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Synthesis, characterization, photophysical and photochemical properties of 7-oxy-3-methyl-4-phenylcoumarin-substituted indium phthalocyanines

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ABSTRACT

The synthesis of tetra- and octa-(7-oxy-3-methyl-4-phenylcoumarin)-substituted indium(III) phthalocyanine complexes obtained from 3-nitrophthalonitrile, 4-nitrophthalonitrile and 4,5-dichlorophthalonitrile substituted with 7-oxy-3-methyl-4-phenylcoumarin are described for the first time in this study. The new compounds have been characterized by elemental analysis, IR, ^{1}H NMR, electronic spectroscopy and mass spectra. The photophysical and photochemical properties of the compounds are also studied in dimethylformamide (DMF). The effects of the number of the substitution and the position on the photophysical and photochemical parameters of the substituted indium(III) phthalocyanine complexes are also reported. Photophysical and photochemical properties of phthalocyanine complexes are very useful for photodynamic therapy (PDT) of cancer applications. In particular, high singlet-oxygen quantum yields are very important for Type II mechanisms. These complexes have good singlet-oxygen quantum yields and show potential as Type II photosensitizers.

1. Introduction

Coumarin and its derivatives have been found to show a wide range of bioactivities such as anticoagulant, estrogenic, dermal photosensitizing, vasodilator, molluscacidal, anthelmintic, sedative, hypnotic, analgesic, hypothermic [1], antimicrobial [2], anti-inflammatory [3], antifungal [4] and antiulcer [5]. 7-Hydroxycoumarin, also known as umbelliferone is a major biotransformed product of coumarin (1,2-benzopyrone), which is a widely distributed natural product [6]. Coumarins and 7-hydroxycoumarins have been also found to exhibit cytotoxic effects against the lung adenocarcinoma cell lines KB [4], A549 [7], SK-LU-1,1.3.15, 3A5A and A-427 [8].

Phthalocyanines are used in a number of applications due to their increased stability, architectural flexibility, diverse coordination properties and improved spectroscopic characteristics. Metallophthalocyanines (MPcs), a family of aromatic macrocycles based on an extensive delocalized 18π electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific research. Some technological applications in fields, such as chemical sensors [9], liquid crystals [10], semiconductors [9b], non-linear optics [11], as photosensitizers in photodynamic therapy (PDT) [12], have shown the increased importance of these macrocycles. The MPcs can be modulated in a plethora of ways by changing the peripherally or non-peripherally substitution, tetra or octa-substituents on the Pc ring in addition to changing the central metal and the axial ligands. Their physicochemical properties can be fine-tuned by changing the metal and/or nature of substituents [13].

Although metallophthalocyanine complexes have been extensively studied, their properties cannot be fully exploited as they have low solubility in most organic solvents and they aggregate. Depending on the polarity of the substituents, Pcs become more soluble in polar or non-polar solvents. Pcs soluble in polar solvents have strong influence on bioavailability whereas Pcs soluble in non-polar solvents have a higher tumor affinity [14]. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework [15]. Tetra-substituted phthalocyanines are usually more soluble than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery [15,16]. According to their substituent positions, two types of tetra-substituted macrocycles, which show significant differences in their chemical and physical behaviors can be distinguished. Substitution at the more sterically crowded non-peripheral position causes reduced aggregation tendencies more than substitution at peripheral position [17].

Metallophthalocyanine complexes have proved to be highly promising as photosensitizers for photodynamic therapy (PDT), due to their intense absorption in the red region of the visible light.

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High triplet state quantum yields and long triplet lifetimes are required for an efficient sensitization. The photophysical properties of the phthalocyanine dyes are strongly influenced by the presence and nature of the central metal ion. Complexation of phthalocyanine with transition metals gives dyes short triplet lifetimes. Closed shell, diamagnetic ions, such as Zn^{2+}, Al^{3+} and In^{3+}, give phthalocyanine complexes both high triplet yields and singlet oxygen generation [18]. Heavy metals, especially diamagnetic metals, play a major role in photosensitizing and optical limiting mechanisms because they enhance intersystem crossing through spin–orbit coupling. This is desirable because it improves the chances of getting a large population in the triplet state. Axial ligands in MPcs are useful in preventing or minimizing intermolecular interactions which result in aggregation in solution. Aggregation can result in the fast decay of the excited states. Indium is a useful central metal in MPc complexes since it is diamagnetic and able to host axial ligands. Indium phthalocyanines have been reported to have good photosensitizing and optical limiting properties [19].

To our knowledge, coumarin tetra-substitution and octa-substitution on indium acetate based phthalocyanines has not been reported before. The rarity of these phthalocyanines has thus prompted us to synthesize coumarin substituted indium phthalocyanines (**9**–**12**) because the development and elucidation of photophysical and photochemical properties of new phthalocyanine complexes are of fundamental importance. Specific phthalocyanines can thus be tailored such that they have certain properties, which are required for various applications, since the possibility of combining an unlimited number and type of substituents with a great number of central metals is infinite.

The aim of our ongoing research is to synthesize indium phthalocyanines as potential PDT agents. Photophysical and photochemical properties of **InPc**s are very useful in applications involving PDT, non-linear optics and optical limiters as these indium macrocycles are known to have remarkable properties [20]. Herein, we report the synthesis, spectroscopic, photophysical and photochemical properties of **InPc** tetra-substituted at the non-peripheral (**9**), peripheral (**10**) and octa-substituted (**11** and **12**) at the peripheral positions with 7-oxy-3-methyl-4-phenylcoumarin (Scheme 1).

2. Results and discussion

2.1. Synthesis and characterization

Tetra- and octa-substituted indium(III) phthalocyanine complexes (**9**–**12**) are prepared by cyclotetramerization of 7-hydoxy-3-methyl-4-phenylcoumarin-substituted phthalonitriles (**5**–**8**). In both cases, a mixture of four possible structural isomers is obtained. The four probable isomers can be designed by their molecular symmetry as C_{4h}, C_{2v}, C_s and D_{2h}. In this study, synthesized tetra-(7-oxy-3-methyl-4-phenyl)coumarin-substituted indium(III) Pc complexes are obtained as isomer mixtures as expected. No attempt was made to separate the isomers of complexes **9** and **10**.

The preparation of substituted phthalonitriles from 3-nitrophthalonitrile (**2**), 4-nitrophthalonitrile (**3**) and 4,5-dichlorophthalonitrile (**4**) were recently used to prepare 3-monosubstituted, 4-monosubstituted and 4,5-disubstituted phthalonitrile derivatives, respectively, through base catalyzed nucleophilic aromatic displacement [21]. The same route was applied to prepare 7-oxy-3-methyl-4-phenylcoumarin-substituted phthalonitriles from 7-hydroxy-3-methyl-4-phenylcoumarin (**1**) and 3-nitrophthalonitrile (**2**), 4-nitrophthalonitrile (**3**) or 4,5-dichlorophthalonitrile (**4**) (Scheme 1). The reactions were carried out in dimethylformamide (DMF) at room temperature and gave yields of about 80–90%.

