FULL PAPER



Synthesis, characterization, and determination of photophysicochemical properties of peripheral and nonperipheral tetra-7-oxy-3,4-dimethylcoumarin substituted zinc, indium phthalocyanines

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Gamze Özgül Artuç, Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Istanbul Yeni Yuzyil University, 34010 Istanbul, Turkey. Email: gamze.ozgul@yeniyuzyil.edu.tr The photochemical and photophysical properties of peripheral and nonperipheral zinc and indium phthalocyanines containing 7-oxy-3,4-dimethylcoumarin synthesized were investigated in this study. 7-Hydroxy-3,4-dimethylcoumarin (1) was synthesized via Pechmann condensation reaction and then the phthalonitrile derivatives [4-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (2) and 3-(7-oxy-3,-4-dimethylcoumarino)phthalonitrile (3)] were synthesized by nucleophilic aromatic substitution. Phthalocyanine compounds containing coumarin units on peripheral (4 and 5) and nonperipheral (6 and 7) positions were prepared via cyclotetramerization of phthalonitrile compounds. All compounds' characterizations were performed by spectroscopic methods and elemental analysis. The phthalocyanine derivatives' (4-7) photochemical and photophysical properties were studied in DMF. The photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yields) properties of these novel phthalocyanines (4-7) were studied in DMF. They produced good singlet oxygen (e.g., $\Phi_{\Delta} = 0.93$ for 7) and showed appropriate photodegradation (in the order of 10^{-5}), which is very important for photodynamic therapy applications.

KEYWORDS

coumarin, photochemical and photophysical properties, phthalocyanine

1 | INTRODUCTION

Phthalocyanines, with an 18π -electron delocalization system, are one of the most extensively studied classes of organic functionals highly conjugated heterocyclic compounds.^[1-6] A great number of properties of phthalocyanines arise from the π -electronic delocalization systems, which makes them valuable in different fields of science and technology such as optical recording,^[7,8] photovoltaics,^[9,10] sensor,^[11,12] catalysis,^[13] liquid

crystals,^[14] and photosensitizer in photodynamic therapy (PDT).^[15-20]

In recent years, PDT has been an important method of cancer treatment and includes three fundamental components: light, oxygen, and photosensitizer.^[21,22] Phthalocyanines are suitable as a photosensitizer for PDT application because of the properties such as low dark toxicity, high singlet oxygen quantum yield, high molar absorption coefficient in the near-infrared wavelength, and long fluorescence lifetimes.^[23,24]

Coumarins are secondary plant metabolite benzo derivatives of pyrone (known as coumarin or 2H-1-benzopyran-2-one), an important class of heterocyclic compounds among the biologically active chromophores with a large number of interesting biological properties.^[25,26] The photophysical, photochemical, and spectroscopic properties of coumarin derivatives depend on different substituent in the coumarin ring.^[27,28] These molecules have been widely used as fluorogenic probe in biological imaging,^[29-31] fluorescent brightening agents,^[32,33] and optical sensors.^[34,35] They have good pharmacological and optical properties such as antibacterial, antifungal, antimicrobial, anticoagulant, and antioxidant properties, and in addition to these, they exhibit anticancer activity due to their unique properties.[36-38] photophysical and photochemical Many compounds containing coumarin subunit exhibit useful and diverse biological activity and find their application in pharmaceuticals.^[39-41] These compounds are found in various bioactive natural and synthetic products.^[42]

In the literature, phthalocyanine compounds containing different coumarin derivatives has been synthesized and physical and chemical properties of these compounds have been investigated. It was observed that the substitution of coumarin derivatives to the peripheral/nonperipheral positions of phthalocyanines improves the photochemical and photophysical properties of phthalocyanines. Another advantage of phthalocyanine compounds containing coumarin units for PDT applications can be their imaging due to fluorescence properties of coumarins. The main disadvantage of phthalocyanines is low solubility in common organic solvents. The solubility of these compounds in organic solvents can be increased by attaching some groups on the phthalocyanine skeleton.^[43-46]

In this study, we combined these two functional materials (coumarin and phthalocyanine) into a single compound, and this time, coumarin skeleton is substituted with two methyl groups at lactone ring. For this purpose, we synthesized 7-oxy-3,4-dimethylcoumarin substituted zinc (II) phthalocyanines (**4**,**6**) and indium (III) Cl phthalocyanines (**5**,**7**) and investigated their photophysical and photochemical properties as potential PDT agents and compared them with the similar earlier reported analogues.

