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## Photophysical, photochemical and liquid-crystalline properties of novel gallium(III) phthalocyanines

Fatma Yuksel<sup>a,\*</sup>, Mahmut Durmuş<sup>a</sup>, Vefa Ahsen<sup>a,b</sup>

<sup>a</sup> Gebze Institute of Technology, Department of Chemistry, PO Box 141, Gebze 41400, Kocaeli, Turkey <sup>b</sup> TUBITAK-Marmara Research Center, Material Institute, PO Box 21, 41470 Gebze, Turkey

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## ABSTRACT

The synthesis, liquid crystalline, photophysical and photochemical properties of the *peripheral-* and *nonperipheral-tetra*-substituted alkylthio gallium(III) phthalocyanines are reported here for the first time. These novel compounds have been characterized by elemental analysis, UV–Vis, IR and <sup>1</sup>H NMR spectroscopy and mass spectrometry. The thermal stabilities of the phthalocyanine compounds have been determined by thermogravimetric analysis. The mesogenic properties of these new materials have been investigated by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction measurements. The investigation of thermotropic behavior showed that all of the new compounds are liquid crystalline over a wide range of temperature. The X-ray diffraction patterns confirm that the phthalocyanines form a hexagonal columnar mesophase. Photophysical (fluorescence and photodegradation quantum yields and fluorescence lifetimes) and photochemical (singlet oxygen quantum yields) properties of these compounds have been investigated in toluene. The fluorescence of the substituted gallium(III) phthalocyanines is effectively quenched by 1,4-benzoquinone.

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## 1. Introduction

Phthalocyanines (Pcs) are highly delocalized  $\pi$ -conjugated organic systems and exhibit wide variety of roles in a various high technological areas such as semiconductor devices [1], liquid crystals [2], sensors [3], catalysts [4], non-linear optics [5], photovoltaic solar cells [6] and photodynamic therapy [7–9]. They are among the most important promising chemicals by advantage of their stability, photophysical, photochemical, redox and coordination properties. The properties of Pcs depend on their molecular composition with the number, position and nature of substituents and type of central metal play an important role in controlling their properties.

The presence of different substituents on the Pc ring also leads to increased solubility and supramolecular organizations with improved physicochemical characteristics. For example, the substitution of the phthalocyanine core with long flexible hydrocarbon chains provides these compounds with thermotropic liquid-crystalline behavior showing discotic mesophase. The first thermotropic discotic liquid-crystalline Pc [10] was reported in 1982 and after that it has been found that numerous Pc derivatives exhibit thermotropic or lyotropic mesomorphism [11–18].

The liquid-crystalline properties of these compounds can be controlled by changing the number, position and nature of substituents and the nature of the central complex-forming ion. In last decade, the alkylthio substitution of Pc core has attracted great attention in terms of mesogenic properties. Wöhrle and co-workers reported the first example of columnar mesomorphism of octakis (octylthio)-substituted zinc and copper Pc complexes [19]. Ohta and co-workers reported the synthesis of a series of octakis-(alkylthio)-phthalocyanines [abbreviated as  $(CnS)_{8}PcH_{2}$ , n = 8, 10, 12, 16] and their copper complexes with investigation of the mesogenic properties [20]. The influence of the sulfur atoms and chain length on the mesomorphism and unique aggregated dimer structures in the columnar mesophase of these compounds were discussed. Adam and co-workers reported that a discotic liquid crystal of triphenylene substituted by alkylthio groups exhibited considerably higher charge carrier mobility in the discotic mesophase, compared with conventional organic semiconductors [21]. Basova and co-workers have noted the influence of molecular organization on the electrical properties of mesogenic octakishexylthio substituted copper phthalocyanine film [22]. From these results; one can expect that the sulfur atoms may significantly influence the conductivity of the mesophase. The other advantage of alkylthio substituted Pcs is that these compounds have relatively lower transition temperatures to the liquid-crystalline state than alkoxy-derivatives and they conserve the columnar hexagonal





<sup>\*</sup> Corresponding author. Tel.: +90 262 6053073; fax: +90 262 6053101. *E-mail address*: fatma@gyte.edu.tr (F. Yuksel).

