of the solvents used for the sample and the standard, respectively. Unsubstituted ZnPc ($\Phi_F = 0.23$) (24) was employed as the standard in THF.

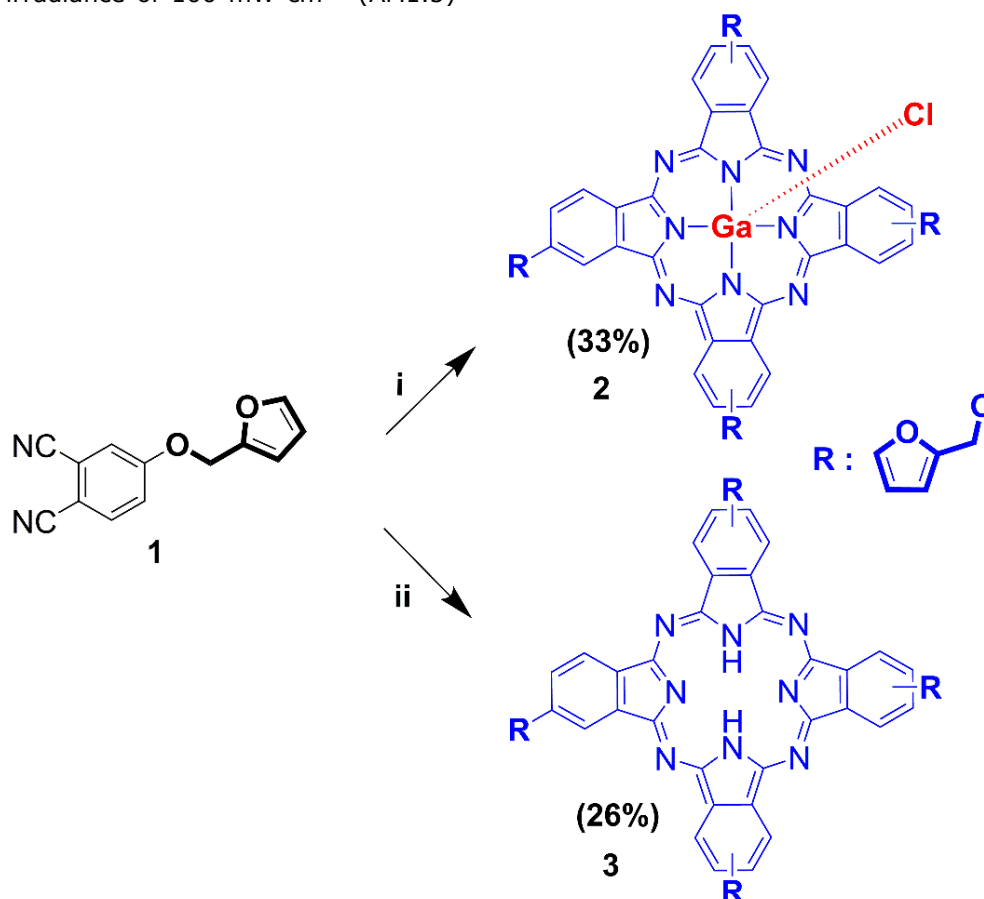
The singlet oxygen generation study carried out under light irradiance of 100 mW cm⁻² (AM1.5)

from a 150 W solar simulator (Newport, 96000) with 650 nm cut-on filter. The irradiation intensity was adjusted using a standard Si detector (Newport, 918D-SL-OD3).

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization

In Scheme 1, the synthetic pathway of tetrakis(2-furylmethoxy)phthalocyanines (M = Ga, **2**; 2H, **3**) at peripheral positions is depicted. Firstly, targeted peripherally substituted gallium (**2**) and metal-free (**3**) compounds were prepared using compound **1**. 2, 9(10), 16(17), 23(24)-tetrakis(2-furylmethoxy)phthalocyaninatogallium (GaPc, **2**) was synthesized by refluxing the precursor ligand and GaCl₃ in quinoline in the presence of DBU, when the color turned to dark green, the reaction was stopped. The crude product was washed with water / methanol series including different ratios of water and methanol to yield a precipitate.



Scheme 1. The synthesis of gallium and metal-free phthalocyanines (**2** and **3**) (i) DBU, Quinoline, GaCl₃, 180 °C. (ii) DBU, n-hexanol, 160 °C.