2 | EXPERIMENTAL

Material, methods, synthesis procedure, equipment details, and photochemical parameters are provided in the supporting information.

2.1 | Synthesis

The coumarin compound (1) was prepared via Pechmann condensation, compounds 2 and 3 were prepared via nucleophilic aromatic substitution, and phthalocyanine compounds (4–7) were prepared via phthalonitrile derivatives' cyclotetramerization according to the literature.^[46–48]

2.1.1 | 7-Hydroxy-3,4-dimethylcoumarin (1)

Yield: 1.77 g (93%) M.p.: 218–219°C. ¹H-NMR (CDCl₃, δ, ppm) aromatic protons: 7.72 (1H, d, *J* 8.4 Hz), 6.71 (1H, dd, *J* 2.2–8.4 Hz), 6.69 (1H, d, *J* 2.2 Hz), aliphatic protons: 2.41 (3H, s) 2.15 (3H, s). ¹³C-NMR (CDCl₃, δ, ppm) (C=O): 161.65, aromatic carbons: 160.58, 151.39, 128.96, 114.26, 113.76, and 102.34, (C=C): 146.85 and 116.32, aliphatic protons: 14.71 and 12.64. FT-IR (ATR, ν_{max} , cm⁻¹) 3298 (Ar OH), 3068 (Ar CH), 2933–2872 (aliphatic CH), 1702 (C=O), 1588 (O–C), 1556–1484 (C=C). Anal. Calculated for C₁₁H₁₀O₃: C (69.40%), H (5.26%) Found: C (69.43%), H (5.24%).

2.1.2 | 4-(7-Oxy-3,4-dimethylcoumarino) phthalonitrile (2)

Yield: 0.98 g (78%) M.p.: 234–236°C. ¹H-NMR (CDCl₃, δ, ppm) aromatic protons: 7.80 (1H, d, J 8.7 Hz), 7.71 (1H, d, J 8.7 Hz), 7.36 (1H, d, J 2.5 Hz), 7.33 (1H, dd, J8.7-2.5 Hz), 7.06 (1H, d, J 2.4 Hz), 7.01 (1H, dd, J 8.7–2.4 Hz) aliphatic protons: 2.45 (3H, s), 2.26 (3H, s). ¹³C-NMR (CDCl₃, δ, ppm) (C=O): 161.34, aromatic carbons: 160.58, 155.15, 153.39, 135.60, 126.50, 122.27, 122.18, 122.09, 118.71, 114.68, 110.07, and 108.54, (C=C): 145.20 and 116.02, (C=N): 116.02 and 115.10, aliphatic protons: 15.25 and 13.50. FT-IR (ATR, v_{max} , cm⁻¹) 3058 (Ar CH), 2930-2862 (aliphatic CH), 2236 (CN), 1712 (C=0).1586 (O-C), 1554-1482 (C=C),1265 (Ar–O–Ar). Anal. Calculated for $C_{19}H_{12}N_2O_3$: С (72.08%), H (3.79%), N (8.85%) Found: C (72.06%), H (3.75%), N (8.87%).

2.1.3 | 3-(7-Oxy-3,4-dimethylcoumarino) phthalonitrile (3)

Yield: 0.87 g (69%) M.p.: 238–240°C. ¹H-NMR (CDCl₃, δ , ppm) aromatic protons: 7.69 (1H, d, *J* 8.7 Hz), 7.66 (1H, brd d, *J* 8.5 Hz), 7.58 (1H, dd, *J* 8.5–2.5 Hz), 7.23 (1H, brd d, *J* 8.5 Hz), 7.05 (1H, dd, *J* 8.7–2.4 Hz), 7.02 (1H, d, *J* 2.4 Hz) aliphatic protons: 2.44 (3H, s), 2.25 (3H, s). ¹³C-NMR (CDCl₃, δ , ppm) (C=O): 161.67, aromatic

