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Investigation of Singlet Oxygen Production Property of Peripherally Tetra-substituted In(III)Cl Phthalocyanine for Photodynamic Therapy

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Abstract: Phthalocyanines (Pcs) are macrocyclic compounds of great importance. Different metals and ligands can be used in the synthesis of Pc compounds and they give different properties to Pcs. Thus, the applications of Pcs have been increasing every day. One of the most important areas of use of Pcs is photodynamic therapy (PDT) application. The scope of this study is synthesis, characterization, and investigation of singlet oxygen generation property of new peripherally tetrakis(benzodioxane) substituted indium(III) chloride phthalocyanine (**InClPc**). The compound may be used as a potential photosensitizer for PDT applications. The new compound was characterized by various techniques such as elemental analysis, FT-IR, ^{1}H NMR, MS, and UV–Vis techniques. Furthermore, photophysical and photochemical properties of the synthesized Pc were investigated for PDT studies. At the same time, the effect of combination of heavy indium atom and benzodioxane groups bearing oxygen atom on solubility and photophysicochemical properties was discussed. The results showed that this compound exhibits good solubility in DMSO and shows high singlet oxygen production (Φ_Δ: 0.76). According to the displayed properties and singlet oxygen production, we can say that this compound is a potential candidate for PDT applications.

Keywords: Photodynamic therapy; phthalocyanine; singlet oxygen; indium(III) ion; photophysicochemical properties.

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INTRODUCTION

Today, cancer is one of the most serious health problems. It is a disease that causes death of millions of people every year despite many completed and ongoing research and millions of people get this disease every year and unfortunately, most of them die (1). Many researchers and research institutions have been working intensively for the treatment of this disease (2). The disease occurs as a result of uncontrolled division and proliferation of cells and therefore it is gene-based. Since all living things have different gene structures, cancer is basically an individual disease (3). Therefore, it is not possible to talk about a single and definitive treatment method. Today, conventional methods such as surgical intervention, chemotherapy and radiotherapy are used (4, 5). As an alternative to these studies, photodynamic therapy (PDT) has become one of the important methods used in cancer treatment (6). It is important to design photosensitizers that will make PDT applications more effective (7, 8). Phthalocyanines (Pcs) are also used as a photosensitizing agent for this treatment method (9-11).

Pcs are of great importance both in application and science and there are many studies in the literature on Pc derivatives (12, 13). Pcs, which have physical and chemical properties that can be changed according to the purpose, are used in many application areas (13). The effective use of Pcs in

Langmuir-Blodgett films, chemical sensors, nonlinear optical and electrode materials, electrochemistry, biomedical agents for imaging and PDT, and solar cell applications has led to increased interest in them (14-17). The properties that make Pcs attractive are their π-electron systems and their physical and chemical behavior. Pcs to be used for PDT applications have primarily high singlet oxygen production, displays selectivity for cancerous cells, show absorption in long wavelengths, prevent aggregation and should be soluble (18, 19). The major disadvantage of unsubstituted Pcs, which is insoluble in organic solvents, is overcome by the addition of various substituents to non-peripherally and peripherally positions of Pc compounds. The solubility of Pcs can be increased by binding some functional groups (crown ethers, alkyl, alkoxy, carboxylate, alkylthio and the donor atoms such as N and O etc.) to peripherally position of Pc ring or by adding some metal ions (Zn, Mg, In etc.) to the interior of Pcs (20-26). Therefore, in this study, benzodioxane ligand containing alkyl and oxygen atoms, which can increase the solubility of Pc compound, was chosen. Pc compounds containing benzodioxane ligand have been reported previously (27-32). Kantekin and co-workers also investigated the photophysical and photochemical properties including singlet oxygen quantum yield of the same Pc molecule bearing different metals (Zn and Mg) (31). However, indium(III) metal ion containing derivative of the same Pc has not been reported. Also, indium(III) Pcs show the potential to be used as a photosensitizer in PDT because of their ideal singlet oxygen quantum yield caused by the heavy atom effect of indium(III) atom (33, 34). Accordingly, indium(III) metal ion was chosen as the central atom in the ring of Pc compound.