Metal-free phthalocyanine compound (H₂Pc, **3**) was obtained by refluxing compound **1** for 8 hours in n-hexanol without using any metal salt. Secondly, 2-furylmethoxy-substituted phthalocyanines were readily purified by column chromatography. The yields of the gallium and metal-free phthalocyanines obtained were 33%

and 26%, respectively. UV-Vis, FT-IR, ¹H-NMR and MS methods were used to characterize compounds **2** and **3**. The structures are in harmony with the spectral data. Unlike unsubstituted phthalocyanines, the synthesized gallium and metal-free phthalocyanine complexes are quite soluble in many organic solvents.

The UV-Vis absorption spectra of deeply green colored peripherally substituted gallium and metal-free compounds in THF show two main peaks, the characteristic ligand-centered $\pi-\pi^*$ transitions of a monomeric metal-free or metallophthalocyanine derivatives **2** and **3** with

the Soret or B-band and Q-band maxima at 702, 358 nm ($\log \epsilon = 4.72$ and 4.55) and 701, 665 and 339 ($\log \epsilon = 4.79$, 4.76 and 4.72), respectively (Figure 1) (25). The Q band splits in metal-free phthalocyanine (**2**) owing to the D_{2h} symmetry.

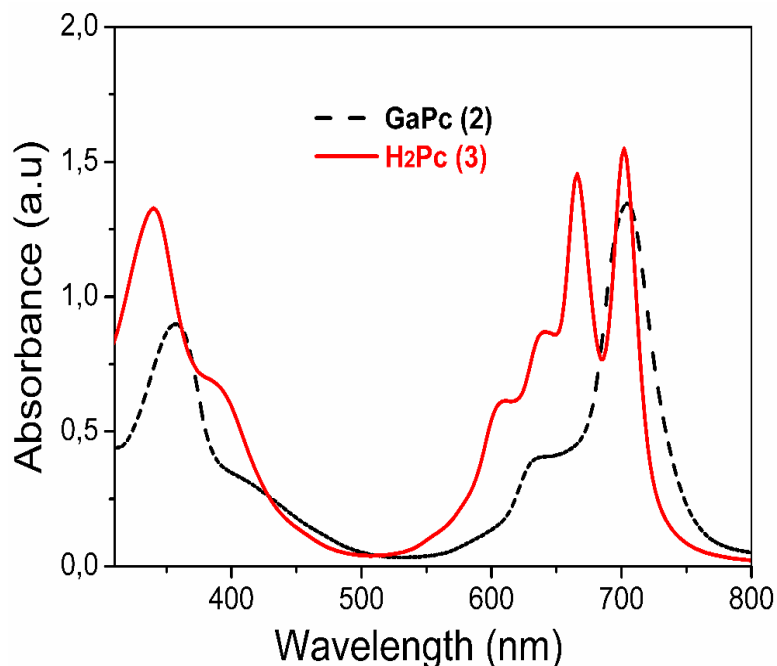


Figure 1. Absorption spectra of **2** (GaPc) and **3** (H₂Pc) in THF ($\sim 2.5 \times 10^{-5}$ mol dm⁻³).

Gallium and metal-free phthalocyanine compounds were confirmed by FT-IR analysis. The formation of phthalocyanine complexes by cyclotetramerization of dinitrile **1** was approved by the absence of sharp ($\text{C}\equiv\text{N}$) vibration at 2227 cm^{-1} . This sharp peak disappeared and the color changed after conversion, indicative of phthalocyanines' formation. FT-IR spectroscopy yielded that the compounds possessed stretching for etheric groups (-C-O-C , at $1274\text{-}1244\text{ cm}^{-1}$), furyl groups (-C-O , at $1142\text{-}1124\text{ cm}^{-1}$), aromatic groups (-C-O , at $1077\text{-}1087\text{ cm}^{-1}$), and aliphatic groups (-CH , at $2965\text{-}2946\text{ cm}^{-1}$). These stretching modes are all visible in the spectra and contributed to the elucidation of the structures. In addition, for metal free complex, the presence of the inner cavity -NH stretches at 1074 and 3266 cm^{-1} supported the structure of metal free phthalocyanine (**3**).