carbons: 158.74, 155.87, 151.45, 132.09, 128.76, 127.36, 114.61, 114.46, 113.12, 111.91, 99.66, and 98.74, (C=C): 145.78 and 116.02, (C=N): 116.09 and 114.09, aliphatic protons: 14.58 and 12.81. FT-IR (ATR, v_{max} , cm⁻¹) 3060 (Ar CH), 2954–2875 (aliphatic CH), 2242 (CN), 1709 (C=O), 1592 (O–C), 1561–1493 (C=C), 1270 (Ar–O–Ar). Anal. Calculated for C₁₉H₁₂N₂O₃: C (72.08%), H (3.79%), N (8.85%) Found: C (72.10%), H (3.74%), N (8.81%).

2.1.4 | 2(3),9(10),16(17),23(24)-Tetra-(7-oxy-3,4-dimethylcoumarino)phthalocyaninato zinc (II) (4)

Yield: 38 mg (38%). M.p. > 300°C. UV–visλ_{max} (nm) (logε) in DMF: 675 (5.08), 343 (4.95). ¹H-NMR (CDCl₃, δ, ppm) aromatic protons: 7.71–6.69 (24H, m) aliphatic protons: 2.45 (12H, brd s) 2.29 (12H, brd s). ¹³C-NMR (CDCl₃, δ, ppm) (C=O): 162.14–159.45 (4C), aromatic carbons: 157.76–100.39 (64C), aliphatic protons: 15.23–12.16 (8C). FT-IR (ATR, v_{max} , cm⁻¹) 3061 (Ar CH), 2935–2842 (aliphatic CH), 1707 (C=O), 1612 (O–C), 1582–1471 (C=C), 1236 (Ar–O–Ar). Anal. Calculated for C₇₆H₄₈N₈O₁₂Zn: C (68.53%), H (4.24%), N (8.42%) Found: C (68.50%), H (4.27%), N (8.45%). MS (MALDI-TOF) *m/z*: Calculated 1330.65; Found 1331.12 [M+H]⁺.

2.1.5 | 2(3),9(10),16(17),23(24)-Tetra-(7-oxy-3,4-dimethylcoumarino)phthalocyaninato indium (III) chloride (5)

Yield: 40 mg (36%). M.p. > 300°C. UV–visλ_{max} (nm) (logε) in DMF: 689 (4.93), 310 (4.82). ¹H-NMR (CDCl₃, δ, ppm) aromatic protons: 7.82–6.71 (24H, m) aliphatic protons: 2.43 (12H, brd s), 2.24 (12H, brd s). ¹³C-NMR (CDCl₃, δ, ppm) (C=O): 161.96–158.79 (4C), aromatic carbons: 157.12–99.97 (64C), aliphatic protons: 14.99–11.92 (8C). FT-IR (ATR, v_{max} , cm⁻¹) 3052 (Ar CH), 2921–2854 (aliphatic CH), 1710 (C=O), 1609 (O–C), 1573–1469 (C=C), 1224 (Ar–O–Ar). Anal. Calculated for C₇₆H₄₈N₈O₁₂InCl: C (64.43%), H (3.39%), N (7.91%) Found: C (64.39%), H (3.36%), N (7.94%). MS (MALDI-TOF) *m/z*: Calculated 1415.51; Found 1415.63 [M]⁺.

2.1.6 | 1(4),8(11),15(18),22(25)-Tetra-(7-oxy-3,4-dimethylcoumarino)phthalocyaninato zinc (II) (6)

Yield: 36 mg (35%). M.p. > 300°C. UV–vis λ_{max} (nm) (loge) in DMF: 689 (4.65), 313 (4.52). ¹H-NMR (CDCl₃, δ , ppm)

aromatic protons: 7.75–6.64 (m, 24H) aliphatic protons: 2.39 (12H, brd s), 2.19 (12H, brd s). ¹³C-NMR (CDCl₃, δ , ppm) (C=O): 160.99–159.32 (4C), aromatic carbons: 158.23–101.12 (64C), aliphatic protons: 15.45–12.12 (8C). FT-IR (ATR, v_{max} , cm⁻¹) 3042 (Ar CH), 2963–2854 (aliphatic CH), 1707 (C=O), 1610 (O–C), 1584–1476 (C=C), 1225 (Ar–O–Ar). Anal. Calculated for C₇₆H₄₈N₈O₁₂Zn: C (68.53%), H (4.24%), N (8.42%) Found: C (68.55%), H (4.22%), N (8.39%). MS (MALDI-TOF) *m/z*: Calculated 1330.65; Found 1332.21 [M+2H]⁺.