Within the scope of this study, chloroindium(III) Pc compound, which can be used as a photo-sensitizing agent for PDT, containing benzodioxane groups was synthesized and its structure was characterized by various techniques. Herein, we aimed to increase the efficiency of the ideal photosensitizer by binding substituents containing oxygen atoms to Pc ring and to increase singlet oxygen production due to the heavy atom effect of indium(III) atom and thus absorption at long wavelengths was provided. These results have been supported with fluorescence, singlet oxygen production, photodegradation, and aggregation properties.

EXPERIMENTAL SECTION

Materials and Equipments

The used chemicals, equipments, materials, photochemical, and photophysical parameters and formulas were given in the supplementary information file.

Synthesis of the Compound

The 4-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy)phthalonitrile compound used as a starting compound in this study was reported in our previous study (27). The new 2(3),9(10),16(17),23(24)-tetrakis-{(2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy) phthalocyaninato chloroindium(III) (**InClPc**) compound was synthesized for the first time according to given procedure in our previous works (27). As the only difference, anhydrous indium(III) chloride (34.5 mg, 0.156 mmol) for **InClPc** were used in the synthesis. The detailed experimental procedure is given in supplementary information file.

*2(3),9(10),16(17),23(24)-tetrakis-{(2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy)} phthalociyaninato indium(III) chloride (***InClPc***)*

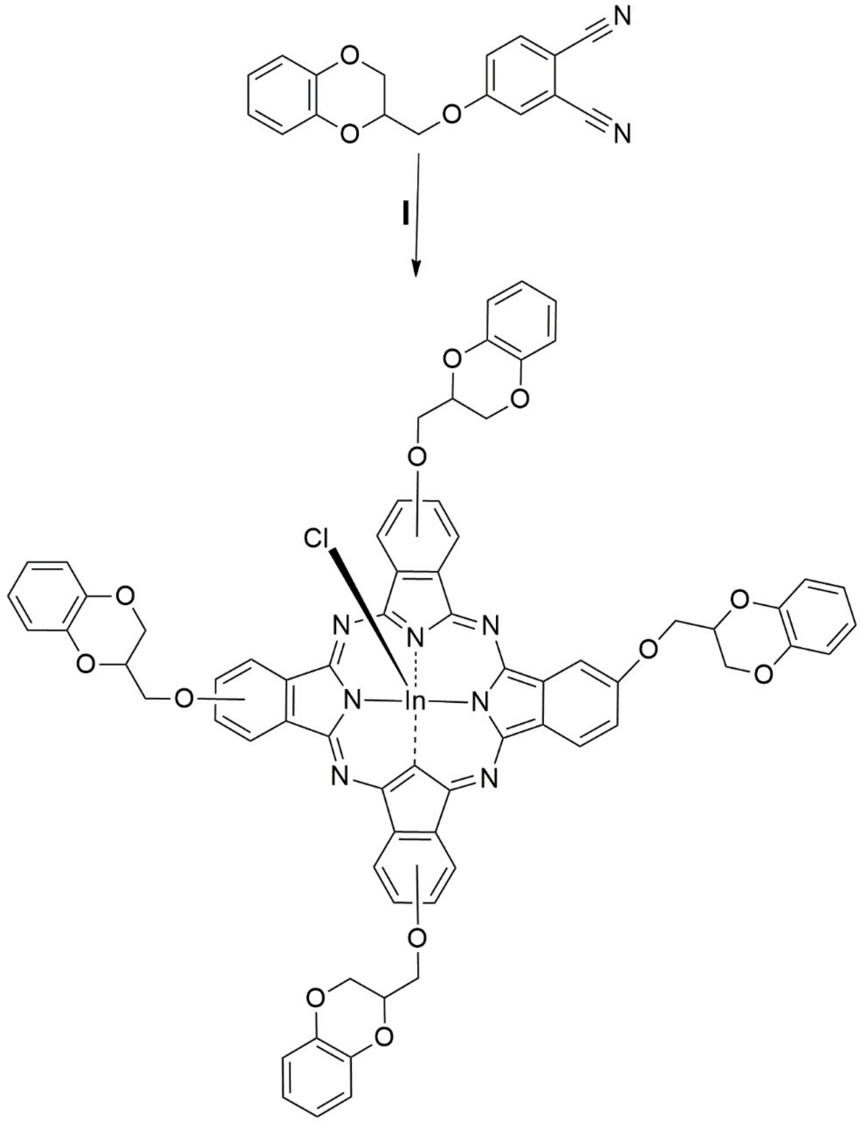
The THF: MeOH (100:6) solvent system was chosen for column chromatography. Yield: 35% (59.18 mg), Mp:>300 °C, Anal. calc. for $C_{68}H_{48}ClInN_8O_{12}$: C, 61.90; H, 3.67; N, 8.49; Found: C, 61.70; H, 3.50; N, 8.22%. FT-IR (ATR, cm^{-1}): 3045-3010 (Ar-CH), 2927-2875 (Aliphatic-CH, CH_2), 1622 (C=N), 1587-1485 (C=C), 1250 (C-O-C). ^{1}H-NMR (400 MHz, $CDCl_3$), (δ: ppm): 7.76-7.65 (bm, 6H, Ar-H), 7.42-7.13 (bm, 6H, Ar-H), 6.93-6.40 (bm, 16H, Ar-H), 4.90 (bs, 4H, Aliphatic-CH), 4.51-4.13 (bm, 16H, Aliphatic-CH_2). UV–Vis (DMSO, 1×10^{-5} M): λ_{max}/nm (log ε): 709 (4.80), 638 (3.78), 368 (4.40). MS (MALDI-TOF), (m/z): Calc.: 1318.216, Found: 1318.425 $[M]^+$.