¹H-NMR investigation of the gallium and metal-free phthalocyanines provided the expected chemical shifts for the structure. In the ¹H-NMR spectrum of the phthalocyanine complexes displayed one multiplet for methylene protons at about $5.02\text{-}5.30$ ppm integrating 8 protons for each complex. The signals for each 8 furan protons observed as two multiplets between $6.45\text{-}6.86$ ppm for these complexes. Also signals observed for 16 protons of furan and phthalocyanines benzene as multiplets between $7.66\text{-}7.75$ ppm and $7.25\text{-}8.02$ ppm for complexes

2 and **3**, respectively. The ¹H-NMR spectra of gallium and metal-free phthalocyanines showed complex patterns since it is a mixture of constitutional isomers. In the ¹H-NMR spectra of **2** and **3**, broader chemical shifts were observed compared to dinitrile derivative **1**. ¹H-NMR spectra of phthalocyanines are of broad nature, because of the presence of four positional isomers which tend to show similar chemical shifts. The second reason for broad signals is that phthalocyanines show an equilibrium of aggregation and disaggregation.

The mass spectra of the complexes, which were obtained by MALDI-TOF technique, confirmed the proposed structures. Highly resolved signals of each species were successfully obtained in MALDI-TOF mass spectra using reflectron mode of the instrument to compare experimental and theoretical monoisotopic m/z values of metal complexes in detail. After evaluation of MALDI-TOF mass spectra, it was concluded that desired complex compounds could be successfully synthesized and purified using the experimental route explained in this study. Additionally, it was found that synthesized metal complexes were sufficiently stable under MALDI-MS conditions to determine their intact structures without significant fragmentation. The molecular ion peaks were observed at m/z : 1002.48 [M]^+ for **2** (Figure 2), m/z : 899.89 [M+H]^+ for **3**.