2.1.7 | 1(4),8(11),15(18),22(25)-Tetra-(7-oxy-3,4-dimethylcoumarino)phthalocyaninato indium (III) chloride (7)

Yield: 35 mg (32%). M.p. > 300°C. UV–visλ_{max} (nm) (logε) in DMF: 707 (5.20), 318 (4.90). ¹H-NMR (CDCl₃, δ, ppm) aromatic protons: 7.69–6.59 (24H, m) aliphatic protons: 2.49 (12H, brd s), 2.29 (12H, brd s). ¹³C-NMR (CDCl₃, δ, ppm) (C=O): 163.52–159.17 (4C), aromatic carbons: 157.72–102.11 (64C), aliphatic protons: 14.98–12.01 (8C). FT-IR (ATR, v_{max} , cm⁻¹) 3064 (Ar CH), 2931–2844 (aliphatic CH), 1704 (C=O), 1612 (O–C), 1596–1478 (C=C), 1239 (Ar–O–Ar). Anal. Calculated for C₇₆H₄₈N₈O₁₂InCl: C (64.43%), H (3.39%), N (7.91%) Found: C (64.41%), H (3.41%), N (7.87%). MS (MALDI-TOF) *m/z*: Calculated 1415.51; Found 1417.45 [M+2H]⁺, 1379.64 [M+2H-Cl]⁺.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization

The synthetic pathway of the coumarin (1), phthalonitrile (2 and 3), and phthalocyanine derivatives (4–7) was shown in Scheme 1. 7-Hydroxy-3,4-dimethylcoumarin (1) was prepared according to the literature, and it was observed that spectroscopic data of the obtained coumarin compound (1) were consistent with the literature.^[48] Details of the synthesis of phthalonitrile (2 and 3) and phthalocyanine (4–7) compounds were given in the supporting information. The obtained compounds' characterizations were performed by spectroscopic methods and elemental analysis. The obtained results were consistent with the proposed structures of the target compounds.

In the FT-IR spectra of 4-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (2) and 3-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (3), the stretching vibrations of nitrile groups are at 2,236 and 2,242 cm⁻¹, respectively. All of the characteristic vibration peaks (aromatic, aliphatic, lactone, ester) of compounds 2 and 3 were seen in FT-IR spectra of compounds. In the ¹H-NMR spectra of 4-(7-oxy-



SCHEME 1 Synthetic route of coumarin (1), phthalonitrile derivatives (2 and 3) and phthalocyanine derivatives (4-7)

4-(7-Oxy-3,4-dimethylcoumarino)phthalonitrile (2)



-3,4-dimethylcoumarino)phthalonitrile (3

3.4-dimethylcoumarino)phthalonitrile (2) and 3-(7-oxy-3,-4-dimethylcoumarino)phthalonitrile (3) in CDCl₃, the aromatic protons appeared at between 7.80-7.01 and 7.69–7.02 ppm, respectively. In the ¹H-NMR spectra of 4-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (2) and 3-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (3)in CDCl₃, the aliphatic protons appeared at between 2.45–2.26 and 2.44–2.25 ppm, respectively. In the ¹³C-NMR spectra of 4-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (2)and 3-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (3)in CDCl₃, C=O, C=C, and C=N aromatic and aliphatic protons were observed at the appropriate chemical shift values. ¹H-NMR (Figure 1a) and ¹³C-NMR (Figure 1b) spectrum of 4-(7-oxy-3,4-dimethylcoumarino)phthalonitrile (2) in CDCl₃ was given in Figure 1 as an example.

In the phthalocyanine derivatives' (4–7) FT-IR spectra, stretching vibration of nitrile groups of compounds 2 and 3 disappeared. The specific C=O vibration of lactone peaks and the other characteristic vibration peaks (aromatic –CH, aliphatic –CH, aromatic C=C, and ester C=O) were seen in the spectra of the phthalocyanine compounds (4–7). Comparison of FT-IR spectra of all compounds was given in Figure 2.

