Peripheral and non-peripheral tetrasubstituted aluminium, gallium and indium phthalocyanines: Synthesis, photophysics and photochemistry

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ABSTRACT

The synthesis, photophysical and photochemical properties of soluble triethyleneoxythia substituted aluminium, gallium and indium phthalocyanines (**6a**–**c** and **7a**–**c**) are reported for the first time. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H NMR spectroscopy, electronic spectroscopy and mass spectra. General trends are described for quantum yields of photodegradation, fluorescence and fluorescence lifetimes as well as singlet oxygen quantum yields of these compounds. The effects of the position of the substituents and the nature of the metal ion on the photophysical and photochemical parameters of the Al(III), Ga(III) and In(III) phthalocyanines (**6a**–**c** and **7a**–**c**) are also reported. Photophysical and photochemical properties of phthalocyanine complexes are very useful for photodynamic therapy (PDT) applications. 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 0.27 to 0.90. The substituted Al(III), Ga(III) and In(III) phthalocyanines showed high singlet oxygen quantum yields. High singlet oxygen quantum yields are very important for Type II mechanism. Thus, these complexes show potential as Type II photosensitizers.

1. Introduction

Phthalocyanines play a major role in modern technology with applications in many fields [1–3], and have been found to be useful phototoxic drugs in medicine [4]. Complexation of phthalocyanines with metal ions has an influence on their photophysical properties. The interest in soluble metal phthalocyaninates mainly relies on their suitability as materials with unusual electrical, optical, catalytic and mesogenic properties, which are strongly dependent on the substitution pattern of the macrocycle. Particularly, they have been studied as dyes and pigments [5], light emitting diodes [6], in optical limiting devices [7–9], in molecular electronics [10], for non-linear optical applications [11], as liquid crystals [12,13], gas sensors [14], semiconductor materials [15], in photovoltaic cells [16,17], photodynamic therapy [18–21], photocatalysts [22] and for electrochromic displays [23,24]. Owing to their strong and long-wavelength absorptions, high efficiency at generating reactive oxygen species (ROS) and ease of chemical modification, phthalocyanines have emerged as a promising class of second-generation photosensitizers for photodynamic therapy (PDT) [18–21]. Over the last decade, a substantial number of phthalocyanine-based

photosensitizers have been prepared and evaluated for their photodynamic activity, with the focus on silicon, zinc and aluminium analogues as a result of their desirable photophysical properties.

The first photosensitizers were hematoporphyrin derivatives and have already been described in detail in several articles [25–26]. Second generation photosensitizers such as phthalocyanines have also been introduced for PDT in research and clinical trials [27]. To date, several phthalocyanine systems such as the silicon(IV) phthalocyanine Pc4 and a liposomal preparation of zinc(II) phthalocyanine have been in clinical trials. Photosens®, which is a mixture of sulfonated aluminium(III) phthalocyanines, is clinically used in Russia for the treatment of a range of cancers [28]. Due to their high molar absorption coefficient in the red part of the spectrum, photostability and long lifetimes of the photoexcited triplet states, phthalocyanines (Pcs) are known to be useful photosensitizers [18–21]. Altering the peripheral substitution of the macrocyclic ring is one way of tailoring the solubility properties of the Pc material. The aggregation properties of Pcs are very important for the development of new phosensitizers [29]. The introduction of either long chains or bulky substitutents to the periphery of the macrocycle should prevent the aggregation [30].

Thiol-derivatized metallophthalocyanine (MPc) complexes show rich spectroscopic and photochemical properties. For example, they are known to absorb at longer wavelengths (>700 nm) [31,32] than other MPc complexes. Therefore, these complexes

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have a very useful feature for applications in optoelectronics, near-IR devices and PDT.

Our previous papers have described synthesis, photophysical and photochemical properties of zinc, gallium and indium phthalocyanines carrying various substituents [33–37]. These phthalocyanine complexes showed fascinating photophysical and photochemical properties especially high singlet oxygen quantum yields which are very important for PDT of cancer. In this work, we report on the effects of the position of substituents and the nature of the metal on the photophysical and photochemical parameters of group 3A (Al, Ga and In) phthalocyanine derivatives in DMSO. Aggregation behaviour, photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties were investigated. Since PDT activity is mainly based on singlet oxygen, its production was determined by the dye-sensitized photooxidation of 1,3-diphenylisobenzofuran (DPBF), a specific scavenger of this toxic species [38]. Studies of the photostability of Al(III), Ga(III) and In(III) phthalocyanines during photosensitized reactions is also of immense importance.

2. Experimental

2.1. Materials and equipment

Quinoline, dimethylsulfoxide (DMSO), methanol, n-hexane, chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), acetone, ethanol and dimethylformamide (DMF) were dried as described in Perrin and Armarego [39] before use. Aluminium(III) chloride, indium(III) chloride were purchased from Aldrich, 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) and 1,3-diphenylisobenzofuran (DPBF) were from Fluka, gallium(III) chloride was from Alfa Aesar and K_2CO_3 was from Merck. Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and bio-beads (BIO-RAD S-X1 200-400 mesh). Preparative thin layer chromatography was performed on silica gel 60 P F$_{254}$. 1-Mercapto-4,7,10-trioxaundecan (**1**) [40], 3-nitrophthalonitrile (**2**) [41], 4-nitrophthalonitrile (**3**) [42] were synthesized and purified according to literature procedures. Zinc phthalocyanine which used as standard was purchased from Aldrich. Unsubstituted Al(III), Ga(III) and In(III) phthalocyanines were synthesized and purified according to literature procedures [43].

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 spectrofluoremeter using 1 cm pathlength cuvettes at room temperature. FT-IR spectra (KBr pellets) were recorded on a Bio-Rad FTS 175C FT-IR spectrometer. The mass spectra were acquired on a Bruker Daltonics (Bremen, Germany) MicrOTOF mass spectrometer equipped with electronspray ionization (ESI) source. The instrument was operated in positive ion mode using a m/z range of 50–3000. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow was 1 bar and drying gas flow 8 mL/min. ^{1}H NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer. Elemental analyses were obtained with a Thermo Finnigan Flash 1112 Instrument.