RESULT AND DISCUSSION

Synthesis and characterization studies

The synthesis procedure for the compound is presented in Scheme 1. The synthesis and characterization studies of 4-(2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy)phthalonitrile compound used as a starting compound in this study were given in our previous work (27). On the other hand, **InClPc** derivative in scope of this study was synthesized for the first time. We carried out nucleophilic substitution reactions between 2-hydroxymethyl-1,4-benzodioxane and 4-nitrophthalonitrile in order to obtain substituted phthalonitrile compound. **InClPc** compound was obtained by cyclotetramerization of this compound in the presence of anhydrous indium(III) chloride and DBU as a catalyst. Purification of **InClPc** was achieved by column chromatography (silica gel) with THF/MeOH solvent mixture. The compound was obtained with 35% yield and exhibited good solubility in DMSO. Various techniques such as FT-IR, elemental analysis, NMR, and MS were used to elucidate the structure of the compound.

In the FT-IR spectrum of **InClPc** formed as a result of the cyclotetramerization of the phthalonitrile compound, the disappearance of the peak of the C≡N group at 2230 cm^{-1} of the phthalonitrile and the formation of the C=N group at 1622 cm^{-1} of Pc ring support the structure. In addition, vibrational bands of aromatic-CH (3045-3010 cm^{-1}), aliphatic-CH, -CH$_2$ groups (2927-2875 cm^{-1}) and C=C (1587-1485 cm^{-1}) and C-O-C (1250 cm^{-1}) bands of the Pc ring and substituted groups support the structure. The NMR spectrum of **InClPc** compound is similar to the phthalonitrile derivative, which is the starting material. Due to the aggregation in Pc ring and deutero solvent, a broad spectrum was obtained according to the NMR spectrum of the phthalonitrile derivative. In the ^{1}H NMR spectrum, the signals of the aromatic protons were observed at around 7.76-6.40 ppm and the signals of aliphatic protons were observed at around 4.90-4.13 ppm. These signals prove the formation of the expected structure. In the MALDI-TOF spectrum of the **InClPc** compound, the presence of the peak at 1318.425 [M]$^+$ confirms the structure. The theoretical and experimental elemental analysis results are compatible with the targeted structure. The spectral data are compatible with the spectral data of previously published Pc compounds (27, 30-32). It is seen that the data obtained from elemental analysis, FT-IR, mass, and ^{1}H NMR analyses of **InClPc** compound are compatible with the synthesized structure.



Scheme 1: General synthesis scheme for **InClPc** (**I**: InCl$_3$, DBU, n-pentanol, 160 °C, 24 h).