The preparation of phthalocyanine derivatives from the aromatic 1,2-dinitriles occurs under different reaction conditions. The syntheses of indium(III) Pc complexes (**9**–**12**) were achieved by treatment of 7-oxy-3-methyl-4-phenylcoumarin-substituted phthalonitriles (**5**–**8**) with anhydrous indium(III) acetate in *N*,*N*-dimethylaminoethanol (DMAE) (Scheme 1). Column chromatography with silica gel was employed to obtain the pure products from the reaction mixtures. Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. All phthalocyanine complexes (**9**–**12**) exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, DMF and DMSO. The new compounds were characterized by UV–Vis, FT-IR and NMR spectroscopies, MALDI-TOF mass spectra and elemental analysis. The analyses are consistent with the predicted structures as shown in Section 3.

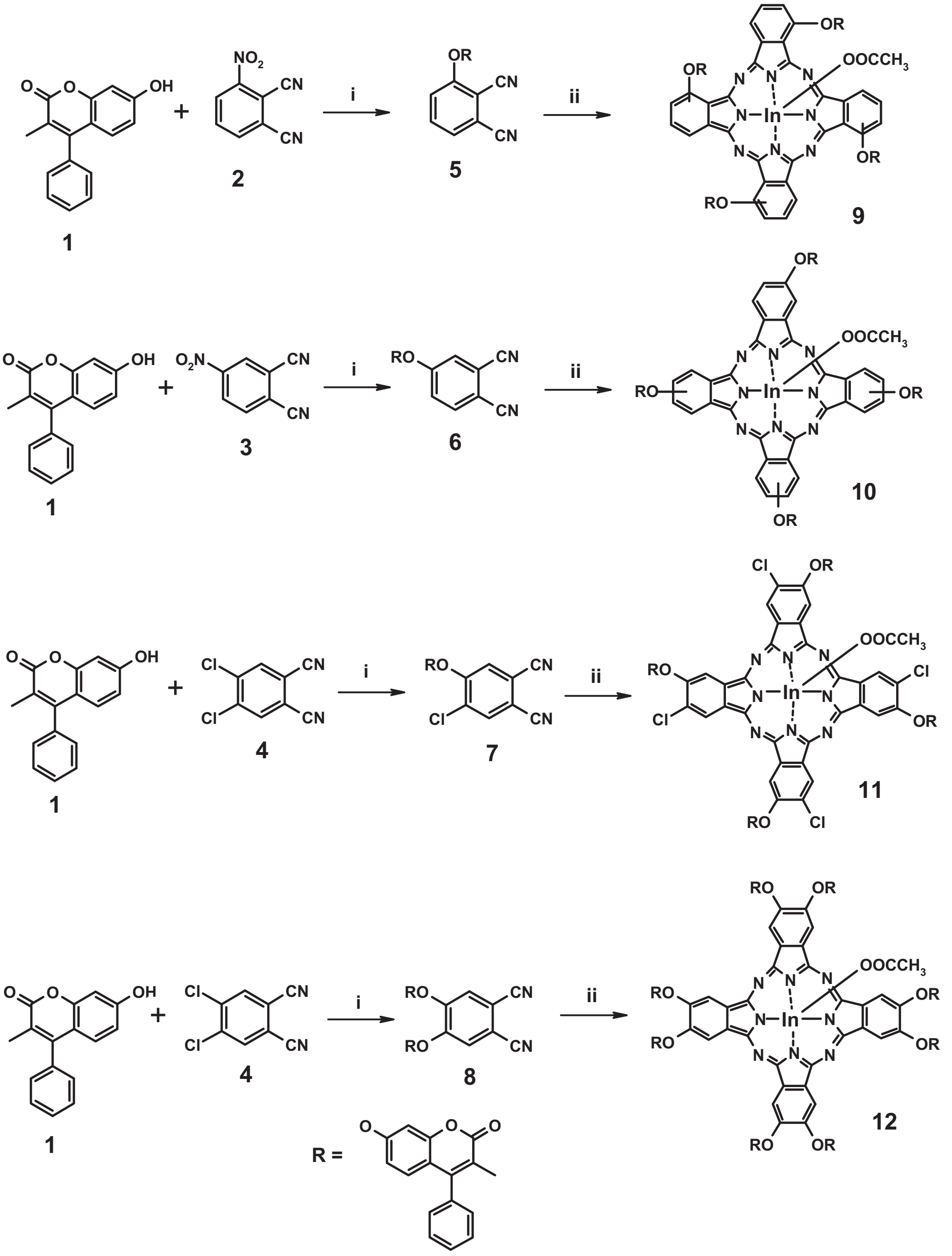
Comparison of the IR spectra at each step gave some insights on the nature of the products. The –OH stretching band of 7-hydroxy-3-methyl-4-phenylcoumarin group at 3141 cm^{-1} disappeared for all the dinitrile compounds in the IR spectra. The IR spectra of the all dinitrile compounds showed a sharp peak at around 2230–2245 cm^{-1} for $C{\equiv}N$ stretching. These peaks disappeared and the color changed to green after conversion, indicative of phthalocyanines formation.

The ^1H NMR spectra of substituted dinitrile compounds (**5**–**8**) were recorded in $CDCl_3$. We were able to obtain good aromatic and methyl protons signals for ^1H NMR spectroscopy. In the ^1H NMR spectra of substituted dinitrile compounds (**5**–**8**), the aromatic protons were observed at between 7.65 and 6.87 ppm for compound **5**, 7.78–6.84 ppm for compound **6**, 7.92–6.82 ppm for compound **7** and 7.55–6.80 ppm for compound **8** integrating totally 11 protons for compounds **5** and **6**, 10 protons for compounds **7** and 18 protons for compound **8**. The aliphatic methyl protons were observed at ~2 ppm for all dinitrile compounds integrating 3 protons for each compound.

In the mass spectra of phthalonitriles obtained by the MALDI-TOF technique, the molecular ion peaks were observed at *m*/*z*: 378.1 $[M]^+$ for **5**, 378.7 $[M]^+$ for **6**, 412.0 $[M]^+$ for **7** and 628.9 $[M]^+$ for **8**.