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, 700 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.

2.2. Photophysical parameters

2.2.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [44–45]

$$\Phi_F = \Phi_F F(\text{Std}) \frac{F A_{\text{Std}}}{F_{\text{Std}} A} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**6a–c** and **7a–c**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [46] was employed as the standard. Both the samples and standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program which uses the Strickler–Berg equation [47]. The fluorescence lifetimes (τ_F) were evaluated using the following equation

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

2.3. Photochemical parameters

2.3.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature [48–50]. Typically, a 3 ml portion of the respective unsubstituted, peripheral and non-peripheral tetrasubstituted aluminium(III), gallium(III) and indium(III) phthalocyanine (**6a–c** and **7a–c**) solutions (absorbance ~1.5 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in Refs. [48–50]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with ZnPc (in DMSO) as references. DPBF was used as chemical quenchers for singlet oxygen in DMSO. Eq. (3) was employed for the calculations:

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{R \; I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} I_{\text{abs}}} \tag{3}$$

where Φ_Δ^{Std} is the singlet oxygen quantum yields for the standard ZnPc ($\Phi_\Delta^{\text{Std}} = 0.67$ in DMSO) [51] R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**6a–c** and **7a–c**) and standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples (**6a–c** and **7a–c**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [52], the concentration of quenchers (DPBF) was lowered to ~3×10^{-5} mol dm^{-3}. Solutions of sensitizer containing DPBF were 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 of 7.05×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

2.3.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [48–50]. Photodegradation quantum yields were determined using the following equation

$$\Phi_d = \frac{(C_0 - C_t) V \, N_A}{I_{\text{abs}} S \, t} \tag{4}$$

where C_0 and C_t are the samples' (**6a–c** and **7a–c**) concentrations before and after irradiation, respectively, V is the reaction volume, N_A the Avogadro's constant, S the irradiated cell area and t is the

irradiation time. I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**6a–c** and **7a–c**). A light intensity of 2.35×10^{16} photons $s^{-1} cm^{-2}$ was employed for Φ_d determinations.

2.4. Synthesis

2.4.1. 3-(4,7,10-Trioxaundecane-1-sulfanyl)phthalonitrile (**4**)

To a solution of 3-nitrophthalonitrile (**2**) (4 g, 0.022 mol) in anhydrous DMF (40 ml) 1-mercapto-4,7,10-trioxaundecane (3.8 g, 0.022 mol) was added under argon atmosphere. After stirring for 10 min, finely ground anhydrous potassium carbonate (8 g, 0.058 mol) was added portionwise in 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at room temperature for 2 days. Then reaction mixture was dropped into ice and filtered with cold filter. Yield: 5.0 g (% 74) mp: 50 °C; FT-IR ν_{max}/cm^{-1} (KBr pellet): 3062 (Ar—CH), 2896 (CH), 2228 (C≡N), 1115 (C—O—C); ^{1}H NMR (CDCl$_3$) δ ppm: 7.77 (dd, 1H, Ar—CH), 7.63 (t, 1H, Ar—CH), 7.59 (dd, 1H, Ar—CH), 3.78 (t, 2H, CH$_2$), 3.65 (m, 2H, CH$_2$), 3.63 (m, 4H, CH$_2$), 3.56 (m, 2H, CH$_2$), 3.38 (s, 3H, CH$_3$), 3.29 (t, 2H, CH$_2$); Calc. for C$_{15}$H$_{18}$N$_2$O$_3$S: %C 58.80, %H 5.92, %N 9.14; Found: %C 58.62, %H 5.46, %N 9.58. MS (ESI-MS) m/z: Calc. 306.4; Found: 329.1 [M+Na]$^+$.

2.4.2. 4-(4,7,10-Trioxaundecane-1-sulfanyl)phthalonitrile (**5**)

Synthesis and purification was as outlined for **4** except 4-nitrophthalonitrile (**3**) was employed instead of **2**. The amounts of the reagents employed were: **3** (4 g, 0.022 mol), 1-mercapto-4,7,10-trioxaundecane (3.8 g, 0.022 mol), potassium carbonate (8 g, 0.058 mol) in DMF (40 ml). Yield: 4.2 g (% 63), mp: 41 °C; FT-IR ν_{max}/cm^{-1} (KBr pellet): 3093 (Ar—CH), 2918–2819 (CH), 2230 (C≡N), 1115 (C—O—C); ^{1}H NMR (CDCl$_3$) δ ppm: 7.70 (d, 1H, Ar—CH), 7.66 (d, 1H, Ar—CH), 7.61 (dd, 1H, Ar—CH), 3.79 (t, 2H, CH$_2$), 3.67 (m, 2H, CH$_2$), 3.63 (t, 4H, CH$_2$), 3.56 (m, 2H, CH$_2$), 3.39 (s, 3H, CH$_3$), 3.25 (t, 2H, CH$_2$); Calc. for C$_{15}$H$_{18}$N$_2$O$_3$S: %C 58.80, %H 5.92, %N 9.14; Found: %C 58.41, %H 5.34, %N 9.76. MS (ESI-MS) m/z: Calc. 306.4; Found: 329.1 [M+Na]$^+$.

2.4.3. 1(4),8(11),15(18),22(25)-Tetrakis-(4,7,10-trioxaundecan-1-sulfanyl) phthalocyaninato aluminium(III) (**6a**)

A mixture of 3-(4,7,10-trioxaundecane-1-sulfanyl) phthalonitrile (**4**) (1 g, 3.26 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.10 ml, 0.7 mmol) and anhydrous aluminium chloride (0.213 g, 1.6 mmol) in quinoline (2,5 ml) was refluxed and stirred under argon atmosphere for 7 h. The resulting green suspension was cooled and crude product was precipitated by addition of n-hexane. The crude green product was purified by column chromatography over bio-beads using CH$_2$Cl$_2$ as eluent. Furthermore this product was purified with preparative TLC (silica gel) using 15:1/CH$_2$Cl$_2$:MeOH as solvent system. TLC: R_f = 0.55. Yield: 0.10 g (10%). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3064 (Ar—CH), 2874–2844 (CH), 1569 (C=C), 1317, 1238, 1104 (C—O—C), 912, 745. ^{1}H NMR (CDCl$_3$) δ ppm: 8.88–7.64 (m, 12H, Ar—CH), 3.75–3.64 (br, 32H, —CH$_2$), 3.51–3.46 (br, 16H, —CH$_2$), 3.31 (s, 12H, —CH$_3$). Calc. for C$_{60}$H$_{72}$N$_8$O$_{12}$S$_4$AlCl: %C 55.95, %H 5.63, %N 8.70; Found: %C 56.12, %H 5.27, %N 8.91. MS (ESI-MS) m/z: Calc. 1286; Found: 1251.6 [M−Cl]$^+$. UV/vis (DMSO): λ, nm (log ε): 725 (5.20), 652 (4.54), 340 (4.78).

