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Novel phthalocyanines bearing 7-oxy-3-(3,5-difluorophenyl)coumarin moieties: Synthesis, characterization, photophysical and photochemical properties

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Two novel phthalonitriles,7-(2,3-dicyanophenoxy)-3-(3,5-difluorophenyl) coumarin (**2**), 7-(3,4-dicyanophenoxy)-3-(3,5-difluorophenyl) coumarin (**3**), and corresponding zinc(II)-, indium(III) phthalocyanines were prepared. Additionally, photophysical (fluorescence quantum yields and lifetimes), photochemical (singlet oxygen generation and photodegradation under light irradiation) and spectral properties of the resulting peripherally/non-peripherally tetra 7-oxy-3-(3,5-difluorophenyl) coumarin substituted zinc (II) and indium (III) phthalocyanines (**4**–**7**) were investigated. All compounds (**1**–**7**) were characterized by elemental analysis, IR, ^{1}H NMR, mass and UV–vis spectral data. The obtained 7-oxy-3-(3,5-difluorophenyl) coumarin bearing pure zinc (II) and indium (III) phthalocyanine complexes were well soluble in organic solvents and displayed good singlet-oxygen generation and appropriate photodegradation.

1. Introduction

Phthalocyanines (Pcs) are azaporphyrin derivatives and have been extensively studied to examine structure–activity relationships and to improve upon some of the unique characteristics of the tetrapyrrolic chromophore [1–3]. Pcs play an important role in research of high technological materials such as solar cells [4], semiconductors [5], optical data storage devices [6], gas sensors [7], photosensitizers in photodynamic therapy (PDT) [8], liquid crystals [9], non-linear optics [10], electrochromic displaying systems [11] and molecular electronics [12]. Pcs have been proposed as the second-generation photosensitizers because of their versatile advantages such as intense absorption in the red visible region, high efficiency to generate singlet oxygen, ease of chemical modification, and low dark toxicity [13,14]. The PDT properties of the Pc dyes are strongly influenced by the presence and nature of the central metal ion. Complex structure of Pc with transition metals gives short triplet lifetimes to these dyes. Closed shell and diamagnetic ions, such as Zn^{2+}, In^{3+}, Ga^{3+} and Si^{4+} give Pc complexes both high triplet yields and long lifetimes [13]. The photophysics and photochemistry of zinc (II) and indium (III) Pc complexes are well documented [14–18]. Porphyrinoids (porphyrin, phthalocyanine, chlorin and corrole) containing fluorine have been researched for the last 20 years and have appeared to be attractive molecules for applications in PDT. The presence of fluorine in the structure of a photosensitizer may enrich the solubility and pharmacokinetic features [19–21].

The benzo derivatives of pyrone are known as coumarin or 2H-1-benzopyran-2-one. Coumarins are an important class of oxygen heterocyclics [22–25]. Coumarin derivatives exhibit unique photochemical and photophysical properties, which render them usefulness in a variety of applications such as optical brighteners, laser dyes, non-linear optical chromophores, solar energy collectors, fluorescent labels and probes in biology and medicine [26–30].

Skillful combination of fluorine substituents with other functional groups in their structures, including coumarins led to novel molecules possessing outstanding phototoxicity in both in vitro and in vivo studies. Pcs constitute the largest group within fluorinated porphyrinoids of potential anticancer and antimicrobial properties [19–21].

In our previous studies, demonstrated that the introduction of coumarin derivatives into the peripheral/nonperipheral ring of phthalocyanines increases the photochemical and photophysical properties of phthalocyanines [31–33]. Fluorinated Pcs show improved photosensitizer activity for PDT when compared to

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non-fluorinated derivatives [34–36]. Therefore in this paper; we have, in particular, combined these two functional materials into a single compound and this time coumarin is substituted with fluorine atom in the skeleton. We report here in this paper synthesis, characterization, photophysical and photochemical properties of novel peripheral and non-peripheral tetra 7-oxy-3-(3,5-difluorophenyl) coumarin substituted zinc (II) Pcs (**4** and **6**) and indium (III) Pcs (**5** and **7**) as potential PDT agents.

2. Experimental

2.1. Materials and equipment

Unsubstituted zinc (II) phthalocyanine (ZnPc), 1,3-diphenylisobenzofuran (DPBF), Triton X-100, zinc(II) acetate [$Zn(OAc)_2$], indium (III) chloride ($InCl_3$), potassium carbonate (K_2CO_3), sodium acetate (NaOAc), 2,4-dihydroxybenzaldehyde and 3,5-difluorophenylacetic acid were purchased from Aldrich. All solvents were dried as described by Perrin and Armarego before use [37]. 7-Hydroxy-3-(3,5-difluorophenyl) coumarin (**1**), 7-(2,3-dicyanophenoxy)-3-(3,5-difluorophenyl) coumarin (**2**) and 7-(3,4-dicyanophenoxy)-3-(3,5-difluorophenyl) coumarin (**3**) were synthesized and purified according to the literature procedures [38].

Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV-2450 UV–visible Spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ^1H NMR spectra were recorded on a Varian Unity Inova 500 MHz NMR Spectrometer. Mass spectra were performed on a Bruker Microflex LT MALDI-TOF Spectrophotometer. Photo-irradiations were performed using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Intor) 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.

The photophysical and photochemical parameters were supplied as Supplementary information.

2.2. Synthesis

*2.2.1. 7-Hydroxy-3-(3,5-difluorophenyl) coumarin (**1**)*

A mixture of 2,4-dihydroxybenzaldehyde (2 g, 14.5 mmol), 3,5-difluorophenylacetic acid (2.49 g, 14.5 mmol), anhydrous NaOAc (1.78 g, 21.75 mmol) and 15 mL acetic anhydride was heated with stirring at 160 °C under nitrogen for 8 h. After removal of acetic acid by distillation, the resulting mixture was treated with 10% HCl/methanol, and the precipitates were collected by filtration. The dried product was purified by recrystallization from methanol.