The $C{\equiv}N$ stretching peaks of the dinitrile compounds at around 2230–2245 cm^{-1} disappeared after formation of the phthalocyanine complexes. In the IR spectra for Pc complexes (**9**–**12**), vibrations bands were observed at: 3038–3075 cm^{-1} for aromatic C–H stretching, 2840–2923 cm^{-1} for aliphatic C–H stretching, 1710–1720 cm^{-1} for C=O vibration of the ester groups, 1582–1678 cm^{-1} for aromatic C=C stretching and 1237–1278 cm^{-1} for Ar–O–Ar stretching. The C=O and C=C bands for indium(III) phthalocyanine complexes (**9**–**12**) in IR spectra were broader and shorter than those of dinitrile compounds (**5**–**8**) because of the H-type aggregation of coumarin moiety.

The ^1H NMR spectra of Pcs (**9**–**12**) were recorded in $CDCl_3$. The ^1H NMR spectra of tetra-substituted phthalocyanine complexes (**9**–**12**) have broad absorptions when compared with that of corresponding phthalonitrile derivatives (**5**–**8**). It is likely that broadness is due to both chemical exchange caused by aggregation–disaggregation equilibrium in $CDCl_3$ and the fact that the product obtained in this reaction is a mixture of four positional isomers (for tetra-substituted complexes) which are expected to show chemical shifts which slightly differ from each other. The 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) Pc complexes were found to be pure by ^1H NMR with all the substituents and ring protons observed in their respective regions. In the ^1H NMR spectra of Pcs (**9**–**12**), the aromatic protons were observed at between 8.01 and 6.92 ppm for compound **9**, 8.25–6.72 ppm for compound **10**, 7.91–6.98 ppm for compound **11** and 7.98–6.76 ppm for compound **12** integrating totally 44, 44, 40, 72 protons for each Pcs, respectively. The aliphatic methyl protons were observed at 2.55, 2.81, 2.54, 2.59 ppm for all Pcs, respectively, integrating 12 protons



Scheme 1. Synthesis of tetra- and octa-(7-oxy-3-methyl-4-phenylcoumarin)-substituted indium(III) phthalocyanine complexes (**9**–**12**). (i) DMF, K_2CO_3, RT; (ii) DMAE, $In(OAc)_3$, reflux.

for each Pcs (**9**, **10** and **11**) and 24 protons (**12**). The indium(III) acetate protons were observed at 2.51, 2.81, 2.60 and 2.12 ppm for all Pcs, respectively, integrating 3 protons for each Pcs (**9**, **10**, **11** and **12**).

In the mass spectra of phthalocyanines obtained by the MALDI-TOF technique, the molecular ion peaks were observed at m/z: 1627.5 for **9**, 1627.4 for **10**, 1766.1 for **11** and 2628.5 for **12** as without axially substituted acetate groups.

2.2. Ground state electronic absorption spectra

The electronic spectra of the 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) Pc complexes (**9**–**12**) showed characteristic absorption in the Q band region at around 677–705 nm in DMF, Table 1. The B bands were observed at around 320 nm (Fig. 1). The spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes in DMF [22]. In DMF, the Q bands were observed at: 705 nm for **9**, 687 nm for **10**, 677 nm for **11** and 683 nm for **12**, Table 1. The red-shifts were observed for indium(III) Pc complexes following substitution. The Q band of the non-peripherally substituted complex (**9**) is red-shifted when compared to the corresponding peripherally tetra-(**10**) and octa-(**11** and **12**) substituted complexes in DMF (Fig. 1). The red-shifts are 18 nm between **9** and **10**, 28 nm between **9** and **11** and 22 nm between **9** and **12**. The observed red spectral shifts are typical of Pcs with substituents at the non-peripheral positions and have been explained in the literature [23], due to linear combination of the atomic orbitals (LCAO)

Table 1
Absorption, excitation and emission spectral data for unsubstituted (**InPc**) and substituted indium phthalocyanines (**9**–**12**) in DMF.

Compound	Q band λ_{max} (nm)	(log ε)	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift Δ_{Stokes} (nm)
InPc[a]	681	5.04	681	696	15
9	705	5.01	713	721	16
10	687	4.68	689	698	11
11	677	4.30	679	684	7
12	683	4.86	682	686	3

[a] Data from Ref. [29].

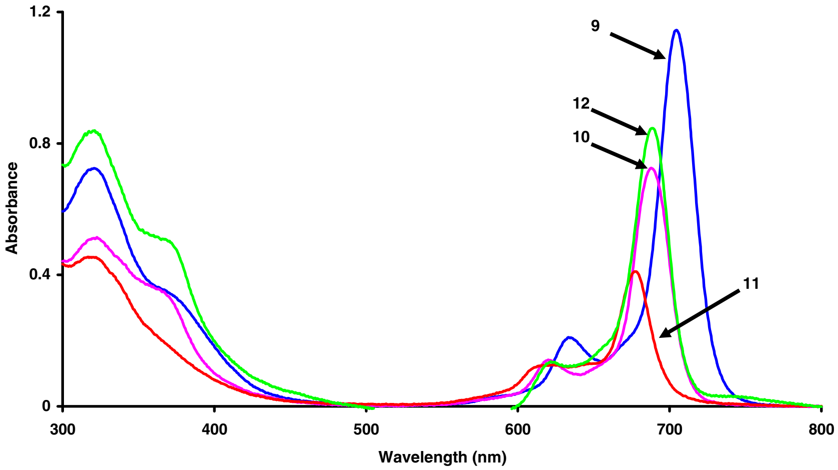


Fig. 1. Absorption spectra of substituted indium phthalocyanine complexes (**9**, **10**, **11** and **12**) in DMF. Concentration = 1×10^{-5} M.

coefficients at the non-peripheral positions of the highest occupied molecular orbital (HOMO) being greater than those at the peripheral positions. As a result, the HOMO level is more destabilized upon non-peripherally substitution than peripherally substitution. Essentially, the energy gap (ΔE) between the HOMO and lowest unoccupied molecular orbital (LUMO) becomes smaller, resulting in a ~20 nm bathochromic shift. The shoulder between 360 and 370 nm may be due to charge transfer from the electron-rich ring to the electron-poor metal. The B-bands are broad due to the superimposition of the B1 and B2 bands in the ~320 nm region.

2.3. Aggregation studies

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [24]. In the aggregated state the electronic structure of the complexed phthalocyanine rings are perturbed resulting in alternation of the ground and excited state electronic structures [25]. In this study, the aggregation behavior of 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) Pc complexes (**9**–**12**) were investigated at different concentrations in DMF (Fig. 2, for complex **10** as an example). The Beer–Lambert law was obeyed for all of these compounds at concentrations ranging from 1.4×10^{-5} to 4×10^{-6} M. The 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) Pc complexes did not show aggregation at these concentration ranging in DMF.