UV-Vis and Aggregation Studies

Generally, UV-Vis spectroscopy is the most specific method used in the characterization of Pcs. Pcs are highly colored compounds thanks to their π electron system originating from benzene rings. This chromaticity causes them to give characteristic absorption bands in the visible and ultraviolet region. There are two characteristic bands in UV-Vis measurements of Pcs. The first of these is observed between 300-400 nm. The band formed in this region is called as B-band or Soret band. The characteristic second band is observed around 600-750 nm and is called the Q band (35). The Q band is caused by π-π* transitions and therefore the absorption density is high. The shoulder in Q band gives information about whether Pc is metal or metal-free. Namely, while the only band observed in Q band indicates that the structure is a metallo Pc, the presence of two bands approximately equal to each other indicates that the structure is a metal-free Pc (36). At the same time, UV-Vis measurements help us to understand whether Pc is aggregated in the solvent from which the spectrum was taken. There are many factors that affect the absorption properties of Pcs. These can be listed as the substituents attached to Pc, the central metal atom, the position of the substituents, the solvent used to dissolve Pc, the aggregation, the conjugation and the symmetry of molecule. When looking the presence of these two bands in the UV-Vis spectrum of the obtained compound, it is seen that **InClPc** is formed (Figure 1). When the UV-Vis spectrum of the compound was examined, Q band at 709 nm and B band at 368 nm were observed. No aggregation was observed in the UV-Vis spectrum of the compound taken in DMSO. The Q band of this compound appears to have shifted to red in the wavelength when compared to other peripherally tetra substituted Pcs containing benzodioxane (27). The important factor in the red shift of the Q band is due to the used heavy indium metal which binds the chlorine atom in the axial position in Pc ring. The red shift of Q band has significant effects on photochemical and photophysical properties.

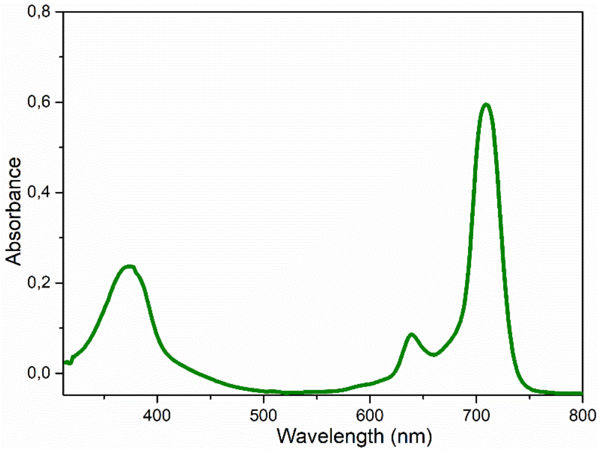


Figure 1: Electronic absorption spectrum of **InClPc** in DMSO (Concentration: $1.0x10^{-5}$ M)

Aggregation is a problem in PDT. Aggregation is not a desirable situation in the application areas of Pcs, as it causes widening and low resolution in the Q band seen in the UV-Vis spectrum of Pcs (37). The UV-Vis spectra of the compound in different concentrations ($2.00x10^{-6}$-$1.20x10^{-5}$ mol/L) of DMSO are given in Figure 2. When the UV-Vis spectrum of the compound was examined, it was observed that the synthesized compound did not show aggregation in DMSO. In addition, it is seen that the molar concentration and the absorption intensity of the Q band change in direct proportion. This result is in accordance with the Lambert-Beer's Law.

Photophysical and photochemical Properties

The photochemical and photophysical properties of the compound in DMSO were investigated to determine whether it is suitable for PDT using UV-Vis and fluorescence spectrophotometers. Photochemical measurements include photodegradation quantum yield (Φ_d) and singlet oxygen quantum yield (Φ_Δ), while photophysical measurements include fluorescence quantum yield (Φ_F) and spectra.