In the phthalocyanine compounds' (4-7) ¹H-NMR spectra, the aromatic protons were observed as multiplet and broad signals because of the aggregation and isomers of phthalocyanines at between 7.80 and 6.50 ppm in a total of 24 proton integrations for each compound. The aliphatic protons were seen at around 2.45 and 2.25 ppm as broad singlet signals for each compound. In the phthalocyanine compounds' (4-7) ¹³C-NMR spectra, the aromatic and carbonil carbons were observed as broad signals because of the aggregation and isomers of phthalocyanines at between 163.52 and 99.97 ppm in a total of 64 carbon integrations for each compound. The aliphatic carbons were seen at between 15.45 and 12.01 ppm in a total of eight carbon integrations as broad signals for each compound.

The molecular ion peaks of the phthalocyanine derivatives (**4**–**7**) were observed at 1331.12 for **4**, 1415.63 for **5**, 1332.21 for **6**, and 1417.45 for **7**. MALDI-TOF-MS spectra of **6** and **7** were given in Figure 3 as an example.

In UV-vis spectra of phthalocyanines in $CHCl_3$, two characteristic bands were observed for each compound. In UV-vis spectra, Q and B bands were observed at 675–710 and 300–350 nm, respectively.



Consequently, elemental analysis data for phthalonitrile (2 and 3) and phthalocyanine (4–7) derivatives confirmed their proposed structure.

3.2 | Electronic absorption spectra and aggregation studies

In ground state absorption spectra of the phthalocyanines, two characteristic strong absorption bands are shown in the UV region and visible region. These characteristic Q and B bands are observed at around 650-750 and 300-350 nm, respectively. Phthalocyanines' affects spectroscopic and solubility their also physical-chemical properties. Phthalocyanine compounds can aggregate in the solvent because of the interactions between their $18-\pi$ electron systems. This tendency to aggregation affects the solubility and hence the spectroscopic properties of phthalocyanine compounds. Also, the solvent, central metal atom, and substituents' positions affect the solubility of the phthalocyanine compounds.[41]



FIGURE 2 Comparison of the FT-IR spectrum of coumarin (1), phthalonitriles (2 and 3), and their phthalocyanine derivatives (4, 5 and 6, 7)

In this study, the compounds' ground state absorption spectra and their aggregation behaviors were determined.

In the compounds' ground state absorption spectra, two characteristic absorption bands (Q and B) were observed for each phthalocyanines. The Q bands of nonperipheral substituted phthalocyanines (6 and 7) were higher wavelength shifted when compared with the peripheral substituted phthalocyanines (4 and 5) because of their atomic orbital coefficients' linear combination at the nonperipheral positions of the highest occupied molecular orbital (HOMO) being higher than the peripheral positions. The Q bands of indium (III) phthalocyanines (**5** and **7**) were also higher wavelength shifted compared with the zinc (II) phthalocyanines (**4** and **6**) because of the nonplanar effect of the larger atomic radius indium metal ion as metal atom in the phthalocyanine center. The observed red shifts are typical for phthalocyanines.^[49] Comparison of the peripheral (**4** and **5**) and nonperipheral (**6** and **7**) substituted phthalocyanines' UV-vis spectra was given in Figure 4.

The phthalocyanines' (4-7) aggregation behaviors were investigated in different organic solvents. The phthalocyanines' Q bands were red shifted in lowpolarity solvents such as chloroform when compared with the high-polarity solvents such as DMF. All compounds did not show any aggregation in DMF and chloroform. DMF was chosen as a solvent for determination of aggregation behaviors and other photophysical-photochemical properties because of the good solubility of compounds in this solvent. In Figure 5, UV-vis spectra of 4 in different solvents were given as an example.

The phthalocyanines' (4–7) aggregation behaviors were also investigated at different concentrations ranging from 1 to 10 μ M in DMF. The absorption intensity for the Q bands also increased while the concentration was increased and any additional bands were not observed for all phthalocyanines. These results showed that all phthalocyanines did not show any aggregation at the working concentration ranging and were compatible with the Beer–Lambert law. In Figure 6, UV–vis spectra of **5** at different concentrations were given as an example.