2.4. Fluorescence spectra

Fig. 3 shows fluorescence emission, absorption and excitation spectra of 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) Pc complexes **10** (Fig. 3a) and **11** (Fig. 3b) in DMF as examples of the studied indium(III) Pc complexes. Fluorescence emission peaks were listed in Table 1. All indium(III) Pc complexes (**9**–**12**) showed similar fluorescence behavior in DMF (Fig. 3 as an example for complexes **10** and **11**). The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for all indium(III) Pc complexes in DMF. The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for all indium(III) Pc complexes suggest that the nuclear configurations of the ground and excited states are similar and not affected by excitation. The fluorescence emission of the chloro octa-substituted indium(III) Pc complex (**11**) is more intense than other studied indium(III) phthalocyanine complexes (**9**, **10** and **12**) in DMF, suggesting that heavy atom effect of the chlorine atoms on the Pc framework instead of H atoms.

2.5. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of the studied indium Pc complexes are given in Table 2. The Φ_F values of indium(III) Pc complexes are lower than other MPc complexes because of the indium is very heavy metal, Table 2. The Φ_F values of the indium Pc complexes are similar and typical of other studied indium Pc complexes in DMF [26], except for chloro octa-substituted indium(III) Pc complex (**11**). This complex showed higher Φ_F value due to the heavy atom effect of the chlorine atom on the Pc framework (Table 2). The Φ_F values of the substituted indium Pc complexes (**9**–**12**) are higher compared to unsubstituted indium Pc complex (**InPc**) in DMF, which implies that the presence of the 7-oxy-3-methyl-4-phenylcoumarin substituents reduced the fluorescence quenching of the molecules. For comparison among the studied indium(III) Pc complexes, the Φ_F values of the octa-substituted indium(III) Pc complexes are higher than tetra-substituted indium(III) Pc complexes which suggesting that the increasing of

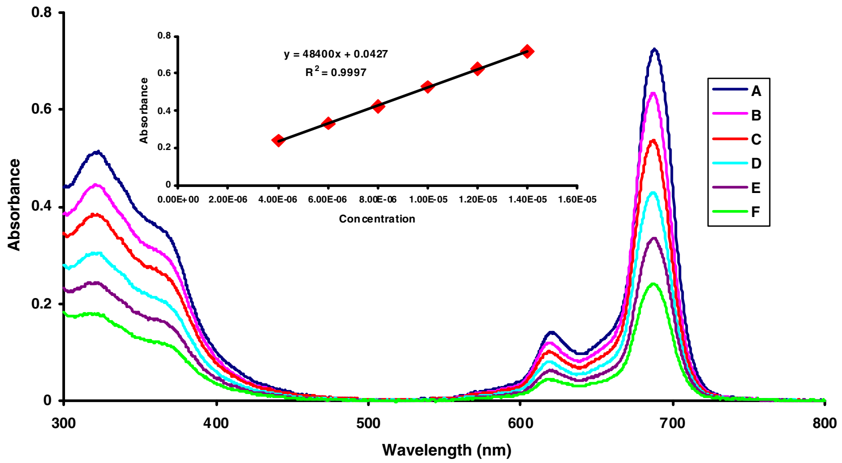


Fig. 2. Aggregation behavior of **10** in DMF at different concentrations: 14 × 10^{-6} (A), 12 × 10^{-6} (B), 10 × 10^{-6} (C), 8 × 10^{-6} (D), 6 × 10^{-6} (E) and 4 × 10^{-6} (F) M. (Inset: plot of absorbance vs. concentration.)

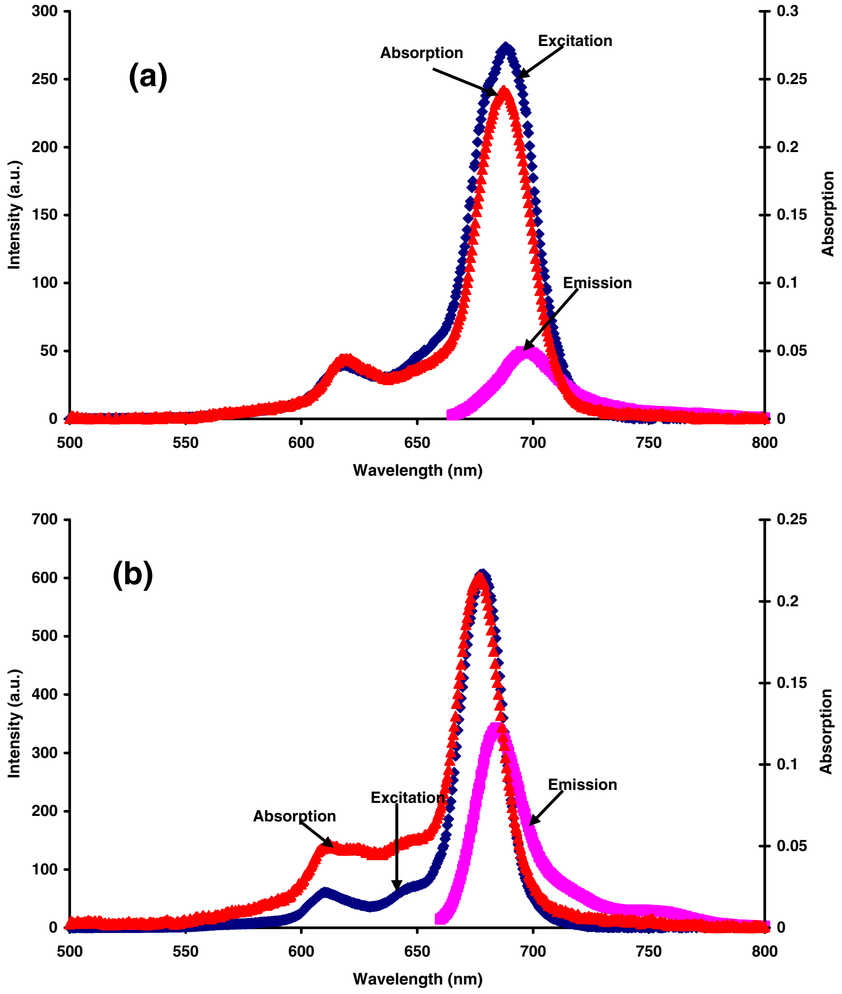


Fig. 3. Absorption, excitation and emission spectra of the compound **10** (a) and **11** (b) in DMF. Excitation wavelength = 655 nm for **10** and 650 nm for **11**.

the number of the substituents reduced fluorescence quenching of the Pc molecules.