Yield: 2.158 g (54.36%), mp: 275 °C. IR (KBr tablet); ν_{max}/cm^{-1}: 3153 (—OH), 3040–3080 (Ar C—H), 1699 (lactone, C═O), 1600 (C═C), 1591–1465 (Ar C═C) and 1120 (Ar C—F). ^1H NMR (DMSO-d_6), (δ:ppm): 7.18 (dd, 1H, J = 8 and 2 Hz, Ar—H), 7.28 (t, 1H, J = 6 Hz, Ar—H), 7.32 (d, 1H, J = 2 Hz, Ar—H), 7.48 (dd, 2H, J = 8 and 2 Hz, Ar—H), 7.83 (d, 1H, J = 8 Hz, Ar—H), 8.35 (s, 1H, coumarin 4-H), 9.32 (bs, 1H, —OH). MS (MALDI-TOF), (m/z): 274.04 $[M]^+$, 275.08 $[M+H]^+$, 276.11 $[M+2H]^+$. $C_{15}H_8F_2O_3$: calcd. C, 65.64; H, 2.92; F, 13.86%; found: C, 65.67; H, 2.89; F, 13.83.

*2.2.2. 7-(2,3-Dicyanophenoxy-) 3-(3,5-difluorophenyl) coumarin (**2**)*

7-Hydroxy-3-(3,5-difluorophenyl) coumarin (**1**) (1 g, 3.66 mmol) and 3-nitrophthalonitrile (0.63 g, 3.66 mmol) were dissolved in dry dimethylformamide (DMF) (25 mL) under nitrogen and anhyd. K_2CO_3 (0.76 g, 5.49 mmol) was added after stirring for 5 days at 50–60 °C, the reaction mixture was treated with diluted HCl under ice cooling. The crude product was filtered, washed with water and dried. The product was purified by silica gel column chromatography using $CHCl_3$ as eluent.

Yield: 0.812 g (55%), mp: 268 °C. IR (KBr tablet); ν_{max}/cm^{-1}: 3042–3084 (Ar C—H), 2231 (Ar—CN), 1699 (lactone, C═O), 1606 (C = C), 1586–1460 (Ar C═C), 1271 (Ar C—O) and 1122 (Ar C—F) cm^{-1}. ^1H NMR (DMSO-d_6), (δ:ppm): 7.26 (dd, 1H, J = 8 and 2 Hz, Ar—H), 7.31 (t, 1H, J = 6 Hz, Ar—H), 7.38 (d, 1H, J = 2 Hz, Ar—H), 7.50 (dd, 2H, J = 8 and 2 Hz, Ar—H), 7.53 (dd, 1H, J = 8 and 2 Hz, Ar—H), 7.86 (dd, 1H, J = 8 and 2 Hz, Ar—H), 7.90 (d, 1H, J = 8 Hz, Ar—H), 7.96 (dd, 1H, J = 8 and 2 Hz, Ar—H), 8.46 (s, 1H, coumarin 4-H). MS (MALDI-TOF), (m/z): 400.07 $[M]^+$, 401.13 $[M+H]^+$, 402.06 $[M+2H]^+$. $C_{23}H_{10}F_2N_2O_3$: calcd. C, 68.94; H, 2.50; F, 9.49; N, 7.00%; found: C, 68.95; H, 2.46; F, 9.45; N, 7.02.

*2.2.3. 7-(3,4-Dicyanophenoxy)-3-(3,5-difluorophenyl) coumarin (**3**)*

Compound **3** was prepared and purified according to the procedure described for **2**, starting from compound **1** (1 g, 3.66 mmol), 4-nitrophthalonitrile (0.63 g, 3.66 mmol) and anhydrous K_2CO_3 (0.76 g, 5.49 mmol).

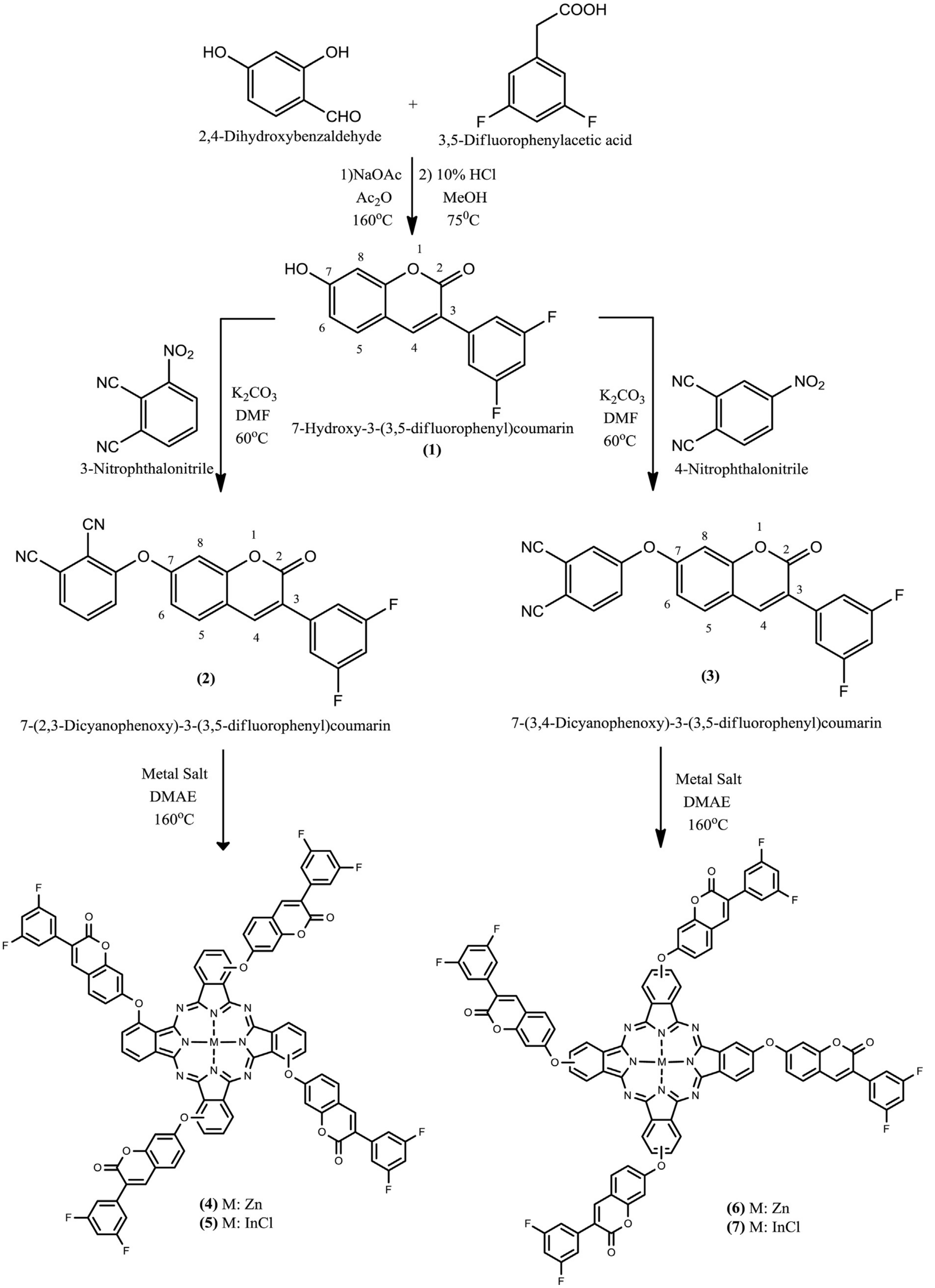
Yield: 0.925 g (62.90%), mp: 273 °C. IR (KBr tablet); ν_{max}/cm^{-1}: 3047–3084 (Ar C—H), 2230 (Ar—CN), 1699 (lactone, C═O), 1603 (C═C), 1576–1454 (Ar C═C), 1255 (Ar C—O) and 1120 (Ar C—F) cm^{-1}. ^1H NMR (DMSO-d_6), (δ:ppm): 7.22 (dd, 1H, J = 8 and 2 Hz, Ar—H), 7.31 (t, 1H, J = 6 Hz, Ar—H), 7.35 (d, 1H, J = 2 Hz, Ar—H), 7.51 (dd, 2H, J = 8 and 2 Hz, Ar—H), 7.59 (dd, 1H, J = 8 and 2 Hz, Ar—H), 7.86 (d, 1H, J = 8 Hz, Ar—H), 7.96 (d, 1H, J = 2 Hz, Ar—H), 8.17 (d, 1H, J = 8 Hz, Ar—H), 8.48 (s, 1H, coumarin 4-H). MS (MALDI-TOF), (m/z): 400.03 $[M]^+$, 401.10 $[M+H]^+$, 402.07 $[M+2H]^+$. $C_{23}H_{10}F_2N_2O_3$: calcd. C, 68.94; H, 2.50; F, 9.49; N, 7.00%; found: C, 68.96; H, 2.43; F, 9.44; N, 7.04.