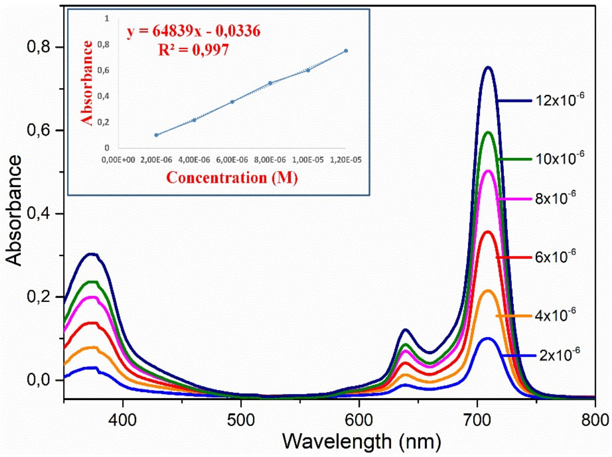


Figure 2: UV-Vis spectra of **InClPc** compound in DMSO and at different concentrations for aggregation properties (Inset: Absorbances versus concentrations)

Fluorescence spectra and quantum yield (Φ_F) properties

The absorbance, emission, and excitation values and spectra of the compound in DMSO are given in Table 1 and Figure 3. According to literature, these fluorescence properties are characteristic for indium(III) Pcs in DMSO (29, 30, 38, 39). According to these values, it has been predicted that the excitation spectra of **InClPc** differ from the absorption spectra because of the loss of symmetry (34) and this demonstrates that the nuclear configuration was changed. Fluorescence spectra were observed at 725 nm for emission and at 713 nm for excitation in DMSO. The Stokes shift value (λ_{ems}-λ_{exc}) of the compound was found as 12 nm.

Table 1: Spectral, photophysical and photochemical data for **InClPc** in DMSO.

Solvent	Q band λ_{max} (nm)	Extinction coefficient (cm^{-1}/M)	logε	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes Shift Δ_{stokes} (nm)	Φ_F	Φ_Δ	Φ_d (10^{-5})
DMSO	709	63150	4.80	713	725	12	0.09	0.76	2.55

Ideal photosensitizers should show some fluorescent behavior in order to be able to follow them in the body. Therefore, it is important to investigate their fluorescent quantum yield (Φ_F) characteristics for PDT applications. The Φ_F of **InClPc** is calculated according to current literature with reference to standard ZnPc (40). Table 1 presents Φ_F value of **InClPc**. The Φ_F efficiency was calculated as 0.09 for **InClPc** in DMSO. The fluorescence efficiency reduces since increasing the atomic number causes more intersystem crossing (41, 42). Therefore, **InClPc** exhibits low values because of the heavy metal effect. **InClPc** displays lower fluorescence quantum values compared to unsubstituted ZnPc (Φ_F=0.20 in DMSO) and Zn(II) and Mg(II) derivatives of the same Pc (31). Owing to the enhancement of inter-system crossing by the presence of a heavy indium atom in **InClPc**, Φ_F value is low as expected (43). This Φ_F value is also similar to other studied InPc compounds (29, 30). The fluorescent behavior of this photosensitizer is appropriate for determination and quantification of photosensitizer in PDT studies.

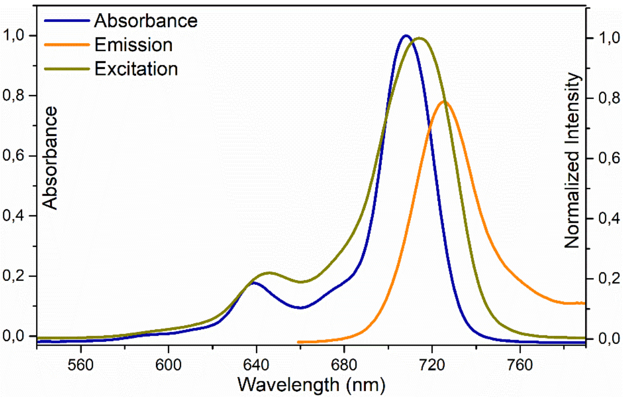


Figure 3: Fluorescent spectra of **InClPc** in DMSO.