Fluorescence lifetime (τ_F) refers to the average time a molecule stays in its excited state before fluorescing, and its value is directly related to that of Φ_F; i.e. the longer the lifetime, the higher the quantum yield of fluorescence. Any factor that shortens the fluorescence lifetime of a fluorophore indirectly reduces the value of Φ_F. Such factors include internal conversion and intersystem crossing. As a result, the nature and the environment of a fluorophore determine its fluorescence lifetime. τ_F values (Table 2) were calculated using the Strickler–Berg equation. The τ_F values of the substituted indium(III) Pc complexes are higher compared to unsubstituted

Table 2
Photophysical and photochemical data for unsubstituted (**InPc**) and substituted indium phthalocyanines (**9**–**12**) in DMF.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	k_F[a] (s^{-1}) ($\times 10^7$)	Φ_d ($\times 10^{-3}$)	Φ_Δ
InPc[b]	0.017	0.11	12.89	15.5	0.01	0.70
9	0.018	0.26	14.53	6.88	1.16	0.83
10	0.033	0.87	26.26	3.80	1.10	0.62
11	0.141	10.51	75.06	1.33	0.23	0.30
12	0.055	0.94	17.13	5.84	0.73	0.76

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.

[b] Data from Ref. [29].

indium(III) Pc complexes in DMF, suggesting less quenching by substitution. τ_F values are lower for tetra-substituted indium Pc complexes (**9** and **10**) when compared to octa-substituted indium Pc complexes (**11** and **12**), Table 2, suggesting more quenching by tetra-substitution compared to octa-substitution. However the τ_F values are typical for indium(III) Pc complexes [26], the τ_F value of chloro octa-substituted indium(III) Pc complex (**11**) is higher than other substituted indium(III) Pc complexes (**9**, **10** and **12**) because of the heavy atom effects of the chlorine atom, again.

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also given in Table 2. The τ_0 values of the substituted indium Pc complexes (**9**–**12**) are higher than unsubstituted indium Pc complex (**InPc**) in DMF. The chloro octa-substituted indium(III) Pc complex showed higher τ_0 value than other substituted indium(III) Pc complexes in DMF (Table 2). The rate constants for fluorescence (k_F) of substituted indium(III) Pc complexes (**9**–**12**) are lower when compared to unsubstituted indium(III) Pc (**InPc**) in DMF. The chloro octa-substituted complex (**11**) showed the lowest k_F value among the substituted indium(III) Pc complexes in DMF (Table 2).

2.6. Singlet oxygen quantum yields

An efficient photosensitizer must be generating singlet oxygen very effectively for application of photodynamic therapy treatment of cancer. Energy transfer between the triplet state of a photosensitizer molecule (such as phthalocyanines) and the ground state of molecular oxygen leads to its conversion into singlet oxygen. This transfer must be as much efficient as possible to generate large amounts of singlet oxygen. This is determined as the singlet oxygen quantum yield (Φ_Δ), a parameter giving an indication of the potential of molecules using as photosensitizers in applications where singlet oxygen is required (e.g., for Type II mechanism) [27]. The Φ_Δ values were determined in DMF using a chemical method and 1,3-diphenylisobenzofuran (DPBF) as a quencher. The disappearance of DPBF absorbance at 417 nm was monitored using UV–Vis spectrophotometer (Fig. 4 for complex **10** as an example).

Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen including; triplet excited state energy, ability of substituents and solvents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen. It is believed that during photosensitization, the phthalocyanine molecule is first excited to the singlet state and through intersystem crossing forms the triplet state, and then transfers the energy to ground state oxygen, $O_2(^3\Sigma_g)$, generating excited singlet state oxygen, $O_2(^1\Delta_g)$, the chief cytotoxic species, which subsequently oxidizes the substrate by Type II mechanism.

There was no change in the Q band intensity during the Φ_Δ determinations, confirming that complexes were not degraded during singlet oxygen studies (Fig. 4 as an example for complex **10**). The Φ_Δ values of the substituted indium(III) Pc complexes (**9**, **10**, **11** and **12**) are given in Table 2. The Φ_Δ values of the substituted indium(III) Pc complexes (**9**, **10** and **12**) are higher when compared to unsubstituted indium(III) Pc (**InPc**) complex, except for chloro octa-substituted complex (**11**) in DMF. The Φ_Δ value of chloro octa-substituted complex (**11**) is lower than other substituted indium(III) Pc complexes in DMF, because this complex contains heavy chlorine atoms and these chlorine atoms reduce intersystem crossing. The non-peripherally tetra-substituted indium(III) Pc complex (**9**) showed the highest Φ_Δ value among the studied indium(III) Pc complexes (Table 2) may be due to their absorption of light at longer wavelength than peripherally substitution.

2.7. Photodegradation studies

Degradation of the molecules under irradiation can be used to study their stability and this is especially important for those molecules intended for use as photocatalysts. The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with photochemical reaction into different forms of MPc absorbing in the visible region.

The spectral changes observed for all the substituted indium Pc (**9**–**12**) during irradiation are as shown in Fig. 5 (using complex **9** as an example in DMF) and hence confirm photodegradation occurred without phototransformation. All the complexes showed about the same stability with Φ_d of the order of 10^{-3}. The Φ_d values, found in this study, are higher than phthalocyanine derivatives having different metals and substituents on the phthalocyanine ring in the literature [28]. Stable zinc phthalocyanine molecules show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [28]. The Φ_d values of the substituted indium(III) Pc complexes (**9**–**12**) are also higher than unsubstituted indium(III) Pc complex in DMF [29]. It seems indium(III) metal and 7-oxy-3-methyl-4-phenylcoumarin groups increases the Φ_d values and decreases the stability of complexes.

3. Experimental

3.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. 7-Hydroxy-3-methyl-4-phenylcoumarin (**1**), indium(III)acetate, K_2CO_3 and unsubstituted zinc phthalocyanine were purchased from the Aldrich Chemical Company. 1,3-Diphenylisobenzofuran (DPBF) was purchased from Fluka. 3-Nitrophthalonitrile (**2**) [30], 4-nitrophthalonitrile (**3**) [31] and 4,5-dichlorophthalonitrile (4) [32] were synthesized and purified according to well known literature.