2.4.4. 2(3),9(10),16(17),23(24)-Tetrakis-(4,7,10-trioxaundecan-1-sulfanyl) phthalocyaninato aluminium(III) (**7a**)

Synthesis and purification was as outlined for **6a** except 4-(4,7,10-trioxaundecane-1-sulfanyl) phthalonitrile (**5**) was employed instead of **4**. The amounts of the reagents employed were: **5** (1 g, 3.26 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.10 ml, 0.7 mmol), anhydrous aluminium(III) chloride

(0.213 g, 1.6 mmol) in quinoline (2.5 ml). TLC (silica gel, using 20:1/CH$_2$Cl$_2$:MeOH as solvent system): R_f = 0.43. Yield: 0.22 g (21%). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3064 (Ar—CH), 2918–2849 (CH), 1602 (C=C), 1450, 1389, 1315, 1080 (C—O—C), 923, 753. ^{1}H NMR (CDCl$_3$) δ ppm: 7.89–7.49 (m, 12H, Ar—CH), 3.59–3.54 (br, 32H, —CH$_2$), 3.50–3.42 (br, 16H, —CH$_2$), 3.27 (s, 12H, —CH$_3$). Calc. for C$_{60}$H$_{72}$N$_8$O$_{12}$S$_4$AlCl: %C, 55.95; %H, 5.63; %N, 8.70; Found: %C 56.41, %H 5.26, %N 8.87 MS (ESI-MS) m/z: Calc. 1286; Found: 1251.6 [M−Cl]$^+$. UV/vis (DMSO): λ, nm (log ε): 705 (5.21), 633 (4.43), 378 (4.76).

2.4.5. 1(4),8(11),15(18),22(25)-Tetrakis-(4,7,10-trioxaundecan-1-sulfanyl) phthalocyaninato gallium(III) (**6b**)

Synthesis and purification was as outlined for **6a**. The amounts of the reagents employed were: **4** (1 g, 3.26 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.10 ml, 0.7 mmol), anhydrous gallium(III) chloride (0.282 g, 1.6 mmol) in quinoline (2.5 ml). TLC (silica gel, using 20:1/CH$_2$Cl$_2$:MeOH as solvent system): R_f = 0.50. Yield: 0.25 g (23%). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3062 (Ar—CH), 2919–2869 (CH), 1570 (C=C), 1334, 1243, 1109 (C—O—C), 909, 742. ^{1}H NMR (CDCl$_3$) δ ppm: 9.01–8.83 (m, 4H, Ar—CH), 7.98–7.89 (m, 8H, Ar—CH), 4.06 (br, 8H, CH$_2$), 3.90 (br, 8H, CH$_2$), 3.84 (br, 8H, CH$_2$), 3.78 (br, 16H, CH$_2$), 3.64 (br, 8H, CH$_2$), 3.44 (s, 12H, CH$_3$). Calc. for C$_{60}$H$_{72}$N$_8$O$_{12}$S$_4$GaCl: %C 54.16, %H 5.45, %N 8.42; Found: %C 54.52, %H 5.33, %N 8.65. MS (ESI-MS) m/z: Calc. 1330; Found: 1295.5[M−Cl]$^+$. UV/vis (DMSO): λ, nm (log ε): 730 (5.22), 654 (4.55), 341 (4.82).
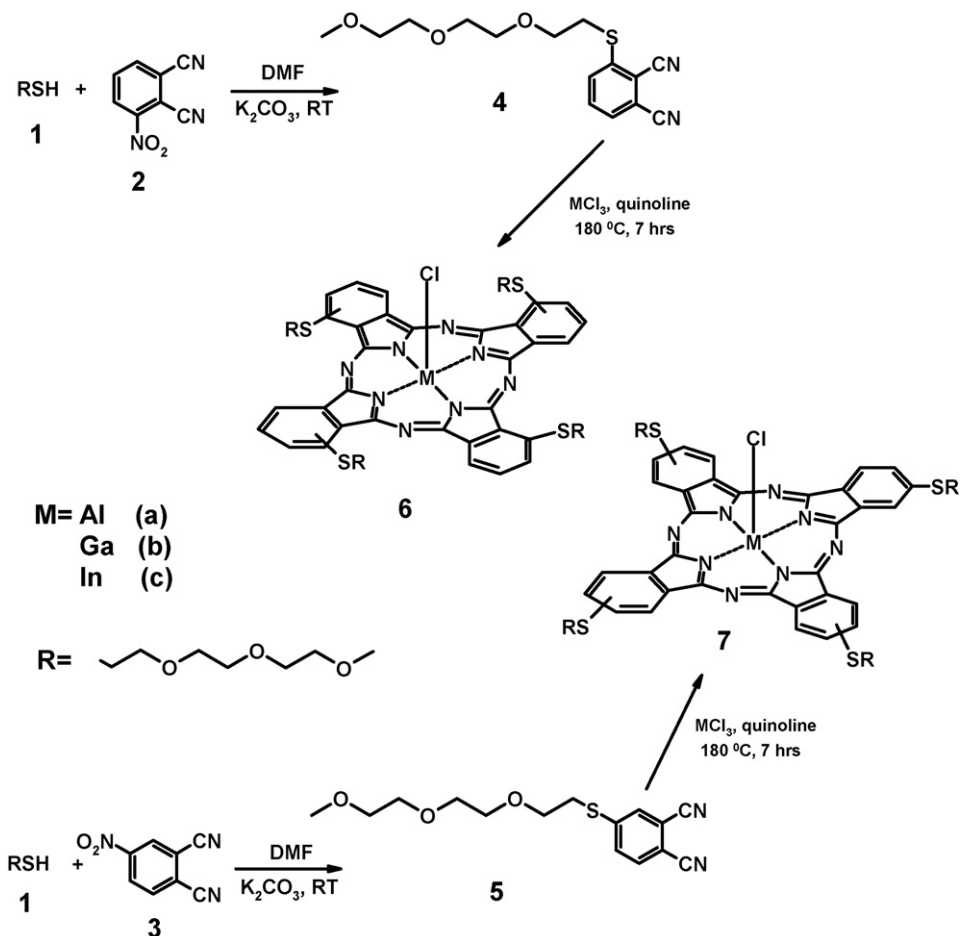
2.4.6. 2(3),9(10),16(17),23(24)-Tetrakis-(4,7,10-trioxaundecan-1-sulfanyl) phthalocyaninato gallium(III) (**7b**)