FIGURE 3 MALDI TOF-MS spectra of compounds 6 and 7



FIGURE 4 Absorption spectra of the synthesized peripheral and nonperipheral phthalocyanine compounds at between 300 and 800 nm



FIGURE 5 UV-vis spectra of 4 in different solvents

3.3 | Fluorescence spectra studies

The fluorescence excitation and emission spectra were determined for phthalocyanine compounds (4-7) in DMF and fluorescence excitation and were given with the emission and absorption maximum peaks in Table 1. The phthalocyanine compounds containing indium in central cavities (5 and 7) showed low fluorescent intensity in DMF because of some properties such as large coordination number and long ionic radius of indium metal. Due to these properties, the indium phthalocyanines (5 and 7) increase the transition between systems to populate triple state, thus reducing the number of fluorescent molecules and quenching them.^[15] As seen in Table 1, it was observed that fluorescence excitation and emission maximum peaks of indium phthalocyanines were longer than the unsubstituted counterparts due to the coumarin substituents on phthalocyanine compounds, but Stokes shifts of these compounds were shorter than the unsubstituted



FIGURE 6 The aggregation behavior of compound **5** at different concentrations ranging from 1 to $10 \ \mu$ M in DMF

counterparts due to the properties of central metal atom. Fluorescence emission, excitation maximum peaks, and Stokes shifts of zinc phthalocyanines ($\mathbf{4}$ and $\mathbf{6}$) in DMF were given in Table 1. Also, fluorescence emission, absorption, and excitation spectra of these compounds were shown in Figure 7. It was observed that Stokes shifts and fluorescence emission peaks of the zinc phthalocyanines ($\mathbf{4}$ and $\mathbf{6}$) were longer than the unsubstituted counterpart as a result of coumarin unit as a substituent on the phthalocyanine skeleton. As seen in Figure 7, the excitation spectra and absorption spectra were similar in the compounds and both were mirror images of the fluorescent spectra. This result showed that the ground and excited states' nuclear configurations were similar and not affected by excitation.

Fluorescence quantum yield ($\Phi_{\rm F}$) is the amount of molecules in the excited state that do return ground state by fluorescence, and it is an important parameter for PDT applications.^[43,46] Fluorescence quantum yield ($\Phi_{\rm F}$) was measured in DMF for the synthesized phthalocvanine compounds (4-7). The phthalocyanines' fluorescence quantum yield ($\Phi_{\rm F}$) values were determined in DMF, and results were given in Table 2. The $\Phi_{\rm F}$ values for 4-7 in DMF were found lower than their unsubstituted counterparts due to more quenching of fluorescence with coumarin substituents on phthalocyanine compounds. And also, the $\Phi_{\rm F}$ values for 4–7 were found lower than their counterparts containing different substituents on coumarin in the literature.^[16,29,46,50] This can be due to more quenching of fluorescence via the substitution of the phthalocyanine compounds with two methyl groups located at 3 and 4 position on coumarin. It was observed that the $\Phi_{\rm F}$ values of zinc phthalocyanines (4 and 6) were higher than the indium phthalocyanines (5 and 7). For indium phthalocyanines (5 and 7), the lowest Φ_F values were observed because of the heavy atom

Samples	λ^{Q}_{max} (loge)	λ^{B}_{max} (loge)	λ_{ex} (nm)	λ_{em} (nm)	$\Delta_{\bar{\upsilon}}$ (cm ⁻¹)
4	675 (5.08)	343 (4.95)	675	684	195
5	689 (4.93)	310 (4.82)	693	701	249
6	689 (4.65)	313 (4.52)	691	699	208
7	707 (5.20)	318 (4.90)	710	717	197
Std ZnPc ^a	670 (5.37)	342 (4.65)	670	676	133
Std InPc ^a	681 (5.04)	359 (4.64)	681	696	317

^aData from Taştemel et al.^[55]

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FIGURE 7 Fluorescence emission and excitation spectra of peripheral zinc (a) and nonperipheral zinc (b)

effect and low fluorescence emission properties of these compounds. Fluorescence emission and excitation spectra of peripheral zinc (4) and nonperipheral zinc (6) phthalocyanines were shown in Figures 7a and 7b, respectively.