3.2. Equipment

Absorption spectra in the UV–Vis region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. IR spectra (KBr pellets) were recorded on a Bio-Rad FTS 175C FT-IR spectrometer. Elemental analyses carried out using a LECO CHN 932 was performed by the Instrumental Analysis Laboratory of TUBITAK Ankara Test and Analysis Laboratory. Mass spectra were performed on a Bruker Autoflex III MALDI-TOF spectrometer. A 2,5-dihydroxybenzoic acid (DHB, 20 mg/mL in THF) was used as matrix. MALDI samples were prepared by mixing the complex (2 mg/mL in THF) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf micro tube. Finally, 1 μL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. ^{1}H NMR spectra

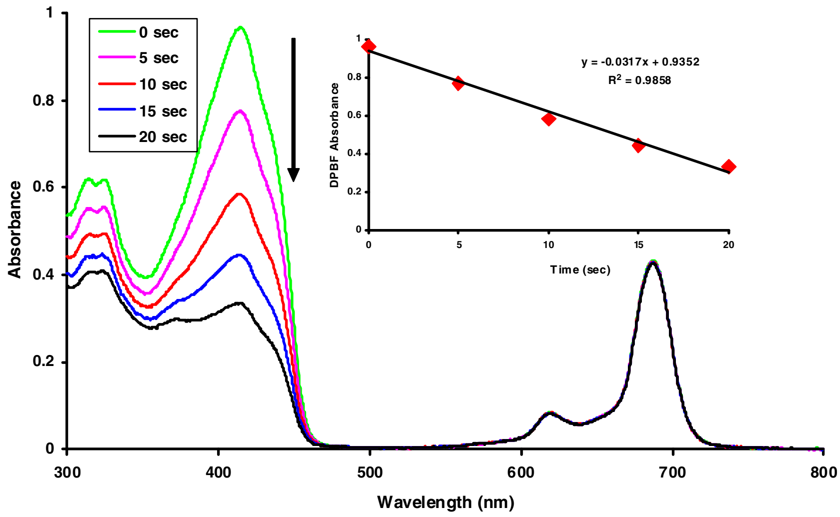


Fig. 4. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **10** in DMF at a concentration of 1×10^{-5} M. (Inset: plot of DPBF absorbance vs. time.)

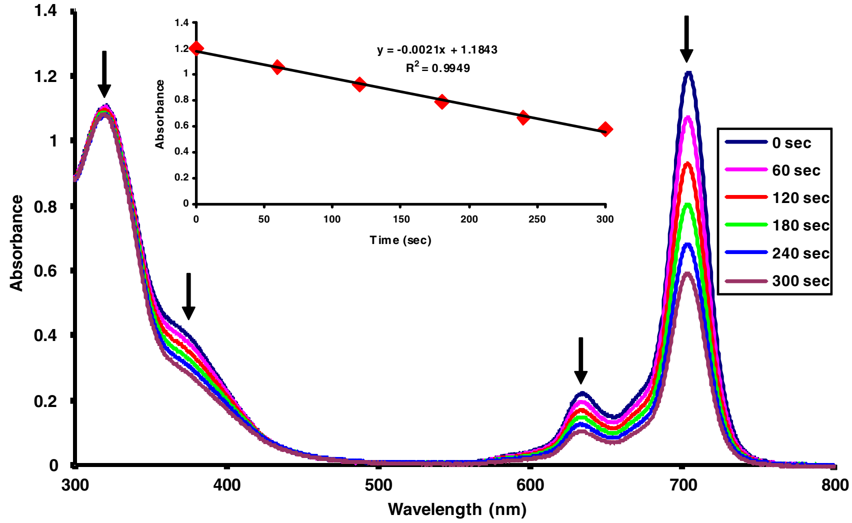


Fig. 5. The photodegradation of compound **9** in DMF showing the disappearance of the Q-band at 1 min intervals. (Inset: plot of absorbance vs. time.)

were recorded in $CDCl_3$ for phthalonitriles (**5**–**8**) and phthalocyanine complexes (**9**–**12**) on a Varian 500 MHz spectrometer.

Photo-irradiations were done using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

3.3. Photophysical parameters

3.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. (1) [33],

$$\Phi_F = \Phi_F(\text{Std})\frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n^2_{\text{Std}}} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**9**–**12**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [34] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative (τ_0) lifetimes were determined using PhotochemCAD program which uses the Strickler–Berg equation [35]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

3.4. Photochemical parameters

3.4.1. Singlet oxygen quantum yields

Singlet oxygen (Φ_Δ) quantum yield determinations were carried out using the experimental set-up described in the literature [36], in DMF. Typically, a 3 mL portion of the respective substituted indium(III) phthalocyanine (**9**–**12**) solutions (absorbance ~1 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in references [36]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with unsubstituted ZnPc (in DMF) as reference. DPBF was used as chemical quenchers for singlet oxygen in DMF. Eq. (3) was employed for the calculations:

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}} \frac{R \cdot I_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}} \cdot I_{\mathrm{abs}}} \tag{3}$$

where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yields for the standard ZnPc ($\Phi_\Delta^{\mathrm{Std}} = 0.56$ in DMF) [34]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**9**–**12**) and standards, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by the samples (**9**–**12**) and standards, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [37], the concentration of quenchers was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (1×10^{-5} M) containing DPBF was prepared in the dark and irradiated in the Q band region using the set-up described above. DPBF degradation at 417 nm was monitored. The light intensity 6.72×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

3.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_{d}) determinations were carried out using the experimental set-up described in the literature [36]. Photodegradation quantum yields were determined using Eq. (4),

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_{\mathrm{A}}}{I_{\mathrm{abs}} \cdot S \cdot t} \tag{4}$$

where C_0 and C_t are the samples (**9**–**12**) concentrations before and after irradiation, respectively, V is the reaction volume, N_{A} is the Avogadro's constant, S *is* the irradiated cell area, t *is* the irradiation time and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**9**–**12**). A light intensity of 2.25×10^{16} photons s^{-1} cm^{-2} was employed for Φ_{d} determinations.

3.5. Synthesis

3.5.1. 3-(3-Methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalonitrile (5, Scheme 1)

7-Hydroxy-3-methyl-4-phenycoumarin (**1**) (0.5 g, 1.98 mmol) and 3-nitrophthalonitrile (**2**) (0.34 g, 1.98 mmol) were dissolved in dry DMF (9 mL) under argon atmosphere. After stirring for 15 min, finely ground anhydrous K_2CO_3 (0.54 g, 3.91 mmol) was added portionwise over 2 h and the ensuing mixture was stirred vigorously at room temperature for a further 48 h. The reaction mixture was then poured into water (150 mL) and the precipitate was filtered off and washed with water to the white product. The compound **5** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.59 g (%79). Mp 126 °C. FT-IR [(KBr) ν_{max}/cm^{-1}]: 3056 (Ar–CH), 2960 (CH), 2229 (C≡N), 1724 (C=O lactone), 1460 (C=C), 1265 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: aromatic protons, 7.65 (t, 1H), 7.57 (d, 7.33 Hz, 1H), 7.55 (d, 7.57 Hz, 1H), 7.54 (d, 8.79 Hz, 2H), 7.51 (t, 1H), 7.25 (d, 8.05 Hz, 2H), 7.23 (d, 8.79 Hz, 1H), 7.06 (d, 2.19 Hz, 1H,), 6.87 (dd, 8.79 Hz, 2.44 Hz, 1H), 2.00 (s, 3H, CH_3). *Anal.* Calc. for $C_{24}H_{14}N_2O_3$ (378.38): C, 76.18; H, 3.73; N, 7.40. Found: C, 76.14; H, 3.77; N, 7.36%. MS (MALDI-TOF) *m*/*z*: 378.10 [M]$^+$.