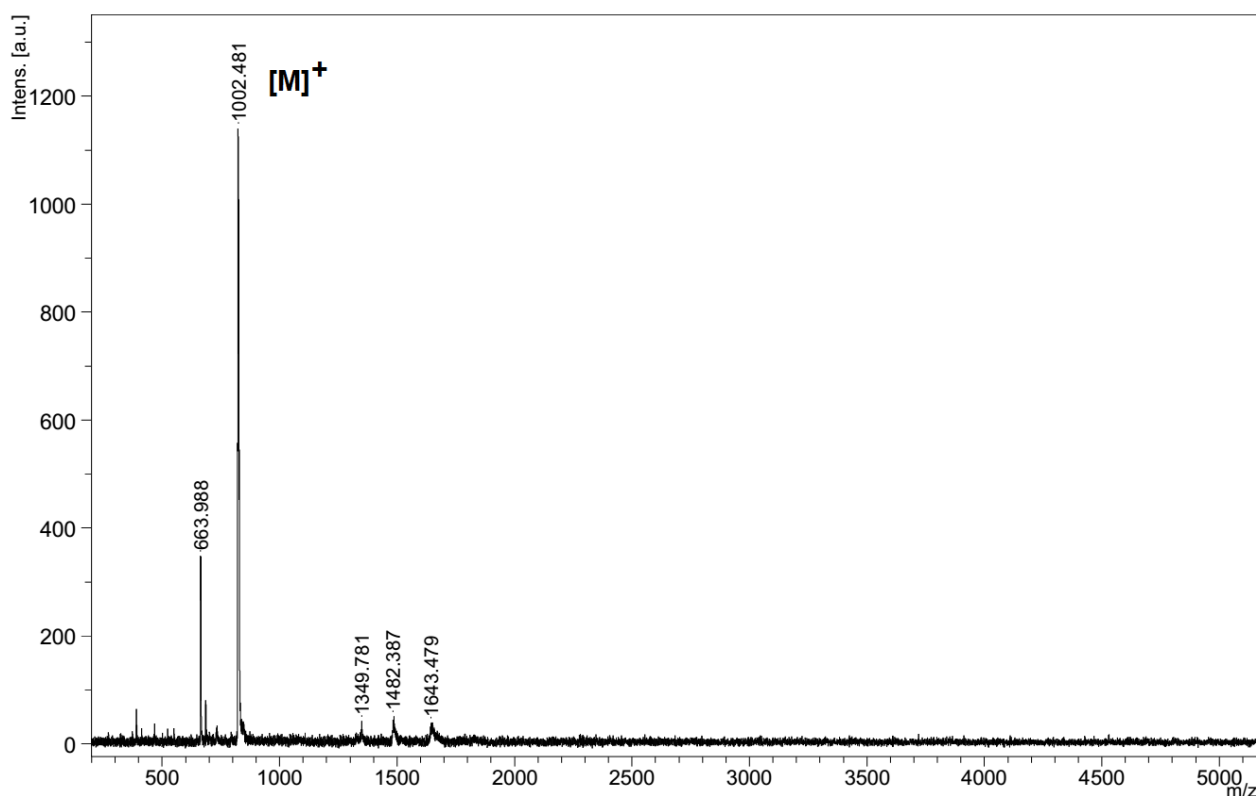


Figure 2: MALDI-TOF mass spectrum of complex **2**.

Aggregation studies

Aggregation can often be explained as the incorporation of monomers, dimers, and rings into higher-order complexes within the solvent. There are a number of parameters for aggregation in phthalocyanines; namely concentration, the nature of the solvent, substituents present at the periphery or non-periphery, the metal ion at the macrocyclic core, and the operation temperature. So as to better evaluate the solubility and aggregation properties of gallium (**2**) and metal-free (**3**) compounds, dilution studies were recorded in THF solvent. As an illustrative example, gallium complex (**2**) was studied using concentrations ranging from 2.5 μM to 40 μM (Figure 3). To demonstrate compliance with the Lambert-Beer law, a linear regression analysis was performed between the density of the Q-band and the concentration of **2**. The peripherally substituted gallium phthalocyanine are essentially free from aggregation in THF at the studied micromolar concentration. Increasing the temperature did not yield new bands on the higher energy side, which would mean the absence of aggregated species, and the absorption intensity obeys Lambert-Beer's law (see the inset of **Figure 3**) (20). Similar behavior

has been observed in metal-free phthalocyanine complex.

Solvents may interact with absorbing species in the solution, which changes the absorption wavelength. This interaction depends on the polarity of the solvent, the refractive index, the coordination power, and the chemical structure of the solute. In general, the Q band wavelength of the phthalocyanine in the solvent shows red-shifting by increasing the refractive index of the solvent. This can best be explained by the Franck-Condon principle. According to this principle, the refraction index and the polarity of the solvent suggest that the species in the solvent can change the absorption wavelength. Thus, it is estimated that the Q band wavelength in a specific solvent is only related to the refractive index of the solvent, unless the solvent reacts with the species in the solution or induces any reaction (26). Non-coordinating solvents (chloroform and dichloromethane) and coordinating solvents (dimethyl sulfoxide and tetrahydrofuran) were investigated in the graph of the Q band plot versus the function $(n^2-1) / (2n^2+1)$, in which n is the refractive index of the given solvent, and the results are plotted in Figure 4.