Fluorescence lifetime (τ_F) is one of the important parameters for PDT applications and refers to the average time that a molecule remains in the stimulated state before emitting the photon.^[43] Fluorescence lifetime (τ_F) is characteristic for fluorescence compounds. Fluorescence lifetime (τ_F) and the natural radiative lifetime (τ_0) values of compounds (**4–7**) were determined in DMF and given in Table 2. It was observed that all of the

TABLE 1Absorption, emission,and excitation values for synthesizedphthalocyanines (4–7) andunsubstituted counterparts (ZnPc andInPc) in DMF

TABLE 2Photophysical and photochemical values of theperipheral and nonperipheral substituted phthalocyaninecompounds (4–7) and unsubstituted counterparts (**ZnPc** and **InPc**)in DMF

Samples	$\Phi_{\rm F}$	$\tau_{\rm F}$	τ_0	k_F^{b}	$\Phi_{\rm d}$	Φ_{Δ}
4	0.08	2.90	36.25	2.76	2.40	0.50
5	0.01	0.41	41.00	2.44	19.35	0.87
6	0.07	2.71	38.71	2.58	40.01	0.64
7	0.01	0.37	37.00	2.70	16.79	0.93
ZnPc ^a	0.17	1.03	6.05	16.53	2.30	0.56
InPc ^a	0.02	0.11	12.89	18.18	1.00	0.70

Note. For lifetime (τ_F) and radiative lifetime (τ_0) , units are in nanosecond (ns). Photodegradation (Φ_d) values were normalized with 10^{-5} . k_F values were normalized with 10^2 .

^aData from Taştemel et al.^[55]

 ${}^{\mathrm{b}}k_F$ is the transition rate constant for fluorescence and calculated using $k_F = \Phi_F / \tau_F$.

fluorescence lifetime (τ_F) and the natural radiative lifetime (τ_0) values of compounds were longer than the unsubstituted counterparts. The τ_F and τ_0 values of zinc phthalocyanines (**4** and **6**) were longer than indium phthalocyanines (**6** and **7**) due to the low fluorescence emission of these compounds. The fluorescence lifetime and natural radiative lifetime of phthalocyanines were observed in the expected range for phthalocyanines.^[40] Time-correlated single photon counting (TCSPC) trace charts for **4** were shown in Figure 8.

3.4 | Singlet oxygen production studies

Singlet oxygen generation is a very important parameter for cancer treatment application via PDT. Singlet oxygen quantum yield (Φ_{Δ}) is the expression of the singlet oxygen generation efficiency of compounds. During the singlet oxygen production processes, a photosensitizer such as phthalocyanine compounds absorbs light in the red region of visible light and turns the ground state oxygen into the excited state oxygen via transferring its energy to



FIGURE 8 Time-correlated single photon counting trace for compound **4** in DMF

the ground state oxygen. The excited state oxygen is the active cytotoxic species resulting in cell death.^[51,52]

The phthalocyanines' (4-7) singlet oxygen quantum vield (Φ_{Λ}) values were investigated in DMF solution via chemical method. In this method, DPBF (1,3-diphenylisobenzofuran) was used as singlet oxygen quencher. The decrease of DPBF absorbance was monitored using UV-vis spectra at 417 nm. During the singlet oxygen studies, it was observed that there was no change in the phthalocyanine compounds' O band intensities. It was also observed that phthalocyanine compounds (4-7) were not degraded by used light irradiation (30 V) during these studies. The singlet oxygen quantum yield (Φ_{Δ}) values of compounds (4–7) were given in Table 2. The Φ_{Λ} values of all the synthesized phthalocyanine compounds except the compound 4 were higher than the unsubstituted counterparts.

It was observed that the Φ_{Δ} values of the nonperipheral substituted phthalocyanine compounds (**6** and **7**) were higher than the peripheral substituted counterparts (**4** and **5**) because of the lower energy transition range between HOMO and the lowest empty molecular orbital (LUMO) in these compounds.