Singlet oxygen production properties

The singlet oxygen generation is an important condition used in PDT. Singlet oxygen generation is the most important behavior of photosensitizer. The singlet oxygen quantum yield (Φ_Δ) which is amount of the produced singlet oxygen is the most important indicator for using of molecules as photosensitizers in PDT applications (44). The Φ_Δ depends on the used solvent. A suitable solvent was biocompatible DMSO. DMSO as a solvent meets the conditions required for the photosensitizers and it is already used as a solvent in the literature for determination of the Φ_Δ (41). The Φ_Δ are found via 1,3-diphenylisobenzofuran (DPBF) compound, which has an absorption at 417 nm, as a quencher. Also, the standard ZnPc is used as reference. The absorbance of DPBF was monitored using UV–Vis spectroscopy after each 5 s of light irradiation. The compound did not degrade against light irradiation, since the compound is resistant to light. The results showing the absorbance change of DPBF are given in Figure 4 and the calculated Φ_Δ value is listed in Table 1. The Φ_Δ value of **InClPc** is 0.76 in DMSO. While **InClPc** showed higher Φ_Δ value than unsubstituted ZnPc and Mg(II) derivative of the same Pc, it showed lower Φ_Δ value than Zn(II) derivative of the same Pc (31). **InClPc** exhibited good singlet oxygen production and it can be potential candidate as potential photosensitizer in PDT. Thanks to the enhancement of intersystem crossing by the heavy atom effect of large In(III) atom, **InClPc** generates high singlet oxygen. When Φ_F and Φ_Δ are evaluated in terms of the heavy atom effect for **InClPc**, decrease in Φ_F value accompanied by increase in Φ_Δ value. **InClPc** demonstrated higher Φ_Δ values than **Std-ZnPc** which means that the substitution of 4-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy) groups to the macrocycle increased singlet oxygen generation. The singlet oxygen generation of this compound is similar with Pc containing different substituents on the Pc ring and In(III) metal ion in Pc cavity (34, 45, 46). The synthesized compound has sufficient singlet oxygen generation for PDT.

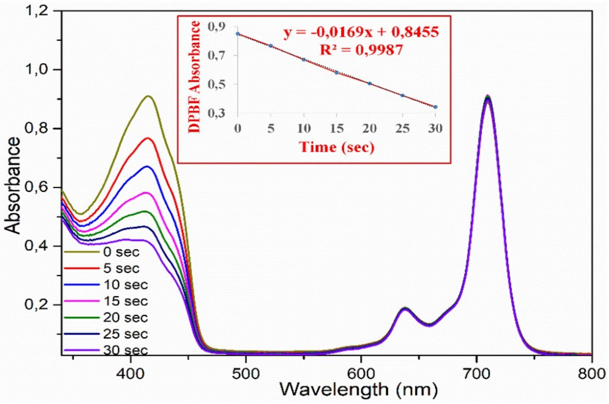


Figure 4: UV-Vis spectral changes of **InClPc** during singlet oxygen production measurements in DMSO (Inset: Plot of DPBF absorbance versus time).

Photodegradation properties

Photodegradation is generally used to determine the stability of Pcs, which is important in photocatalytic application reactions as well as in PDT. Photodegradation is the oxidative decomposition of the photosensitizer under light irradiation and this photodegradation is studied by quantum efficiency. The photodegradation quantum yield (Φ_d) of photosensitizer play a key role in PDT. The Φ_d value gives the stability of the compound against the light irradiation. After exposure to light for every 5 min of the compound, the photodegradation studies in DMSO were performed by monitoring the decrease of the absorbance of the compound. Figure 5 presents the changes in Q band of the compound. The Q band intensity of compound was not disturbed in DMSO under light irradiation. As we know from the literature, the Φ_d of the stable photosensitizer are between 10^{-3} and 10^{-6} (47). The Φ_d value of compound presents in Table 1 and it showed about the same stability with order of 10^{-5}. The Φ_d value of **InClPc** in DMSO was calculated as $2.55\text{x}10^{-5}$. The obtained Φ_d value of **InClPc** are similar with Zn(II) and Mg(II) derivatives of the same Pc (31). **InClPc** demonstrated lower Φ_d values than **Std-ZnPc** which means that the substitution of 4-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy)groups to the macrocycle increased the stability of this phthalocyanine against light irradiation. The results indicate that this compound has moderate stability to photochemical degradation. The photodegradation quantum yields (Φ_d) are in harmony with other InPcs (30, 33, 48) and the stability of the compound are suitable for PDT.