*2.2.4. General procedures for non-peripheral zinc (II) phthalocyanine (**4**) and indium (III) chloride phthalocyanine (**5**)*

A mixture of compound 2 (0.15 g, 0.375 mmol) and metal salt [$Zn(OAc)_2$ (0.017 g, 0.095 mmol), $InCl_3$ (0.021 g, 0.095 mmol)] was heated at 170 °C with 4 mL dry 2-dimethylaminoethanol (DMAE) in a sealed glass tube, and stirred for 24 h under a N_2 atmosphere. After cooling to room temperature, the green solution treated with methanol (5 mL) and the product was filtered off and washed with water, methanol and ethanol.

2.2.4.1. 1,8,15,22-Tetrakis[3-(3,5-difluorophenyl)-7-oxycoumarino] phthalocyaninato zinc (II) (4). Yield: 0.066 g (42.31%), mp > 300 °C. IR (KBr tablet); ν_{max}/cm^{-1}: 3060–3075 (Ar C—H), 1724 (lactone, C═O), 1602 (C═C), 1508–1464 (Ar C═C), 1239 (Ar C—O) and 1120 (Ar C—F) cm^{-1}. ^1H NMR (DMSO-d_6), (δ:ppm): 6.99–8.44 (m, 40H, Ar—H). MS (MALDI-TOF), (m/z): 1665.20 $[M]^+$, 1664.19 $[M–H]^+$. UV/Vis (DMF) λ_{max}/nm (log ε): 690 (5.19), 621 (shoulder, 4.15), 340 (4.15). $C_{92}H_{40}F_8N_8O_{12}Zn$: calcd. C, 66.28; H, 2.40; F, 9.12; N, 6.72; found: C, 66.32; H, 2.40; F, 9.11; N, 6.78.

2.2.4.2. 1,8,15,22-Tetrakis[3-(3,5 difluorophenyl)-7-oxycoumarino] phthalocyaninato indium(III) chloride (5). Yield: 0.062 g (37.81%), mp > 300 °C. IR (KBr tablet); ν_{max}/cm^{-1}: 3055–3075 (Ar C—H), 1724 (lactone, C═O), 1603 (C═C), 1505–1479 (Ar C═C), 1239 (Ar C—O) and 1120 (Ar C—F) cm^{-1}. ^1H NMR (DMSO-d_6), (δ:ppm): 7.03–8.43 (m, 40H, Ar—H). MS (MALDI-TOF), (m/z): 1750.05 $[M]^+$, 1714.55 $[M–Cl]^+$. UV/Vis (DMF) λ_{max}/nm (log ε): 706 (5.25) 635 (shoulder, 4.25), 340 (4.15). $C_{92}H_{40}F_8N_8O_{12}InCl$: calcd. C, 63.06; H, 2.28; F, 8.68; N, 6.40; found: C, 63.10; H, 2.28; F, 8.65; N, 6.48.



Scheme 1. Synthesis of new phthalonitriles (**2** and **3**), zinc (II) Pcs (**4** and **6**) and indium (III) Pcs (**5** and **7**) substituted with 7-oxy-3-(3,5-difluorophenyl) coumarin.

*2.2.5. General procedures for peripheral zinc (II) phthalocyanine (**6**) and indium (III) chloride phthalocyanine (**7**)*

A mixture of compound 3 (0.15 g, 0.375 mmol) and metal salt [Zn(OAc)$_2$ (0.017 g, 0.095 mmol), InCl$_3$ (0.021 g, 0.095 mmol)] was heated at 170 °C with 4 mL dry DMAE in a sealed glass tube, and stirred for 24 h under a N$_2$ atmosphere. After cooling to room temperature, the green solution treated with methanol (5 mL) and the product was filtered off and washed with water, methanol and ethanol.