3.5.2. 4-(3-Methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalonitrile (6, Scheme 1)

7-Hydroxy-3-methyl-4-phenylcoumarin (**1**) (0.5 g, 1.98 mmol) and 4-nitrophthalonitrile (**3**) (0.34 g, 1.98 mmol) were dissolved in dry DMF (9 mL) under argon atmosphere. After stirring for 15 min, finely ground anhydrous K_2CO_3 (0.54 g, 3.91 mmol) was added portionwise over 2 h and the ensuing mixture was stirred vigorously at room temperature for a further 48 h. The reaction mixture was then poured into water (150 mL) and the precipitate was filtered off and washed with water to the white product. The compound **6** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.60 g (%80). Mp 115 °C. FT-IR [(KBr) ν_{max}/cm^{-1}]: 3065 (Ar–CH), 2957–2804 (CH), 2239 (C≡N), 1704 (C=O lactone), 1576 and 1470 (C=C), 1254 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: aromatic protons, 7.78 (d, 8.30 Hz, 1H), 7.58 (d, 2.44 Hz, 1H), 7.57 (d, 7.81 Hz, 1H), 7.53 (t, 1H), 7.33 (d, 8.54 Hz, 2H), 7.26 (d, 8.05 Hz, 2H), 7.10 (d, 8.54 Hz, 1H), 7.09 (d, 2.20 Hz, 1H), 6.84 (dd, 8.79 Hz, 2.44 Hz, 1H), 2.02 (s, 3H, CH_3). *Anal.* Calc. for $C_{24}H_{14}N_2O_3$ (378.38): C, 76.18; H, 3.73; N, 7.40. Found: C, 76.15; H, 3.76; N, 7.37%. MS (MALDI-TOF) *m*/*z*: 378.79 [M]$^+$.

3.5.3. 4-Chloro-5-(3-methyl-4-phenyl-2H-chromen-7-yloxy)phthalonitrile (7, Scheme 1)

7-Hydroxy-3-methyl-4-phenylcoumarin (**1**) (0.5 g, 1.98 mmol) and 4,5- dichlorophthalonitrile (**4**) (0.39 g, 1.98 mmol) were dissolved in dry DMF (9 mL) under argon atmosphere. After stirring for 10 min; finely ground anhydrous K_2CO_3 (0.54 g, 3.96 mmol) was added with stirring. The reaction mixture was stirred at room temperature for 48 h under argon atmosphere. The reaction mixture was then poured into water (150 mL) and the precipitate was filtered off and washed with water to the white product. The compound **7** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.65 g (79%). Mp 103 °C. FT-IR [(KBr) ν_{max}/cm^{-1}]: 3062 (Ar–CH), 2920 (CH), 2245 (C≡N), 1730 (C=O lactone), 1580 (C=C), 1252 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: aromatic protons: 7.92 (s, 1H), 7.58 (d, 8.30 Hz, 2H), 7.54 (d, 8.55 Hz, 2H), 7.52 (t, 1H), 7.19 (s, 1H), 7.12 (d, 8.79 Hz, 1H), 7.08 (d, 1.46 Hz, 1H), 6.82 (dd, 8.79 Hz, 1.46 Hz, 1H), 2.02 (s, 3H, CH_3). *Anal.* Calc. for $C_{24}H_{13}ClN_2O_3$ (412.82): C, 69.83; H, 3.17; N, 6.79. Found: C, 69.73; H, 3.19; N, 6.6%. MS (MALDI-TOF) *m*/*z*: 412.06 [M]$^+$.

3.5.4. 4,5-Bis(3-methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalonitrile (8, Scheme 1)

7-Hydroxy-3-methyl-4-phenylcoumarin (**1**) (0.6 g, 2.38 mmol) and 4,5-dichlorophthalonitrile (**4**) (0.19 g, 1.19 mmol) were dissolved in dry DMF (12 mL) under argon atmosphere. After stirring for 10 min; finely ground anhydrous K_2CO_3 (1.09 g, 9.52 mmol) was added with stirring. The reaction mixture was stirred at room temperature for 72 h under argon atmosphere. The reaction mixture was then poured into water (150 mL) and the precipitate was filtered off and washed with water to the white product. The compound **8** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.58 g (77%). Mp 121 °C. FT-IR [(KBr) ν_{max}/cm^{-1}]: 3040 (Ar–CH), 2880–2946 (CH), 2240 (C≡N), 1720 (C=O, lactone), 1480 (C=C), 1254 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$): δ, ppm: aromatic protons, 7.55 (d, 7.57 Hz, 4H), 7.51 (t, 2H), 7.35 (s, 2H), 7.26 (d, 8.06 Hz, 4H), 7.07 (d, 8.79, 2H), 7.01 (d, 2.20 Hz, 2H), 6.80 (dd, 8.79 Hz, 2.20 Hz, 2H), 2.00 (s, 6H, CH_3). *Anal.* Calc. for $C_{40}H_{24}N_2O_6$ (628.63): C, 76.42; H, 3.85; N, 4.46. Found: C, 75.90; H, 3.92; N, 4.38%. MS (MALDI-TOF) *m*/*z*: 628.98 [M]$^+$.

3.5.5. 1(4),8(11),15(18),22(25)-Tetrakis(3-methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalocyaninato indium(III) acetate (9, Scheme 1)

The compound **5** (0.5 g, 1.32 mmol), anhydrous indium(III)acetate (0.19 g, 0.65 mmol) and dried *N*,*N*-dimethylamino ethanol (2 mL) were refluxed with stirring under argon atmosphere for

24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid product was precipitated and collected by filtration and washed with several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and dried. The green product was purified by passing through a silica gel column using chloroform as the eluting solvent. The compound **9** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.17 g (31%). Mp > 300 °C. UV–Vis λ_{max} (nm) (log ε) (DMF): 320 (4.81), 632 (4.27), 705 (5.01). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3038 (Ar–H), 2923–2840 (CH), 1710 (C=O, lactone), 1607 (C=C), 1582 (C=C), 1274 (Ar–O–Ar). ^{1}H NMR (CDCl$_3$): δ, ppm: aromatic protons, at 8.01–6.92 (m, 44H), In-OCOCH_3 at 2.55 (s, 12H) and alkyl protons on the coumarin group at 2.51 (s, 3H). *Anal.* Calc. for $C_{98}H_{59}InN_8O_{14}$ (1687.38): C, 69.76; H, 3.52; N, 6.64. Found: C, 70.68; H, 3.57; N, 6.80%. MS (MALDI-TOF) *m*/*z*: 1627.46 [M-acetate]$^+$.