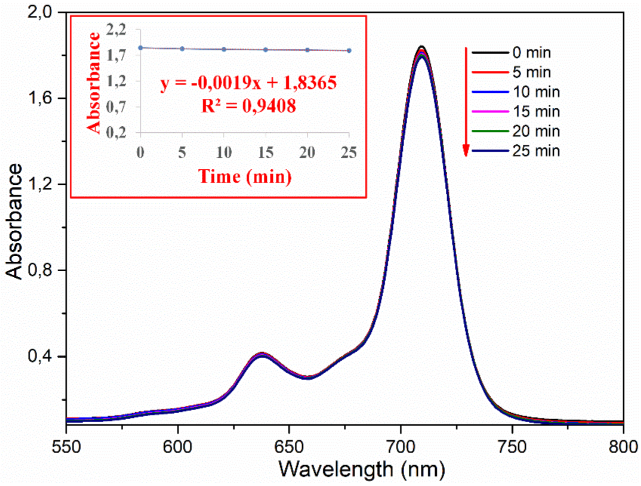


Figure 5: UV-Vis spectral change of **InClPc** during photodegradation measurements in DMSO (Inset: plot of Q band absorbance versus time)

CONCLUSIONS

In this study, new tetra-substituted chloroindium(III) Pc bearing benzodioxane groups was synthesized and characterized by using elemental analysis, UV-Vis, FT-IR, ^{1}H NMR and MALDI-TOF MS techniques. At the same time, the photophysicochemical properties of the compound were researched in order to understand whether it is suitable for PDT. According to the UV-Vis measurements, we observed that this compound dissolves very well in DMSO, does not aggregate, and gives Q band around 709 nm and B band around 368 nm. In addition, we observed that the ratio between absorption and concentration in the Q band changes in accordance with the Lambert-Beer law. The fluorescence spectral results show that the excitation spectrum of this compound differs from the absorption spectra and this demonstrates that the nuclear configuration was changed. The fluorescence quantum yield of the obtained compound (0.09) is lower than the unsubstituted ZnPc compound. When singlet oxygen quantum yield was examined, we observed that the compound show higher result than unsubstituted ZnPc. This situation is due to indium(III) ion being a heavy atom and increasing the transition between systems. In addition, the used benzodioxane substituted groups may have an effect on high singlet oxygen production compared to unsubstituted ZnPc compound. According to the photodegradation results, it is seen that the synthesized compound is stable to light. As a result, with this study, a candidate molecule that can be used as a potential photosensitizer in PDT applications has been reported in the literature.

Conflict of interest: The authors declare that they have no conflict of interest.

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SUPPORTING INFORMATION

Investigation of Singlet Oxygen Production Property of Peripherally Tetra-substituted In(III)Cl Phthalocyanine for Photodynamic Therapy

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EXPERIMENTAL SECTION

Materials

N,N-dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), chloroform ($CHCl_3$), diethylether, methanol (MeOH), tetrahydrofuran (THF), ethanol (EtOH), dichloromethane (DCM), *n*-hexane, n-pentanol, and acetone were purchased from MERCK. 4-Nitrophthalonitrile, 2-hydroxymethyl-1,4-benzodioxan, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), potassium carbonate (K_2CO_3), anhydrous indium(III) chloride were purchased from Aldrich. All chemicals were of reagent grade. All solvents were dried and stored over molecular sieves. The progress of the reactions was monitored by thin layer chromatography (TLC).

Equipments

Melting points of compounds were determined via an electrothermal Gallenkamp device. The UV-vis measurements were made on a Shimadzu UV-2001 UV–Vis spectrophotometer. Elemental analysis studies were performed by a LECO TRUSPEC CHN 932 instrument. The IR spectra of the compounds were registered using a Thermo Fisher scientific NICOLET İS10 spectrometer (ATR sampling accessory). A Bruker Avance III 400 MHz spectrometer was used for ^{1}H-NMR analyses. MALDI-TOF mass measurements were carried out by a Bruker Microflex LT MALDI-TOF-MS. Fluorescence spectra, were registered by Varian Eclipse spectrophotometer using 1 cm path length cuvettes at room temperature. General electric quartz line lamp (300 W) was used to perform photochemical measurements. Ultraviolet and infrared radiations were filtered using A 600 nm glass cut off filter (Schott) and a water filter, respectively. An extra interference filter (Intor, 670 or 700 nm with a band width of 40 nm) was placed through the light path before the sample. A POWER MAX5100 (Molelectron detector incorporated) power meter was utilized to determine light intensities.