Also, it was observed that the Φ_{Δ} values of indium phthalocyanine compounds (**5** and **7**) were higher than the zinc phthalocyanine compounds (**4** and **6**) because of the presence of greater coordination number, long ionic radius, and trivalent heavy indium ion in the central cavity of these compounds. The indium phthalocyanines (**5** and **7**) showed higher singlet oxygen production than the similar coumarin-containing phthalocyanines in the literature.^[46,50]

UV-vis spectra of **4** for the investigation of singlet oxygen quantum yield (Φ_{Δ}) by chemical method using DPBF was given in Figure 9a as an example. Also, the decrease of DPBF absorbance at 417 nm for all compounds (**4–7**) during the singlet oxygen studies was given in Figure 9b.

3.5 | Photodegradation studies

In photodegradation process, a compound is degraded under light irradiation. This is very significant for compounds designed for use as photosensitizers. The investigation of photosensitizers' photodegradation behaviors is also important for PDT application because a good photosensitizer candidate should be staying in an average time in the organism for PDT activity.^[53,54]

The photodegradation stabilities of all phthalocyanine compounds (4–7) were investigated in DMF by monitoring the decrease of the Q band intensity of phthalocyanines under light irradiation (100 V) with increasing



FIGURE 9 (a) UV-vis spectra of **4** for the determination of singlet oxygen quantum yield (Φ_{Δ}) by chemical method using DPBF. (b) Disappearance of DPBF absorbance at 417 nm for phthalocyanines



FIGURE 10 Photodegradation of compound **5** under light irradiation with increasing time in DMF

time. The appropriate Φ_d values for PDT application should be between 10^{-3} and 10^{-6} for phthalocyanine photosensitizers.^[43] Photodegradation quantum yield (Φ_d) values for the phthalocyanines were given in Table 2, and these values showed that all studied phthalocyanine compounds (**4–7**) had high stability in DMF and appropriate for PDT application. The decreasing of the Q band intensity of **5** under light irradiation with increasing time was given in Figure 10 as an example.

4 | CONCLUSION

The phthalocyanine compounds containing 7-oxy-3,-4-dimethylcoumarin units were synthesized in this study. The obtained compounds' characterizations were performed by spectroscopic methods and elemental analysis. All studied phthalocyanine compounds showed good solubility in common organic solvents such as THF, chloroform, and DMF. The phthalocyanines' aggregation behaviors were determined, and it was observed that all of the phthalocyanines did not show aggregation in DMF.

The photophysical and photochemical properties of phthalocyanines compounds (4–7) were compared with their counterparts given in the literature. Photochemical and photophysical properties (singlet oxygen production, photodegradation stability, fluorescence quantum yield, fluorescence lifetime) of the obtained phthalocyanines (4–7) were investigated in DMF. Photophysical and photochemical measurement processes were shown in Figure S1. The phthalocyanine compounds' fluorescence quantum yield and lifetime values showed similar or better results than the coumarin substituted phthalocyanine compounds studied before. Synthesized phthalocyanine compounds except compound 4 showed higher singlet

oxygen quantum yields than the unsubstituted counterparts. In particular, **5** and **7** showed higher singlet oxygen quantum yield (Φ_{Δ}) values than the similar coumarincontaining phthalocyanines in the literature.^[45,46,50] According to the results, it was observed that the singlet oxygen quantum yield of compound **7** ($\Phi_{\Delta} = 0.93$) was higher than many phthalocyanine compounds containing coumarin derivatives in the literature.^[46,50] The phthalocyanine compounds' (**4**–**7**) high photodegradation quantum yields showed that all of the compounds had high stability under light irradiation. The synthesized phthalocyanine compounds showed higher photodegradation quantum yield (Φ_d) values than the unsubstituted counterparts.

In conclusion, these photophysicochemical properties of the synthesized zinc (II) and indium (III) phthalocyanine compounds containing 7-oxy-3,4-dimethylcoumarin units in this study indicate that these compounds may be new promising photosensitizers in PTD applications.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

AUTHOR CONTRIBUTIONS

Gamze Özgül Artuç: Investigation; methodology. Begümhan Karapınar: Investigation; methodology. Mücahit Özdemir: Investigation; methodology. Mustafa Bulut: Investigation; methodology.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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