Synthesis and purification was as outlined for **6a** except 4-(4,7,10-trioxaundecane-1-sulfanyl) phthalonitrile (**5**) was employed instead of **4**. The amounts of the reagents employed were: **5** (1 g, 3.26 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.10 ml, 0.7 mmol), anhydrous gallium(III) chloride (0.282 g, 1.6 mmol) in quinoline (2.5 ml). TLC (silica gel, using 15:1/CH$_2$Cl$_2$:MeOH as solvent system): R_f = 0.31. Yield: 0.51 g (48%). IR [(KBr pellet) ν_{max}/cm^{-1}]: 3064 (Ar—CH), 2868 (CH), 1599 (C=C), 1449, 1396, 1333, 1104 (C—O—C), 919, 744. ^{1}H NMR (CDCl$_3$) δ ppm: 8.86–8.77 (m, 8H, Ar—CH), 8.04–7.93 (m, 4H, Ar—CH), 3.96 (br, 8H, CH$_2$), 3.75 (br, 8H, CH$_2$), 3.70 (br, 8H, CH$_2$), 3.63 (br, 16H, CH$_2$), 3.50 (br, 8H, CH$_2$), 3.30 (s, 12H, CH$_3$). Calc. for C$_{60}$H$_{72}$N$_8$O$_{12}$S$_4$GaCl: %C 54.16, %H 5.45, %N 8.42; Found: %C 54.46, %H 5.19, %N 8.80. MS (ESI-MS) m/z: Calc. 1330; Found: 1296.3[M−Cl]$^+$. UV/vis (DMSO): λ, nm (log ε): 702 (5.20), 632 (4.46), 365 (4.73).

2.4.7. 1(4),8(11),15(18),22(25)-Tetrakis-(4,7,10-trioxaundecan-1-sulfanyl) phthalocyaninato indium(III) (**6c**)

Synthesis and purification was as outlined for **6a**. The amounts of the reagents employed were: **4** (1 g, 3.26 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.10 ml, 0.7 mmol), anhydrous indium(III) chloride (0.354 g, 1.6 mmol) in quinoline (2.5 ml). TLC (silica gel, using 10:1/CH$_2$Cl$_2$:MeOH as solvent system): R_f = 0.54. Yield: 0.31 g (% 29). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3064 (Ar—CH), 2917–2879 (CH), 1569 (C=C), 1332, 1239, 1113 (C—O—C), 900, 740. ^{1}H NMR (CDCl$_3$) δ ppm: 9.34–9.19 (m, 4H, Ar—CH), 8.15–8.07 (m, 8H, Ar—CH), 4.20 (br, 8H, CH$_2$), 3.90 (br, 8H, CH$_2$), 3.84 (br, 8H, CH$_2$), 3.78 (br, 16H, CH$_2$), 3.64 (br, 8H, CH$_2$), 3.44 (s, 12H, CH$_3$). Calc. for C$_{60}$H$_{72}$N$_8$O$_{12}$S$_4$InCl: C 52.38, H 5.27, N 8.14; Found: C 52.84, H 5.01, N 8.59. MS (ESI-MS) m/z: Calc. 1374; Found: 1397.5 [M+Na]$^+$, 1339.5 [M−Cl]$^+$. UV/vis (DMSO): λ, nm (log ε): 726 (5.18), 652 (4.50), 346 (4.70).

Scheme 1. Synthesis of tetrasubstituted triethyleneoxythia(phthalocyaninato)aluminium(III), gallium(III) and indium(III) substituted at the α and β positions.

2.4.8. 2(3),9(10),16(17),23(24)-Tetrakis-(4,7,10-trioxaundecan-1-sulfanyl) phthalocyaninato indium(III) (7c)

Synthesis and purification was as outlined for **6a** except 4-(4,7,10-trioxaundecane-1-sulfanyl) phthalonitrile (**5**) was employed instead of **4**. The amounts of the reagents employed were: **5** (1 g, 3.26 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.10 ml, 0.7 mmol), anhydrous indium(III) chloride (0.354 g, 1.6 mmol) in quinoline (2.5 ml). TLC (silica gel, using 10:1/CH$_2$Cl$_2$:MeOH as solvent system): R_f = 0.45. Yield: 0.74 g (% 45). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3067 (Ar—CH), 2923–2872 (CH), 1599 (C=C), 1448, 1387, 1327, 1102 (C—O—C), 911, 741. ^{1}H NMR (CDCl$_3$) δ ppm: 9.17–8.95 (m, 8H, Ar—CH), 8.18–8.06 (m, 4H, Ar—CH), 4.06 (br, 8H, CH$_2$), 3.84 (br, 8H, CH$_2$), 3.79 (br, 8H, CH$_2$), 3.72 (br, 16H, CH$_2$), 3.59 (br, 8H, CH$_2$), 3.39 (s, 12H, CH$_3$). Calc. for C$_{60}$H$_{72}$N$_8$O$_{12}$S$_4$InCl: %C 52.38, %H 5.27, %N 8.14; Found: %C 52.67, %H 5.09, %N 8.50. MS (ESI-MS) m/z: Calc. 1374; Found: 1421.6 [M+2Na]$^+$, 1339.6 [M−Cl]$^+$. UV/vis (DMSO): λ, nm (log ε): 706 (5.24), 634 (4.46), 368 (4.73).