2.2.5.1. 2,9,16,23-Tetrakis[3-(3,5-difluorophenyl)-7-oxycoumarino] phthalocyaninato zinc (II) (6). Yield: 0.060 g (38.46%), mp > 300 °C. IR (KBr tablet); ν_{max}/cm^{-1}: 3050–3066 (Ar C—H), 1721 (lactone, C=O), 1606 (C=C), 1507–1458 (Ar C=C), 1237 (Ar C—O) and 1122 (Ar C—F) cm^{-1}. ^{1}H NMR (DMSO-d$_6$), (δ:ppm): 7.00–8.34 (m, 40H, Ar—H); MS (MALDI-TOF): *m*/*z*: 1665.12 [M]$^+$. UV/Vis (DMF) λ_{max}/nm (log ε): 678 (5.18), 608 (shoulder, 4.18), 350 (4.22). $C_{92}H_{40}F_8N_8O_{12}Zn$: calcd. C, 66.28; H, 2.40; F, 9.12; N, 6.72; found: C, 66.33; H, 2.41; F, 9.10; N, 6.80.

2.2.5.2. 2,9,16,23-Tetrakis[3-(3,5-difluorophenyl)-7-oxycoumarino] phthalocyaninato indium(III) chloride (7). Yield: 0.064 g (39.02%), mp > 300 °C. IR (KBr tablet); ν_{max}/cm^{-1}: 3061–3084 (Ar C—H), 1722 (lactone, C=O), 1605 (C=C), 1508–1452 (Ar C=C), 1238 (Ar C—O) and 1121 (Ar C—F). ^{1}H NMR (DMSO-d$_6$), (δ:ppm): 7.10–8.40 (m, 40H, Ar—H). MS (MALDI-TOF), (*m*/*z*): 1750.14 [M]$^+$, 1714.64 [M–Cl]$^+$. UV/Vis (DMF) λ_{max}/nm (log ε): 688 (5.19) 621 (shoulder, 4.27), 350 (4.23). $C_{92}H_{40}F_8N_8O_{12}InCl$: calcd. C, 63.06; H, 2.28; F, 8.68; N, 6.40; found: C, 63.11; H, 2.29; F, 8.68; N, 6.41.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows the synthetic route for the target phthalonitriles (**2** and **3**) and peripheral and non-peripheral tetra 7-oxy-3-(3,5-difluorophenyl) coumarin substituted zinc (II) Pcs (**4** and **6**) and indium (III) Pcs (**5** and **7**) derivatives. 7-Hydroxy-3-(3,5-difluorophenyl) coumarin (**1**) was prepared by the Perkin condensation of 2,4-dihydroxybenzaldehyde with 3,5-difluorophenylacetic acid. The phthalonitrile precursors (**2** and **3**) were prepared from the aromatic nucleophilic substitution reaction between 3-nitrophthalonitrile (for **2**) or 4-nitrophthalonitrile (for **3**) with 7-hydroxy-3-(3,5-difluorophenyl) coumarin (**1**). The synthesis of Zn (II) and In (III) Pcs (**4–7**) was achieved by metal-ion mediated cyclotetramerization reaction of the corresponding precursors (**2** or **3**) in dry dimethylaminoethanol (DMAE) using anhydrous Zn(OAc)$_2$ or InCl$_3$. Synthesized Pcs with fluorinated coumarins (**4–7**) have good solubility in organic solvents such as acetone, tetrahydrofuran (THF), DMF and dimethylsulfoxide (Me$_2$SO). The various characterization techniques such as UV–Vis IR, ^{1}H NMR, MS spectroscopic data and elemental analysis gave results consistent with the proposed structures for all the prepared complexes along with their satisfactory purities.

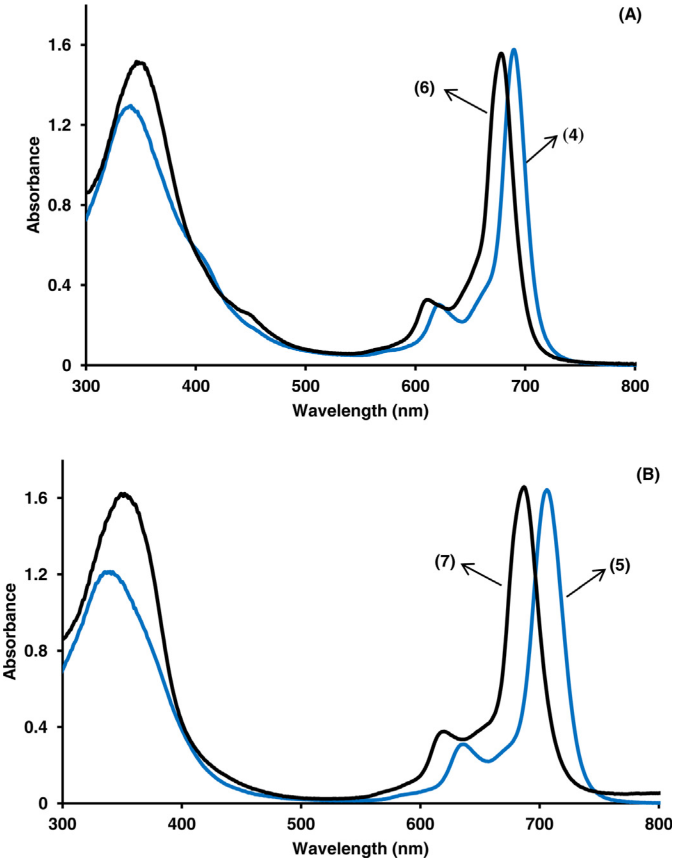


Fig. 1. Absorption spectra of: (A) non-peripheral and peripheral substituted Zn (II) Pc complexes (**4** and **6**) and (B) non-peripheral and peripheral substituted In (III) Pc complexes (**5** and **7**) in DMF. Concentration = 1.0 × 10^{-5} M.