Photophysical and Photochemical Measurements

Fluorescence quantum yield (Φ_F) measurements

The Φ_F values were calculated by the comparative method (**Eq. 1**) [1, 2] using unsubstituted ZnPc as the reference. The Φ_F value of unsubstituted ZnPc is 0.20 in DMSO [3, 4]. Both the synthesized Pcs and the standard were excited at convenient wavelength.

$$\Phi_F = \Phi_F(Std)\frac{F \times A_{Std} \times n^2}{F_{Std} \times A \times n_{Std}^2} \qquad \textbf{(Eq. 1)}$$

In Eq. 1, F and F_{Std} are the areas under the fluorescence emission curves of the synthesized Pc and standard unsubstituted ZnPc, respectively. A and A_{Std} are the absorbances of the synthesized Pc and standard unsubstituted ZnPc at the excitation wavelengths, respectively. The η and η_{std} are the refractive indices of used solvents for the synthesized Pc and standard unsubstituted ZnPc, respectively.

Singlet oxygen quantum yield (Φ_Δ) measurements

The Φ_Δ measurements were performed using the experimental setup described in previous studies [4, 5] with standard unsubstituted ZnPc (in DMSO) as the reference. 2 mL of the synthesized Pc solution (C=1.0×10^{-5} M) containing the singlet oxygen scavenger was irradiated in the Q-band region using the photoirradiation setup described in the literature. The Φ_Δ values were calculated via the relative method with DPBF (singlet oxygen chemical scavenger) in DMSO using **Eq. 2**.

$$\Phi_\Delta = \Phi_\Delta^{Std}\frac{R \,.\, I_{abs}^{Std}}{R^{Std} \,.\, I_{abs}} \qquad \textbf{(Eq. 2)}$$

Φ_Δ^{std} is Φ_Δ for the standard unsubstituted ZnPc (Φ_Δ^{std} =0.67 in DMSO) [1, 6]. R and R_{Std} are DPBF photobleaching rates in the presence of the synthesized Pc and standard unsubstituted ZnPc, respectively. I_{abs} and I_{abs}^{std} are the rates of light absorption by the synthesized Pc and standard unsubstituted ZnPc, respectively. The concentration of DPBF was lowered to ~3×10^{-5} M to avoid chain reactions formed by DPBF in the presence of singlet oxygen [7]. Solutions of the photosensitizer including DPBF were prepared in the dark environment and irradiated in the Q-band region using the described setup in the measurements part. Degradation of DPBF at 417 nm was monitored. The used light intensity in Φ_Δ value measurements is 7.05×10^{15} photons.s^{-1}.cm^{-2}.

Photodegradation quantum yield (Φ_d) measurements

The Φ_d measurements were performed by the experimental setup described in previous studies [8]. $\boldsymbol{\Phi_d}$ values of the synthesized Pcs were calculated via **Eq. 3**.

$$\Phi_d = \frac{(C_0 - C_t)\times V \times N_A}{I_{\text{abs}}\times S \times t} \quad (\textbf{Eq. 3})$$

In Equation 3, S is the irradiated cell area, t is the irradiation time, C_0 and C_t are the sample concentration before and after irradiation, respectively, V is the used volume of solution in measurement, N_A is the Avogadro's constant and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the synthesized Pc. The used light intensity in Φ_d value measurements is 2.20×10^{16} photons.s^{-1}.cm^{-2}.

Synthesis of 2(3),9(10),16(17),23(24)-tetrakis-{(2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy) phthalociyaninato chloro indium(III) (InClPc)

The compound was synthesized according to given procedure in our previous works [9]. The mixture of 4-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methoxy)phthalonitrile compound (0.2 g, 0.69 mmol), n-pentanol (4 mL), 1,8-diazabicyclo[4.5.0]undec-7-ene (DBU) (5 drops), equivalent amounts of anhydrous $InCl_3$ heated to 160 °C and stirred for 24 h at this temperature under N_2 atmosphere. Then cooling to room temperature, the reaction mixture was precipitated by the addition of n-hexane and filtered off. After washing with hot MeOH and hot EtOH, the product was purified with column chromatography by using silica gel and THF/MeOH solvent system. Solvent system for column chromatography was THF/MeOH (100:6).

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