3. Results and discussion

3.1. Synthesis and characterization

Non-peripheral and peripheral substituted aluminium (**6a** and **7a**), gallium (**6b** and **7b**) and indium (**6c** and **7c**) phthalocyanines are prepared by cyclotetramerization of triethyleneoxythia substituted phthalonitriles (**4** and **5**). 2(3),9(10),16(17),23(24)-Tetrasubstituted (peripheral position) phthalocyanines can be synthesized from 4-substituted phthalonitriles while 1(4),8(11),15(18),22(25)-tetrasubstituted (non-peripheral position) phthalocyanines are obtained from 3-substituted analogues [1]. 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}. The 2(3)-substituted compounds always occur in the expected statistical mixture of 12.5% C_{4h}-, 25% C_{2v}-, 50% C_s- and 12.5% D_{2h}-isomer. But for the 1(4)-substituted ones the composition depends on the central metal ion and the structure of the peripheral substituent [13]. In this study, synthesized tetra-(triethyleneoxythia) substituted phthalocyanine compounds are obtained as isomer mixtures as expected. No attempt was made to separate the isomers of complexes **6a–c** and **7a–c**.

The preparation of substituted phthalonitriles from 3-nitro-1,2-dicyanobenzene (**2**) and 4-nitro-1,2-dicyanobenzene (**3**) were recently used to prepare 3-monosubstituted and 4-monosubstituted phthalonitrile derivatives, respectively, through base catalysed nucleophilic aromatic displacement [53,54]. The same route was applied to prepare 3-(4,7,10-trioxaundecane-1-sulfanyl)phthalonitrile (**4**) from 1-mercapto-4,7,10-trioxaundecane (**1**) and 3-nitro-1,2-dicyanobenzene (**2**) (Scheme 1). Similarly, the reaction of 1-mercapto-4,7,10-trioxaundecane (**1**) under the same conditions with 4-nitro-1,2-dicyanobenzene (**3**) resulted in the expected compound **5** (Scheme 1). The reactions were carried out in dimethyl formamide at room temperature and gave yields of about 70–80%.

The preparation of phthalocyanine derivatives from the aromatic nitriles occurs under different reaction conditions. The syntheses of metallophthalocyanine complexes (**6a–c** and **7a–c**) were achieved by treatment of phthalonitriles **4** and **5** with

anhydrous $AlCl_3$, $InCl_3$ or $GaCl_3$ in freshly distilled quinoline (Scheme 1). Complexes **6a–c** are non-peripheral (α) substituted, whereas complexes **7a–c** are peripheral (β) substituted. Column chromatography with bio-beads (BIO-RAD S-X1 200-400 mesh) and preparative thin layer 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 (**6a–c** and **7a–c**) exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, toluene, DMF, DMSO and methanol. For comparative purposes, the triethyleneoxythia groups were tetrasubstituted at the α and β positions of the ring. The new compounds were characterized by UV–vis, FT-IR and NMR spectroscopies, mass spectra and elemental analysis and the analyses are consistent with the predicted structures as shown in Section 2.

In the mass spectra of phthalonitriles obtained by the relatively soft ESI-MS technique, the molecular ion peaks were observed at m/z 329.1 $[M+Na]^+$ for **4** and **5** with Na ion.

The ^1H NMR spectra of tetrasubstituted phthalocyanine complexes (**6a–c** and **7a–c**) have broad absorptions when compared with that of corresponding phthalonitrile derivatives (**4** and **5**). 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 which are expected to show chemical shifts which slightly differ from each other. The triethyleneoxythia substituted phthalocyanines were found to be pure by ^1H NMR with all the substituents and ring protons observed in their respective regions.

In the mass spectra of phthalocyanines obtained by the relatively soft ESI-MS technique, the molecular ion peaks were observed at m/z 1251.6 for **6a**, 1295.5 for **6b**, 1339.5 for **6c**, 1251.6 for **7a**, 1296.3 for **7b** and 1339.6 for **7c** as without axially substituted chlorine atoms [55].

3.2. Ground state electronic absorption and fluorescence spectra

The ground state electronic absorption spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes, Fig. 1 [56]. In DMSO, the Q bands were observed at: 725 (**6a**), 730 (**6b**), 726 (**6c**), 705 (**7a**), 702 (**7b**) and 706 (**7c**). The Q bands of the non-peripheral tetra-substituted complexes (**6a–c**) are red-shifted by 28–20 nm, when compared to the corresponding peripheral tetrasubstituted (**7a–c**)
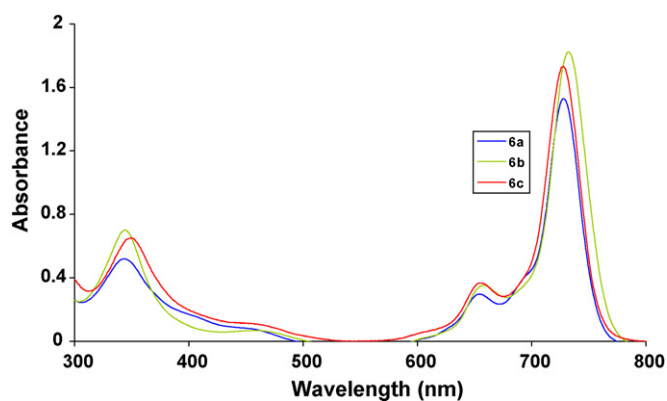

Fig. 1. Absorption spectra of **6a–c** in DMSO. Concentration $\sim 1 \times 10^{-5}$ mol dm^{-3}.

complexes in DMSO. The observed red spectral shift is typical of phthalocyanines with substituents at the non-peripheral positions and has been explained [57–58] to be due to linear combinations of the atomic orbitals (LCAO) 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 destabilized more at the non-peripheral position that it is at the peripheral position. Essentially, the energy gap (ΔE) between the HOMO and lowest unoccupied molecular orbital (LUMO) becomes smaller, resulting in a bathochromic shift. The shoulder between 400 and 450 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 B_1 and B_2 bands in the 340–380 nm region [57].