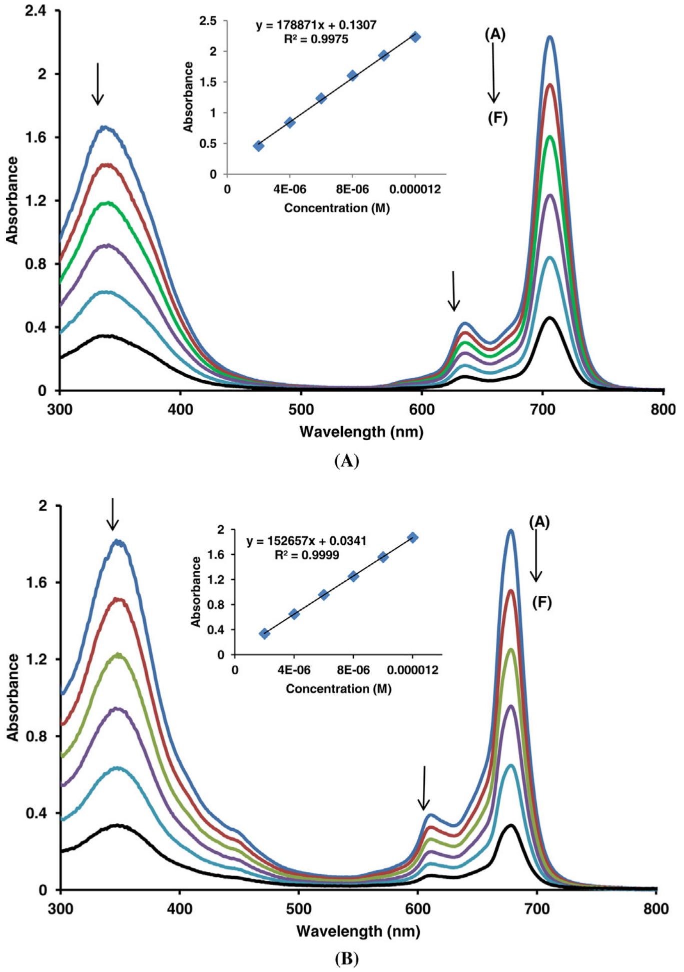
The IR spectrum of 7-hydroxy-3-(3,5-difluorophenyl) coumarin (**1**) exhibits the characteristic frequencies at 3153 (—OH), 3080–3040 (Ar C—H), 1699 (C=O, lactone), 1600 (C=C), 1591–1465 (Ar C=C) and 1120 (Ar C—F) cm^{-1}. Comparison of the IR spectral data clearly indicated the formation of phthalonitriles (**2** and **3**) by the disappearance of the —OH band of **1** and appearance intense absorption band at 2231 (for **2**) and 2230 (for **3**) cm^{-1} corresponding to the C≡N stretching. In the ^{1}H NMR analysis of coumarin (**1**) and phthalonitriles (**2** and **3**) in DMSO-d$_6$, the proton of coumarin lactone ring at the 4- position appeared as singlet at 8.35, 8.46 and 8.48 ppm, respectively. The ^{1}H NMR spectrum of **1**, the —OH proton appeared at 9.32 ppm as broad singlet. The mass spectrum of **1** which showed molecular ion peak at *m*/*z* = 274.04 [M]$^+$ supports the proposed formula for this compound. The mass spectra of phthalonitriles which showed

Table 1
Absorption, excitation and emission spectral data for non-peripherally and peripherally substituted Pcs in DMF.

Compound	Q band λ_{max}, (nm)	log ε	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift $\Delta_{Stokes,}$ (nm)
4	690	5.14	690	713	23
5	706	5.25	709	723	17
6	678	5.18	678	700	22
7	688	5.19	691	712	24
InPc[a]	686	4.46	689	700	14
ZnPc[b]	670	5.37	670	676	6

[a] Data from Ref. [45]

[b] Data from Ref. [46]



(A)

(B)

Fig. 2. Aggregation behaviour of: (A) non-peripheral substituted In (III) Pc complex **5** and (B) peripheral substituted Zn (II) Pc complex **6** in DMF at different concentrations: 1.2×10^{-5} M (A), 1.0×10^{-5} M (B), 0.8×10^{-5} M (C), 0.6×10^{-5} M (D), 0.4×10^{-5} M (E), 0.2×10^{-5} M (F), (Inset: Plot of absorbance versus concentration).

molecular ion peaks at $m/z = 400.07$ $[M]^+$ for **2** and $m/z = 400.03$ $[M]^+$ for **3** supports the proposed formula for these compounds.

The corresponding vibrations for the C=N groups in the IR spectra of phthalonitriles **2** and **3** disappeared after conversion into Zn (II) and In (III) Pcs (**4–7**). In the IR spectra of all Pcs weak bands observed at 3084–3050 cm^{-1} are due to aromatic C—H stretchings. The characteristic carbonyl vibrations of coumarin lactone ring and aromatic C–F vibrations were observed at around 1721 cm^{-1} and 1120 cm^{-1}, respectively.

The ^{1}H NMR spectra of Pcs (**4–7**) are almost identical to that of the starting compounds (**2** and **3**) except for broadening due to chemical exchange caused by an aggregation–disaggregation equilibrium in DMSO-d$_6$ and the presence of a mixture of four positional isomers with chemical shifts which differ slightly from each other. In the ^{1}H NMR spectra of Pc complexes, the aromatic and Pc protons (integrating for 40H) were appeared at between 6.99 and 8.44 ppm (for **4**), 7.03 and 8.43 ppm (for **5**), 7.00 and 8.34 ppm (for **6**) and 7.10 and 8.40 ppm (for **7**). In the mass spectra of Pc complexes, the presence of molecular ion peaks at $m/z = 1665.20$ $[M]^+$ for **4**, $m/z = 1750.05$ $[M]^+$ for **5**, $m/z = 1665.12$ $[M]^+$ for **6** and $m/z = 1750.14$ $[M]^+$ for **7**, confirmed the proposed structures. Elemental analysis results are in good agreement with the assigned structures.