3.5.6. 2(3),9(10),16(17),23(24)-Tetrakis(3-methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalocyaninato indium(III) acetate (**10**, Scheme 1)

The compound **6** (0.5 g, 1.32 mmol), anhydrous indium(III)acetate (0.19 g, 0.65 mmol) and dried *N*,*N*-dimethylaminoethanol (2 mL) were refluxed with stirring under argon atmosphere for 24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid product was precipitated and collected by filtration and washed with several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and dried. The green product was purified by passing through a silica gel column using chloroform as the eluting solvent. The compound **10** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.16 g (29%). Mp >300 °C. UV–Vis λ_{max} (nm) (log ε) (DMF): 320 (4.52), 618 (3.98), 687 (4.68). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3059 (Ar–CH), 2922–2852 (CH), 1714 (C=O, lactone), 1656 (C=C), 1601(C=C), 1237 (Ar–O–Ar). ^{1}H NMR (CDCl$_3$): δ, ppm: aromatic protons, at 8.25–6.72 (m, 44H), In-OCOCH_3 (s, 3H) at 2.81 and alkyl protons on the coumarin group at 2.51 (s, 12H). *Anal.* Calc. for $C_{98}H_{59}InN_8O_{14}$ (1687.38): C, 69.76; H, 3.52; N, 6.64. Found: C, 70.67; H, 3.55; N, 6.79%. MS (MALDI-TOF) *m*/*z*: 1627.50 [M-acetate]$^+$.

3.5.7. Octakis{[2,9,16,23-(3-methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)3,10,17,24-chloro]}phthalocyaninato indium(III) acetate (**11**, Scheme 1)

The compound **7** (0.5 g, 1.21 mmol), anhydrous indium(III)acetate (0.19 g, 0.65 mmol) and dried *N*,*N*-dimethylaminoethanol (2 mL) were refluxed with stirring under argon atmosphere for 24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid product was precipitated and collected by filtration and washed several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and dried. The green product was purified by passing through a silica gel column, using chloroform as the eluting solvent. The compound **11** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.15 g (27%). Mp >300 °C. UV–Vis λ_{max} (nm) (log ε) (DMF): 317 (4.38), 615 (3.86), 677 (4.30). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3075 (Ar–CH), 2919–2850 (CH), 1717 (C=O, lactone), 1602 (C=C), 1433 (C=C), 1273 (Ar–O–Ar). ^{1}H NMR (CDCl$_3$): δ, ppm: aromatic protons, at 7.91–6.98 (m, 40H), In-OCOCH_3 at 2.60 (s, 3H) and alkyl protons at 2.54 (s, 12H). *Anal.* Calc. for $C_{98}H_{55}Cl_4InN_8O_{14}$ (1825.16): C, 64.49; H, 3.04; N, 6.29. Found: C, 65.13; H, 2.98; N, 6.43%. MS (MALDI-TOF) *m*/*z*: 1766.15 [M-acetate]$^+$.

3.5.8. 2,3,9,10,16,17,23,24-Octakis(3-methyl-2-oxo-4-phenyl-2H-chromen-7-yloxy)phthalocyaninato indium(III) acetate (**12**, Scheme 1)

The compound **8** (0.5 g, 0.79 mmol), anhydrous indium(III) acetate (0.19 g, 0.65 mmol) and dried *N*,*N*-dimethylaminoethanol (2 mL) were refluxed with stirring under argon atmosphere for 24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid product was precipitated and collected by filtration and washed several times with hot methanol, ethanol, ethyl acetate, acetonitrile, acetone, diethyl ether and dried. The green product was purified by passing through a silica gel column, using chloroform as the eluting solvent. The compound **12** is soluble in chloroform, dichloromethane, tetrahydrofurane, dimethylformamide and dimethylsulfoxide. Yield: 0.14 g (26%). Mp >300 °C. UV–Vis λ_{max} (nm) (log ε) (DMF): 317 (4.86), 620 (4.04), 683 (4.86). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3063 (Ar–CH), 2920–2851 (CH), 1713 (C=O, lactone), 1678–1600 (C=C), 1278 (Ar–O–Ar). ^{1}H NMR (CDCl$_3$): δ, ppm: aromatic protons, at 7.98–6.76 (m, 72H), In-OCOCH_3 at 2.59 (s, 24H) and alkyl protons on the coumarin group at 2.12 (s, 3H). *Anal.* Calc. for $C_{162}H_{99}InN_8O_{26}$ (2688.38): C, 73.09; H, 3.68; N, 4.26. Found: C, 72.95; H, 3.74; N, 4.41%. MS (MALDI-TOF) *m*/*z*: 2628.55 [M-acetate]$^+$.

4. Conclusions

In the presented work, the syntheses of new non-peripherally tetra-(**9**), peripherally tetra-(**10**), peripherally chloro octa-(**11**) and peripherally octa-(**12**) 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) phthalocyanine complexes were described and new compounds were characterized by standard methods (elemental analysis, ^{1}H NMR, MALDI-TOF, IR, UV–Vis and fluorescence spectral data). The photophysical and photochemical properties of these indium(III) Pc complexes were also described in DMF for comparison of the effects of the number of the substituents and their position on the phthalocyanine framework. All the studied indium(III) Pc complexes are soluble in general organic solvents (such as chloroform, dichloromethane, THF, DMF and DMSO). In solution, the absorption spectra of the studied indium(III) complexes showed monomeric behavior evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes in DMF. All indium(III) Pc complexes (**9**–**12**) showed similar fluorescence behavior in DMF. The excitation spectra of these complexes were similar to absorption spectra and both were mirror images of the fluorescent spectra. Although, the fluorescence quantum yield of the complexes **9**, **10** and **11** are typical for indium(III) Pc complexes, the fluorescence quantum yield of the chloro octa-substituted complex (**11**) is higher than indium(III) Pc complexes due to due to the heavy atom effect of the chlorine atom. The 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) Pc complexes (**9**–**12**) have good singlet oxygen quantum yields (Φ_Δ), especially non-peripherally tetra-substituted complex (**9**) results in the highest value. Heavy chlorine atom on the Pc ring decreased the Φ_Δ value for complex **11** in DMF. The value of Φ_Δ ranged from 0.30 to 0.83 gives an indication of the potential of the compounds as photosensitizers in applications where singlet oxygen is required such as Type II mechanism. The studied 7-oxy-3-methyl-4-phenylcoumarin-substituted indium(III) Pc complexes (**9**–**12**) show similar Φ_d values and stabilities to the indium(III) Pc complexes applicable in PDT.

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