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. In this study, the aggregation behaviour of the phthalocyanine complexes (**6a–c** and **7a–c**) are investigated in different solvents (toluene, DMF, THF, chloroform, DMSO, methanol) (Fig. 2 for complex **7a**). While all the synthesized complexes did not show aggregation in toluene, DMF, THF, $CHCl_3$ and DMSO, they showed aggregation in methanol. For a particular MPc complex, the Q band position changes with the solvent. It has been well established that the Q band position of an MPc complex is a function of the solvent's refractive index [59]. The inset of Fig. 2 shows the plot of Q absorption band positions
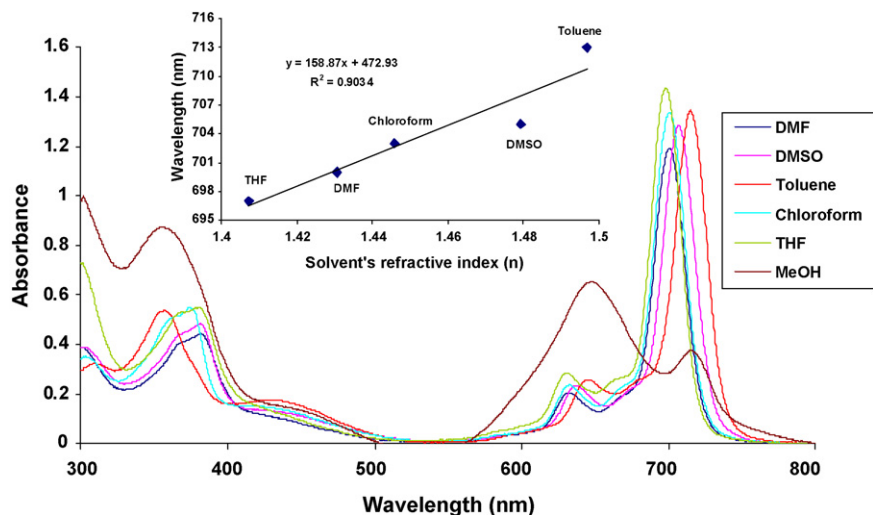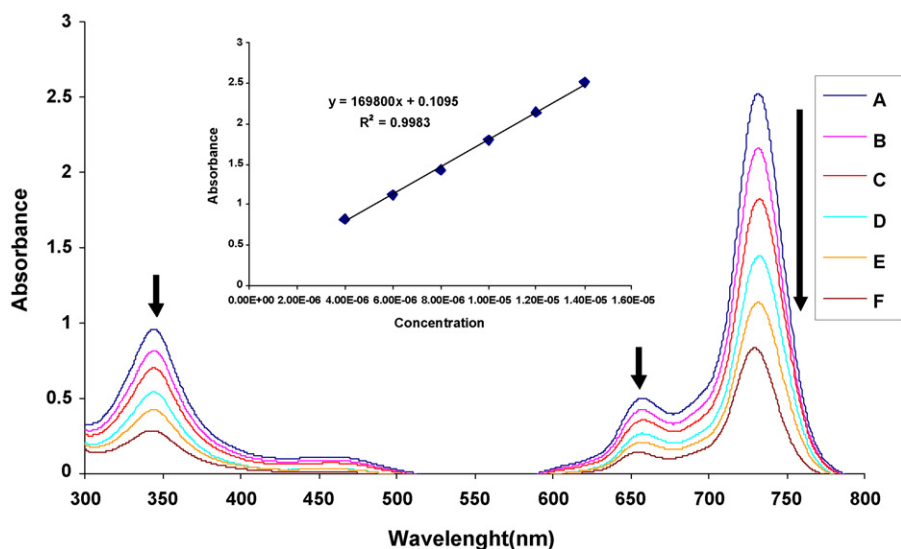

Fig. 2. UV–vis spectrum of **7a** in different solvents. Concentration = 4.00×10^{-6} mol dm^{-3}. (Inset: Q band position of **7a** as a function of solvent's refractive index.)

Fig. 3. Aggregation behaviour of **6b** in DMSO 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) mol dm^{-3}. (Inset: plot of absorbance versus concentration.)

of **7a** versus solvents' refractive indices, where it could be inferred that the Q band wavelength varies directly as the refractive index of the solvent. The aggregation behaviour of the phthalocyanine complexes (**6a–c** and **7a–c**) was also investigated at different concentrations in DMSO. In DMSO, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to the aggregated species for the all complexes (**6a–c** and **7a–c**) (Fig. 3 for complex **6b**). Beer–Lambert law was obeyed for all of the compounds in the concentrations ranging from 1.4×10^{-5} to 4×10^{-6} mol dm^{-3}.

The Al(III) and Ga(III) phthalocyanine derivatives (**6a, b** and **7a, b**) showed the same fluorescence behaviour, which was different from the In(III) phthalocyanine derivatives. The latter complexes (**6c** and **7c**) also showed fluorescence behaviour which was similar to each other. Fig. 4 shows fluorescence emission, absorption and excitation spectra for complex **7b** as an example in DMSO. Fluorescence emission peaks were observed at: 726 nm for **6a**, 752 nm for **6b**, 745 nm for **6c**, 706 nm for **7a**, 723 nm for **7b** and 725 nm for **7c** in DMSO (Table 1). The observed Stokes shifts of 8, 1 and 1 nm for Al(III) complexes, 11, 22 and 21 nm for Ga(III) complexes and 14, 19 and 19 nm for In(III) complexes (Table 1).