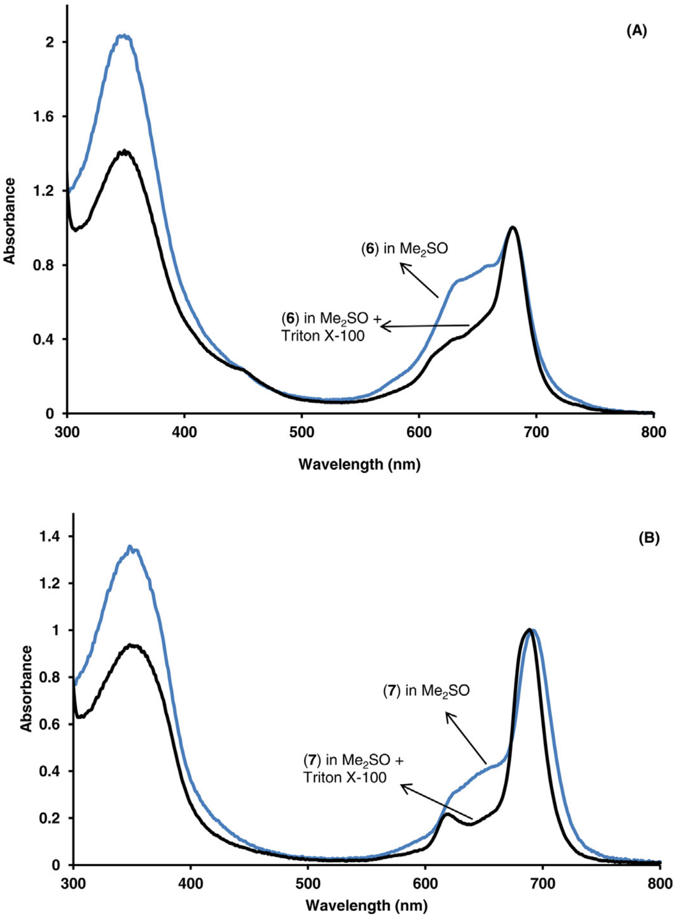


Fig. 3. Absorption spectra of: (A) peripheral substituted Zn (II) Pc complex **6** and (B) peripheral substituted In (III) Pc complex **7** in Me$_2$SO and Me$_2$SO + Triton X-100 solutions. Concentration = 1.0×10^{-5} M.

3.2. Electronic absorption spectra

The electronic absorption spectra of synthesized Pc complexes in DMF are shown in Table 1. The Q-band absorptions are observed as a single (narrow) band at 690 (**4**), 706 (**5**), 678 (**6**) and 688 nm (**7**) (Fig. 1).

Red-shifts were observed for studied Pc complexes (**4–7**) following coumarin substitution compared to unsubstituted Zn (II) and In (III) Pcs. Also non-peripheral substitution greatly influences the energy levels of molecular orbitals and hence the absorption spectrum, whereas peripheral substitution has a smaller effect on the Q-band position [39,40]. The Q bands of the non-peripheral substituted complexes are red shifted when compared to the corresponding peripheral substituted complexes (Fig. 1). The red shifts are 12 nm between **4** and **6**, 18 nm between **5** and **7**. The B (Soret) bands of these complexes exist at 334 nm for **4**, 332 nm for **5**, 343 nm for **6** and 345 nm for **7**.

In this study, the aggregation properties of the Pc complexes were investigated in DMF and DMSO at different concentrations. For investigation of the aggregation behaviors, the UV–Vis spectra of Pc complexes (**4–7**) were measured between 1.2×10^{-5} and 0.2×10^{-5} M in DMF (Fig. 2 for complexes **5** and **6**). All the Pc complexes showed monomeric behavior between defined concentrations and Beer–Lambert law was obeyed. Fig. 2 shows that the complexes are not significantly aggregated within this concentration range in DMF. DMF was preferred as the solvent for studies of photophysical and photochemical properties of

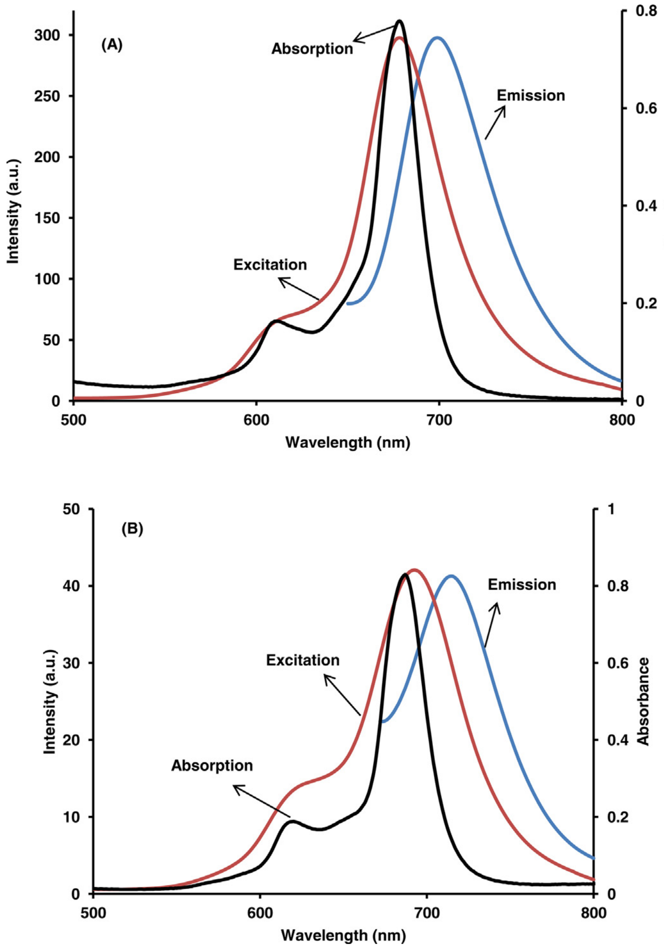


Fig. 4. Absorption, excitation and emission spectra of: (A) peripheral substituted Zn (II) Pc complex **6** and (B) peripheral substituted In (III) Pc complex **7** in DMF. Excitation wavelengths: 640 nm for **6** and **7**. Concentration = 2.0×10^{-6} M.

studied Pc complexes due to the non-aggregated solutions were observed in this solvent. The peripheral substituted Pc complexes (**6** and **7**) showed a little aggregation in Me_2SO (Fig. 3). Non-peripheral substituted Pcs are known to show less aggregation than peripheral substituted ones [41]. Addition of Triton X-100 (0.1 mL) to solutions of Pc complexes (**6** and **7**) in Me_2SO (concentrations: 1.0×10^{-5} M, a solvent in which they are aggregated), resulted considerable increase in intensity of the low energy side of the Q band (Fig. 3), suggesting that the molecules were aggregated and the addition of Triton X-100 breaked up the aggregates between the Pc molecules.