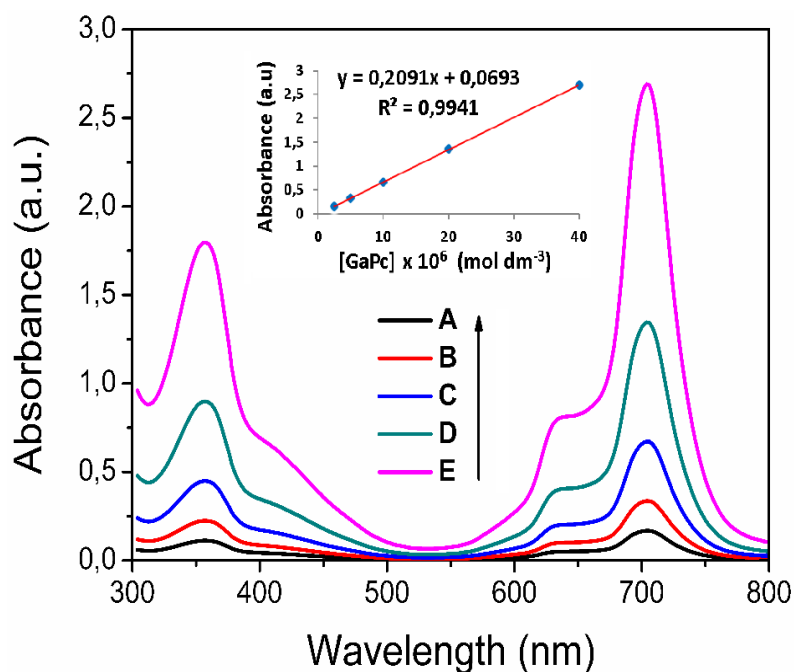


Figure 3. UV-Vis dilution studies of **2** in THF at different concentrations: (E) 40×10^{-6} , (D) 20×10^{-6} , (C) 10×10^{-6} , (B) 5×10^{-6} , (A) 2.5×10^{-6} mol dm⁻³. The inset refers to the calibration values for the Q band maximum value.

It can be seen that Q-band frequencies are linearly related to this function, which explains that Q-band wavelengths are directly changed by interactions with the solution. However, oxygen-containing solvents (DMSO and THF) exhibit a similar tendency, which clearly indicates a coordination between complex **2** and these solvents.

Fluorescence studies

The first property that must be investigated in order for a photosensitizer be used in

photodynamic therapy is fluorescence behavior and fluorescence quantum yields. The fluorescence quantum yield (Φ_F) shows the efficiency of the fluorescence process. In this manner, the fluorescence emission and excitation spectra of novel peripherally tetra-substituted gallium phthalocyanine (**2**) and metal-free phthalocyanine (**3**) investigated and these complexes showed similar fluorescence behavior in THF (Figures 5 and 6).

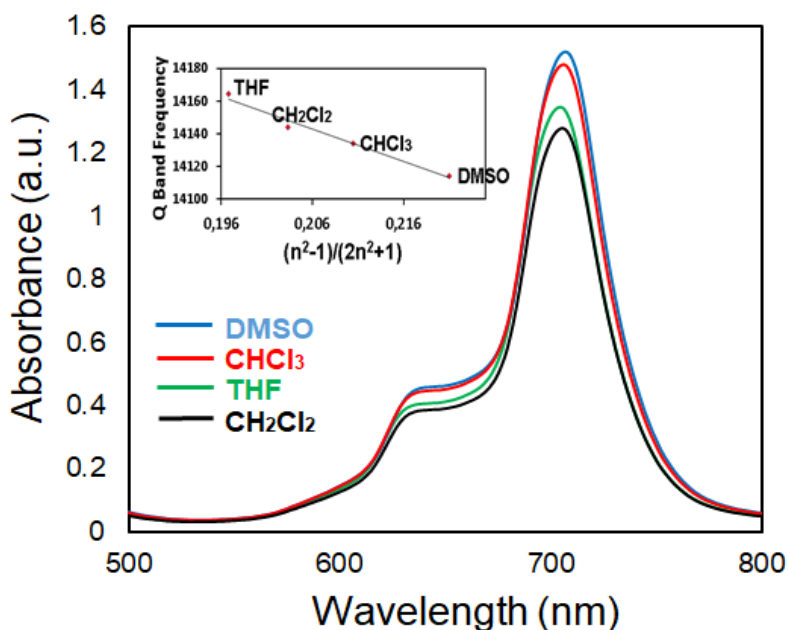


Figure 4. Electronic absorption spectra of **2** in various solvents (15×10^{-6} mol dm⁻³).