The shape of the excitation spectra was similar to absorption spectra and both were mirror images of the fluorescent spectra for the both Al(III) and Ga(III) phthalocyanine complexes (Fig. 4, as an example for **7b**). However, in terms of wavelength, the excitation spectra were slightly red-shifted for Ga(III) and In(III) complexes and blue-shifted for Al(III) complexes when compared to the absorption spectra. For the In(III) phthalocyanine complexes
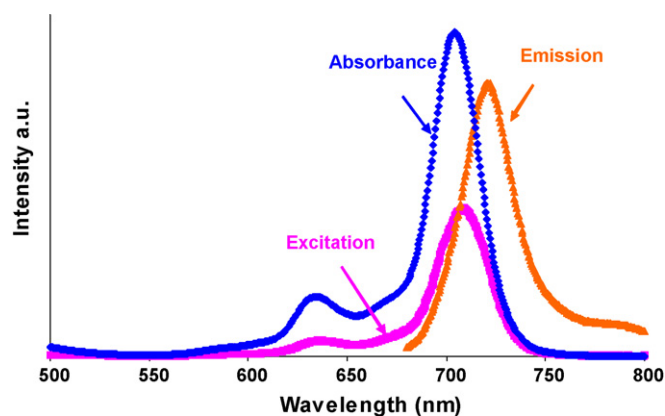
Fig. 4. Absorption, excitation and emission spectra for compound **7b** in DMSO. Excitation wavelength = 670 nm.

(**6c** and **7c**), the shape of excitation spectra was different from the absorption spectra. While the absorption spectra showed as narrow Q band, the excitation spectra showed as unlike narrow Q band. This suggests that there are changes in the molecule following excitation most likely due to loss of symmetry. The fluorescence spectra of complexes **6c** and **7c** were also broad. The difference in the behaviours of Al(III) and Ga(III) phthalocyanine complexes (**6a, b** and **7a, b**) from In(III) phthalocyanine complexes (**6c** and **7c**) on excitation could be due to the larger indium metal being

Table 1

Absorption, excitation and emission spectral data for unsubstituted, non-peripheral and peripheral substituted aluminium, gallium and indium phthalocyanine complexes in DMSO.

Compound	Q band, λ_{max} (nm)	log ε	Excitation, λ_{Ex} (nm)	Emission, λ_{Em} (nm)	Stokes shift, Δ_{Stokes} (nm)
ClAlPc	680	5.00	683	688	8
6a	725	5.20	716	726	1
7a	705	5.21	699	706	1
ClGaPc	680[a]	5.15[a]	680[a]	691[a]	11[a]
6b	730	5.22	737	752	22
7b	702	5.20	711	723	21
ClInPc	686[a]	4.46[a]	689[a]	700[a]	14[a]
6c	726	5.18	741	745	19
7c	706	5.24	719	725	19

[a] Ref. [35].

Table 2
Photophysical and photochemical parameters of unsubstituted, non-peripheral and peripheral tetrasubstituted aluminium, gallium and indium phthalocyanine complexes in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	k_F^a (s^{-1}) ($\times 10^8$)	Φ_d ($\times 10^{-3}$)	Φ_Δ
ClAlPc	0.37	6.09	16.47	0.60	3.21	0.24
6a	0.26	2.04	7.87	1.27	1.97	0.29
7a	0.13	1.04	7.99	1.25	3.41	0.27
ClGaPc	0.30[a]	3.71[a]	11.96[b]	0.83[a]	0.27[a]	0.41[a]
6b	0.15	1.08	7.24	1.37	6.31	0.81
7b	0.30	2.94	8.40	1.19	6.90	0.68
ClInPc	0.018[a]	0.90[a]	50.20[b]	1.99[a]	0.99[a]	0.61[a]
6c	0.013	0.11	8.65	1.15	1.37	0.90
7c	0.027	0.19	7.65	1.30	0.34	0.82

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Ref. [65].

more out of the plane of the phthalocyanine ring. Absorption and fluorescence excitation spectra were recorded with different instruments. The difference between the fluorescence excitation and absorption spectra of the complexes could have been caused instrumental factors and/or different settings of the spectrometer slit widths.

3.3. Photophysical and photochemical properties

3.3.1. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of Al(III) and Ga(III) phthalocyanine complexes (**6a, b** and **7a, b**) are typical of MPc complexes, Table 2. The peripheral tetrasubstituted Ga(III) complex **7b** show marginally larger Φ_F values among studied substituted complexes. For the In(III) phthalocyanine complexes (**6c** and **7c**), the Φ_F values were very low due to enhancement of intersystem crossing (ISC) by the presence of a heavier indium atom in these complexes.

Fluorescence lifetimes (τ_F, Table 2) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been [45] found between experimentally and the theoretically determined lifetimes for the unaggregated molecules as is the case in this work. Thus we suggest that the values obtained using this equation are appropriate measures of fluorescence lifetimes. The τ_F values were within the range reported for MPc complexes [45]. τ_F values were lower for substituted complexes **6a–c** and **7a–c** when compared to unsubstituted derivatives Table 2, again suggesting quenching of fluorescence by the ring substituents. The τ_F values reported in this work for Al(III) and

Ga(III) phthalocyanine derivatives are within the same range for MPcs. The τ_F values for In(III) phthalocyanine derivatives are smaller than Al(III) and Ga(III) phthalocyanine derivatives in DMSO by the presence of a heavier indium atom in the complexes again.

The rate constants for fluorescence (k_F) however increased on going from unsubstituted Al(III) and Ga(III) phthalocyanine derivatives to the corresponding substituted complexes **6a, b** and **7a, b**, but decreased from unsubstituted In(III) derivative to corresponding substituted complexes **6c** and **7c**, Table 2. Substituted complexes **6a–c** and **7a–c** also showed smaller natural radiative lifetime (τ_0, Table 2), compared to unsubstituted derivatives.

Fluorescence quantum yield (Φ_F) and lifetime (τ_F) values of employed Al, Ga and In phthalocyanine complexes (**6a–c** and **7a–c**) are resembling with those of polyoxy substituted Zn phthalocyanine complexes in the literature that ranged from 0.10 to 0.22 [33,34,60,61]. The Φ_F and τ_F values, obtained as a result of this study, are almost similar with Al, Ga and In phthalocyanine derivatives having different substituents on the phthalocyanine ring in literature [35–37,59,62,63].