Table 2
Photophysical, photochemical parameters and fluorescence quenching data for non-peripherally and peripherally substituted Pcs in DMF.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	k_F[a] (s^{-1}) ($x10^7$)	Φ_d ($x10^{-5}$)	Φ_Δ	K_{SV}^{BQ} (M^{-1})	$K_q^{BQ}/10^{10}$ ($M^{-1}\,s^{-1}$)
4	0.05	0.50	10.56	9.48	2.79	0.83	24.04	4.85
5	0.004	0.04	8.49	1.18	3.52	0.71	–	–
6	0.05	0.38	10.23	12.15	2.32	0.56	26.66	5.41
7	0.002	0.02	9.05	1.04	3.62	0.87	–	–
InPc[b]	0.018	0.90	50.20	1.90	3.43	0.61	–	–
ZnPc[c]	0.17	1.03	6.05	16.53	2.30	0.56	57.60	5.59

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$
[b] Data from Ref. [45]
[c] Data from Ref. [46]

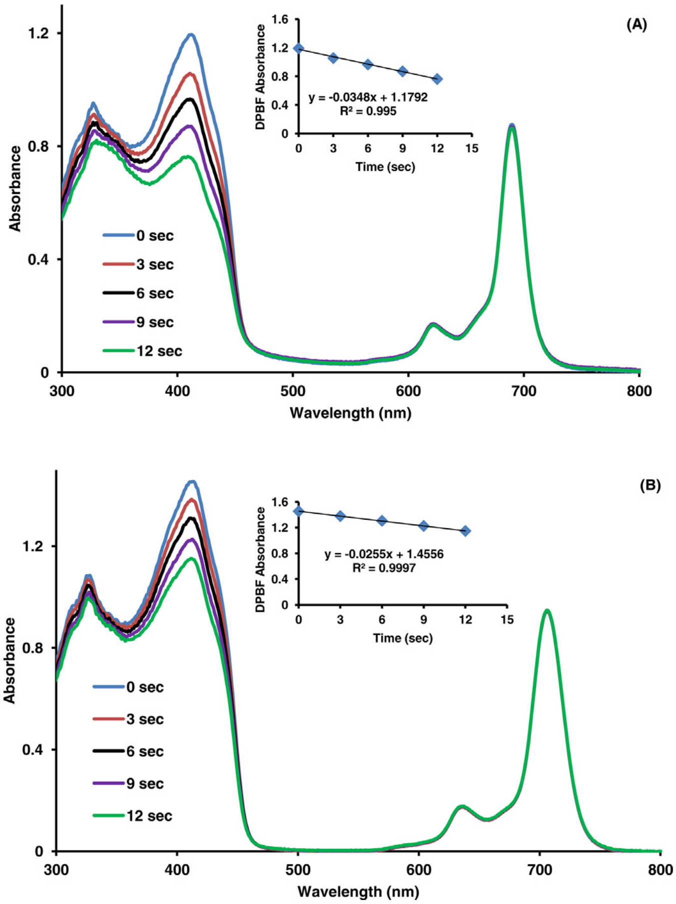


Fig. 5. A typical spectra for the determination of singlet oxygen quantum yield of (A) non-peripheral substituted Zn (II) Pc complex **4** and (B) non-peripheral substituted In (III) Pc complex **5** in in DMF using DPBF as a singlet oxygen quencher. Concentration = 1.0×10^{-5} M. (Inset: plots of DPBF absorbance versus time).

3.3. Fluorescence spectra, fluorescence quantum yields and lifetimes

Fluorescence behaviors of the Pc complexes were investigated in DMF at room temperature (Fig. 4 as examples **6** and **7**). The fluorescence excitation and emission maximum bands and Stokes shift values are given in Table 1. Fluorescence emission peaks were observed at 713 nm for **4**, 723 nm for **5**, 700 nm for **6** and 712 nm for **7** (Table 1). As seen in Fig. 4, the excitation spectra were similar to absorption spectra in the complexes. The fluorescence spectra were mirror images of the excitation spectra for complexes **4**–**7**. ZnPc complexes (**4** and **6**) showed strong fluorescence signal after excitation with a shape of the fluorescence emission spectra while the studied InPc complexes (**5** and **7**) showed low fluorescence emission. As seen from the Table 1, the 7-oxy-3-(3,5-difluorophenyl) coumarin substituted zinc (II) and indium (III) Pcs exhibit a spectral shift in emission wavelength than those of the unsubstituted ZnPc or InPc. This shows that there is an effect of the coumarin substituents on the fluorescence emission from the excited state of the Pc core.

The fluorescence quantum yield (Φ_F) is the fraction of molecules in the excited state that do return to ground state via fluorescence. The fluorescence quantum yields (Φ_F) are given in Table 2. The fluorescence quantum yields (Φ_F) values of Pc complexes **4**–**7** are 0.05, 0.004, 0.05 and 0.002, respectively. The Φ_F values of all studied Pc complexes are lower than unsubstituted ZnPc ($\Phi_F = 0.17$) and InPc ($\Phi_F = 0.018$) in DMF. Moreover, these values are lower than previous works made with similar Pc lacking a fluorine atom. According to literature, electronegative atoms

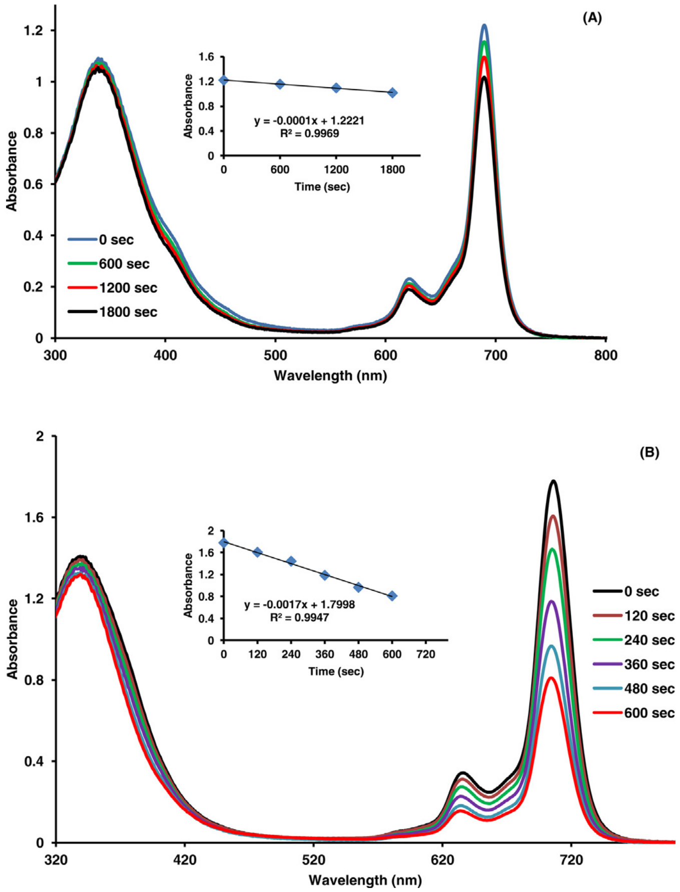


Fig. 6. The photodegradation of (A) non-peripheral substituted Zn (II) Pc complex **4** and (B) non-peripheral substituted In (III) Pc complex **5** in DMF showing the disappearance of the Q band. Concentration = 1.0 × 10^{-5} M. (Inset: plot of Q band absorbance versus time).

such as fluorine on the benzene ring (Pc) increase intensity (hence fluorescence quantum yield) [42]. For InPc complexes, this is due to intersystem crossing enhanced by the presence of the heavy atom indium [40]. This situation may occur in the presence of electron withdrawing fluoro atoms which increase the fluorescence quenching for ZnPc complexes [43]. The Φ_F values of the InPc complexes (**5** and **7**) are lower than those of the analogues ZnPc complexes (**4** and **6**).