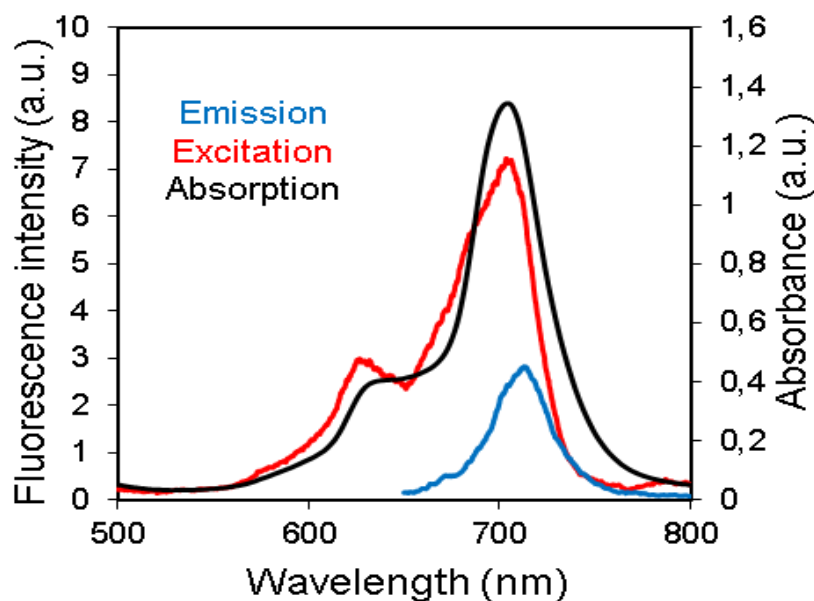


Figure 5. Electronic absorption, fluorescence emission and excitation spectra of **2** (GaPc) in THF. (Excitation wavelength = 630 nm)

The UV-Vis absorption, emission, excitation and fluorescence quantum yield (Φ_F) of the complexes **2** and **3** are summarized in Table 1. Fluorescence emission maxima were observed at 711 nm for complex **2**, at 713 nm for compound **3** in THF. The Stokes shifts of the compounds were

observed within the same region as the typical phthalocyanines. The Stokes shifts observed indicate that the structural change between the ground and excited states in phthalocyanines is very small.

Table 1. Optical and fluorescence properties of the phthalocyanine complexes in THF.

Phthalocyanine	λ_{\max} (nm) ^a	(log ϵ)	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes Shift Δ_{Stokes} (nm)	Fluorescence quantum yield(Φ_F)
2 (GaPc)	702	4.72	706	714	12	0.04
3 (H ₂ Pc)	701,665	4.79,4.76	670,706	714	13	0.15
ZnPc ^b	666	5.19	666	673	7	0.23

^a Absorption maximum wavelength (λ_{\max}) in THF solution.

^b Using unsubstituted ZnPc in THF as the reference (24).

Both photosensitizers show similar Q band absorption and Q band maxima of the excitation spectra. This suggests that the ground and

excited states' nuclear configurations show a similarity and excitation in THF did not affect them.

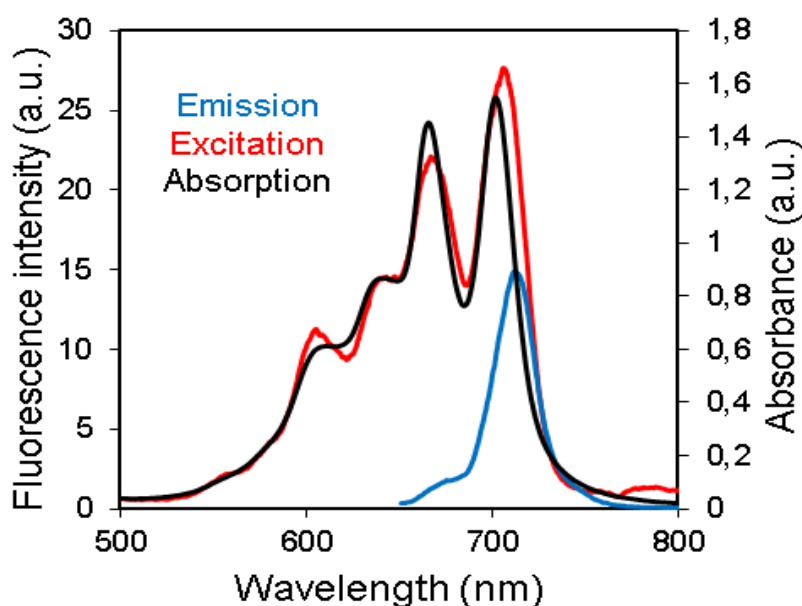


Figure 6. Electronic absorption, fluorescence emission and excitation spectra of **3** (H₂Pc) in THF. (Excitation wavelength = 640 nm)

Fluorescence quantum yield was determined using the comparative method. ZnPc in THF ($\Phi_F = 0.23$) was used as the standard (24). The measured fluorescence quantum yields for **2** and **3** were lower than that for standard ZnPc. This means that the presence of peripheral 2-furylmethoxy substituents induced fluorescence quenching of the parent **2** and **3**. Fluorescence measurements showed that phthalocyanines having the same substituent; the metal-free complex showed a higher fluorescence quantum yield than gallium complex due to heavy atom effect of the gallium atom which enhances the number of triplet state species and induces quenching of fluorescence (27).