3.3.2. Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using DPBF as a chemical quencher. The disappearance of DBPF was monitored using UV–vis spectrometer. 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
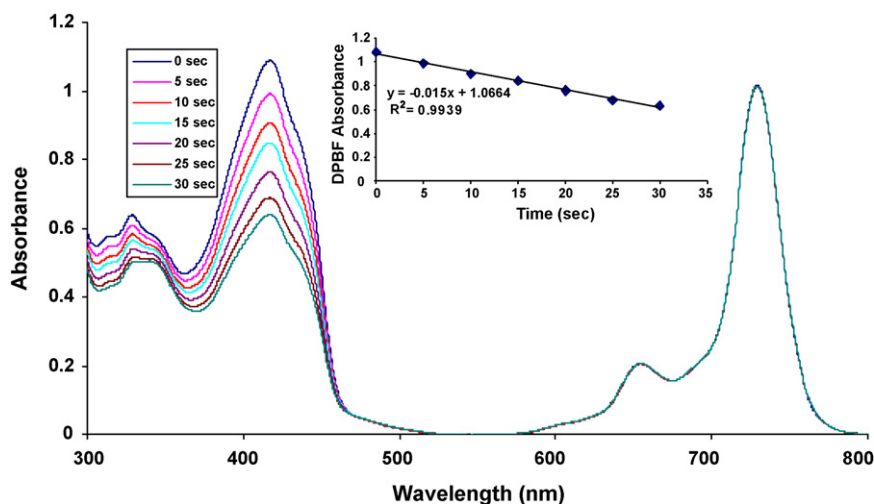
Fig. 5. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **6b** in DMSO at a concentration of 1×10^{-5} mol dm^{-3}. (Inset: plot of DPBF absorbance versus time.)
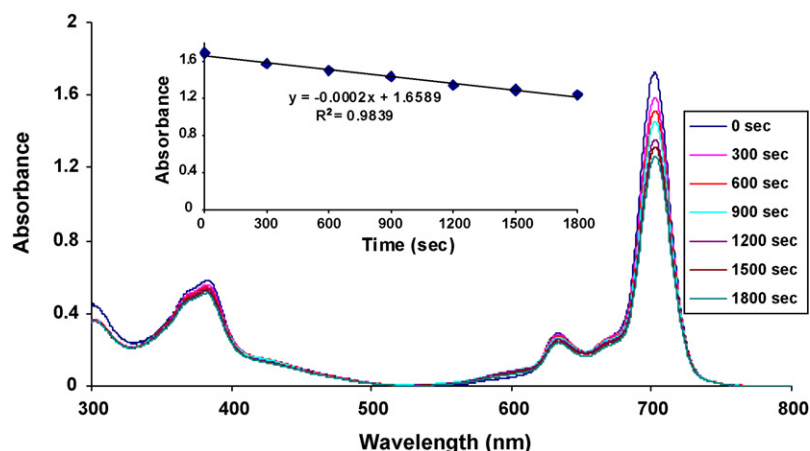
Fig. 6. The photodegradation of compound **7a** in DMSO showing the disappearance of the Q-band at 5 min intervals. (Inset: plot of absorbance versus time.)

excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen.

Because of the presence of oxygen during the determination of singlet oxygen quantum yields (Φ_Δ) the photodegradation of complexes was not observed during singlet oxygen studies as shown by Fig. 5 for complex **6b** (as an example) in DMSO. There was no decrease in the Q band or formation of new bands. The values of Φ_Δ were higher for substituted complexes (**6a**–**c** and **7a**–**c**) when compared to respective unsubstituted Al(III), Ga(III) or In(III) phthalocyanine complexes. The trend of singlet oxygen quantum yields among the corresponding substituted complexes was non-peripheral tetrasubstituted (**6a**–**c**) > peripheral tetrasubstituted (**7a**–**c**) for all of the substituted aluminium, gallium and indium phthalocyanine complexes in DMSO. This suggests that the higher Φ_Δ values of non-peripheral tetrasubstituted phthalocyanine complexes (**6a**–**c**) could be due to red-shift of the Q-bands for these complexes when compared to the peripheral tetrasubstituted phthalocyanine complexes (**7a**–**c**).

Singlet oxygen quantum yield (Φ_Δ) values of employed Al, Ga and In phthalocyanines, ranged from 0.27 to 0.90, have similar Φ_Δ values compared to their corresponding polyoxy substituted Zn phthalocyanine derivatives in literature that ranged from 0.54 to 0.72 [33,34,60,61]. The Φ_Δ values, found in this study, are almost similar with Al, Ga and In phthalocyanine derivatives having different substituents on the phthalocyanine ring in literature [35–37,59,62,63].

3.3.3. 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 phototransformation. The spectral changes observed for all the complexes (**6a**–**c** and **7a**–**c**) during irradiation are as shown in Fig. 6 (using complex **7a** as an example in DMSO) 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 Al, Ga and In phthalocyanine derivatives having different substituents on the phthalocyanine ring in literature [35–37,59,62,63]. 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 [64]. It seems group (III) metals and polyoxy chains increases the Φ_d values and decreases the stability of complexes.

4. Conclusion

In conclusion, we have synthesized peripheral and non-peripheral tetra-triethyleneoxythia substituted 3A group (aluminium, gallium and indium) phthalocyanines. These phthalocyanine complexes are monomeric in DMSO solution. The Al(III) and Ga(III) phthalocyanine derivatives (**6a**, **b** and **7a**, **b**) showed the same fluorescence behaviour, which was different from the In(III) phthalocyanine derivatives. This difference for In(III) complexes on excitation could be due to the larger indium metal being more out of the plane of the phthalocyanine ring. Although the fluorescence quantum yields (Φ_F) of Al(III) and Ga(III) phthalocyanine complexes are typical of MPc complexes, the Φ_F values for the In(III) complexes were very low due to presence of a heavier indium atom in these complexes. Especially, triethyleneoxythia substituted Ga(III) and In(III) phthalocyanine complexes (**6b**, **c** and **7b**, **c**) gave good singlet oxygen quantum yields ranging from 0.68 (for **7b**) and 0.90 (for **6c**). 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 0.27 to 0.90. Thus, these complexes show potential as Type II photosensitizers for PDT of cancer.

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