Fluorescence lifetime (τ_F) is the average time a molecule stays in its excited state before fluorescence, and this value is directly related to that of fluorescence quantum yield (Φ_F). Lifetimes of fluorescence (τ_F) were calculated using the Strickler-Berg formula. The fluorescence lifetime (τ_F), the natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values of Pc complexes are also investigated in DMF (Table 2). The τ_F, τ_0 and k_F values of the ZnPcs are higher compared to those of InPcs. Once again, this is due to the heavy atom effect [44].

3.4. Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) were determined using decomposition of its chemical scavenger 1,3-diphenylisobenzofuran (DPBF) in DMF. Singlet oxygen is considered as the main phototoxic species in PDT and that is why a rate of its production belongs among the important parameters of all new photosensitizers. The disappearance of DPBF was monitored using UV–vis spectral changes. We did not observed any changes in the Q band intensities of complexes during the Φ_Δ determination, confirming that complexes are not degraded during singlet oxygen studies (Fig. 5 as examples for **4** and **5**).

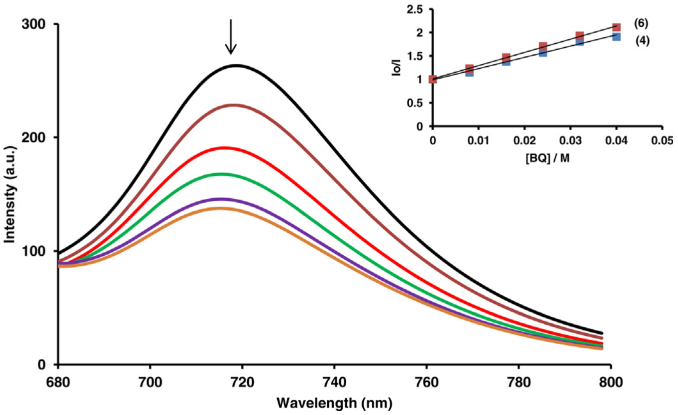


Fig. 7. Fluorescence emission spectral changes of **4** (1.0 × 10^{-5} M) on addition of different concentrations of BQ in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M. (Inset: Stern–Volmer plots for BQ quenching of **4** and **6**).

The values of Φ_Δ were higher for Pc complexes (Φ_Δ = 0.83 for **4**, Φ_Δ = 0.71 for **5**, (Φ_Δ = 0.56 for **6** and Φ_Δ = 0.87 for **7**) when compared to respective unsubstituted ZnPc (Φ_Δ = 0.56) or InPc (Φ_Δ = 0.61) complexes. Insertion of coumarin moieties substituted with fluorine atoms on the Pc rings increases the efficiency of singlet oxygen creation for Pc complexes. All Pc complexes gave good singlet oxygen quantum yields (Φ_Δ) which are indicating the potential of the complexes as photosensitizers in applications of PDT.

3.5. Photodegradation studies

Photodegradation or photobleaching (Φ_d) is used to determine the photostability of MPc molecules and is identified by a decrease in the intensity of the absorption spectra without the appearance of new peaks. The photobleaching stabilities of studied Pc complexes were evaluated in DMF.

All the studied Pc complexes (**4**–**7**) were less stable to degradation compared to unsubstituted ZnPc or InPc because the Φ_d values of all studied Pc complexes were higher than ZnPc or InPc in DMF (Table 2). The spectral changes observed for the Pc complexes during irradiation are as shown in Fig. 6 (using complexes **4** and **5** as examples in DMF). All the complexes showed same stability as compared to ZnPc and InPc [17] with Φ_d of the order of 10^{-5}. Stable ZnPc molecules show values as low as 10^{-6} and for unstable molecules, values of the order 10^{-3} have been reported [17]. The Φ_d values of the 7-oxy-3-(3,5-difluorophenyl) coumarin substituted indium(III) Pc complexes (**5** and **7**) are also higher than zinc(II) Pc complexes (**4** and **6**) in DMF. It seems indium(III) metal and 7-oxy-3-(3,5-difluorophenyl) coumarin groups increase the Φ_d values and decreases the stability of complexes. The difference in the behaviors of indium(III) Pc complexes (**5** and **7**) on degradation could be due to the larger In metal being more displaced from the core of the Pc ring, and the displacement being more pronounced on degradation, hence causing a loss of symmetry [44]. Φ_d of studied Pc complexes show good stability under the light applied.

3.6. Fluorescence quenching studies by benzoquinone (BQ)

Quenching of the ZnPc complexes (**4** and **6**) excited states by BQ was investigated. The InPc complexes behaviour was not studied because of the very low fluorescence emission. Fig. 7 shows the quenching of non-peripherally tetra-substituted zinc(II) Pc complex (**4**) by BQ in DMF solution. The fluorescence quenching of this complex was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. The slope of the plot shown at inset of Fig. 7 gave Stern–Volmer constant (K_{SV}) values of the peripherally and non-peripherally ZnPc complexes. The K_{SV} values of the studied ZnPc complexes were lower than unsubstituted ZnPc. The substitution with coumarin seems to decrease the K_{SV} values of the complexes in DMF. The bimolecular quenching constant (k_q) values of the substituted ZnPc complexes (**4** and **6**) were also lower than for unsubstituted ZnPc.

4. Conclusion

This work described synthesis, characterization, spectral, photophysical and photochemical properties of novel 7-oxy-3-(3,5-difluorophenyl) coumarin substituted non-peripheral/peripheral zinc (II) and indium (III) phthalocyanine complexes. The singlet oxygen quantum yields (Φ_Δ), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.56 to 0.87. In addition, their photodegradation parameters are suitable for potential photodynamic therapy agents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2014.12.005.

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