Singlet oxygen generation studies

It is presumed that by triggering the chemiluminescence reaction, the excited states of the species transferred their energy to a photosensitizer compound in the medium. The changes that occur during the quenching of the resulting excited state species can easily be monitored by spectroscopic methods. Diphenylisobenzofuran (DPBF) is known to be a singlet oxygen quencher with chemical addition reaction by forming endoperoxide species with singlet oxygen in the solution medium.

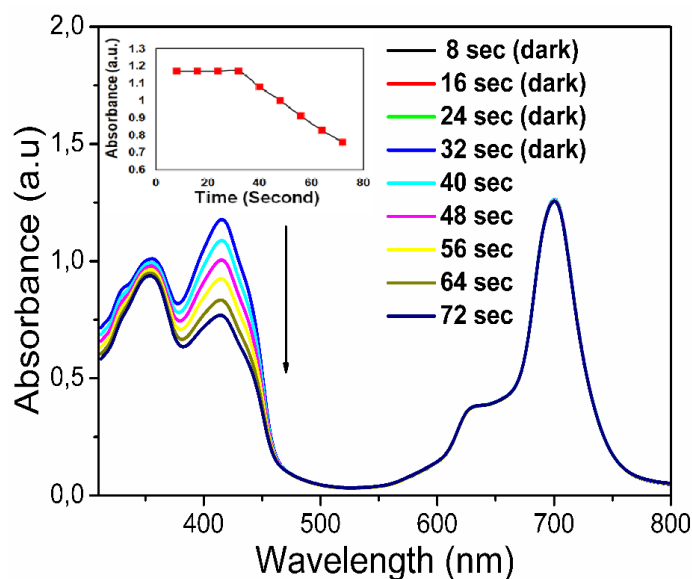


Figure 7. Reaction of singlet oxygen formed by gallium phthalocyanine complex (**2**) dissolved in DMSO with 1,3-diphenylisobenzofuran (DPBF). For the first 32 sec, the solution was kept in the dark; thereafter, it was irradiated with a light source (650 nm cut on filter) for 40 sec. The total volume of the solution was set to 3 mL. The absorption spectra were recorded every 8 seconds.

In order to demonstrate that the peripherally substituted gallium and metal-free phthalocyanines are satisfactory as effective photosensitizers, the phthalocyanine solutions were prepared in DMSO containing DPBF. Experiments have been performed by removing other potential sources of media that may affect the absorption decline. It was observed that there was no significant changing in the absorption spectrum when kept in the dark for 32 seconds (Figure 7). On irradiation with a red light (with 650 nm glass cut on filter, flow rate 16 mW/cm²), however, the absorption peak owing to the trapping compound DPBF swiftly disappeared within 40 seconds.

CONCLUSION

In summary, synthesis, characterization, and investigation of the optical, fluorescence and singlet oxygen generation properties of furan-2-ylmethoxy-substituted gallium and metal-free phthalocyanine complexes have been reported. Not only the gallium phthalocyanine but also the metal-free phthalocyanine are essentially free from aggregation in THF at the studied micromolar concentration which makes important for PDT (photodynamic therapy) applications. The fluorescence quantum yields (Φ_F) of the phthalocyanine photosensitizers investigated for photophysical properties were determined and compared with an unsubstituted ZnPc. In THF, the fluorescence quantum yields (Φ_F) for photosensitizers (**2** and **3**) were found to be lower than unsubstituted ZnPc. This suggests that the existence of peripheral 2-furylmethoxy substituents induced some fluorescence quenching of the parent (**2** and **3**). Singlet oxygen generation studies showed that the phthalocyanine complexes containing the furan-2-ylmethoxy group indicated a high level of photosensitization and singlet oxygen generation capacity. As a consequence, these gallium and metal-free phthalocyanines are favorable photosensitizers for photodynamic cancer therapy applications.

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