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mesophase over a wide temperature range including room temperature [23].

The main aim of this study was the development of novel polyfunctional materials which have mesogenic, photophysical and photochemical properties to achieve potential application in high technology areas such as liquid-crystalline displays. On account of this aim, we have designed here the first example of liquid crystal Ga(III)Pcs which are *tetra*-substituted with alkylthio groups. It was expected that the alkylthio substitution and the presence of gallium metal in the core would improve the unique mesogenic, photophysical and photochemical properties of phthalocyanine unit.

Despite, Ga(III)Pcs have excellent photophysical and photochemical properties and they have been investigated as potential non-linear optical materials [24–27] and photodynamic therapy agents [28–31], gallium has been relatively little studied for complexation with phthalocyanines. Although, many studies concerning the liquid-crystalline properties of Pc complexes, to the best of our knowledge, liquid crystal Ga(III)Pcs have not been reported before. Similarly, the substitution of the alkylthio groups on the phthalocyanine core improve its mesogenic, spectroscopic and photochemical properties such as mesogenic phase transition in lower temperature and absorption of light at longer wavelength than other corresponding substituted metallophthalocyanine complexes. Nevertheless, the reports of alkylthio substitution on gallium based Pcs are scarce in the literature [32].

We present here the syntheses of the Ga(III)Pcs which are *tetra*substituted with alkylthio groups. The characterization, thermotropic and lyotropic mesophase behavior, photophysical and photochemical properties of novel compounds have been investigated and the results were reported in this work.

## 2. Experimental

### 2.1. Materials

All solvents were reagent-grade quality, obtained from commercial suppliers. Gallium(III) chloride, K<sub>2</sub>CO<sub>3</sub>, 1,3-diphenylisobenzofuran (DPBF), 1,5-diazabicyclo[4.3.0]non-5-ene (DBU), deuterated CDCl<sub>3</sub>, 1-mercaptododecane and 1-mercaptohexadecane were purchased from commercial suppliers. Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and preparative thin layer chromatography was performed on silica gel 60 P F<sub>254</sub>.

#### 2.2. Measurements

Elemental analyses were obtained from Thermo Finnigan Flash 1112. Infrared spectra in KBr pellets were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer. Optical spectra in the UV-visible region were recorded with a Shimadzu 2001 UV spectrophotometer using a 10 mm pathlength cuvette at room temperature. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Mass spectra were recorded on a MALDI (Matrix Assisted Laser Desorption Ionization) BRUKER Microflex LT using a 2,5-dihydroxybenzoic acid (DHB) as matrix or on a LCQ-ion trap (Thermofinnigan, San Jose, CA, USA), equipped with an Electrospray (ES) source. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> solutions on a Varian 500 MHz spectrometer. The phase transition behavior of Ga(III)Pc complexes was observed by means of polarizing microscope (Leitz Wetzler Orthoplan-pol.) equipped with the hot stage (Linkam TMS 93) and temperature-controller (Linkam LNP). Thermogravimetric analyses and the determination of transition temperatures were carried out on Mettler Toledo Star<sup>e</sup> Thermal Analysis System/DSC 822<sup>e</sup> with scan rate of 10 °C min<sup>-1</sup>. The differential scanning calorimeter system was calibrated with indium from 4 to 7 mg samples under nitrogen atmosphere. X-ray diffraction measurements (Cu-K $\alpha$ -radiation) were performed using a Bruker Advanced D8 diffractometer.

Photo-irradiations were performed 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 radiation 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.

## 2.3. Photophysical parameters

#### 2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields ( $\Phi_F$ ) were determined by the comparative method (Equation (1)) [33,34]

$$\Phi_{\rm F} = \Phi_{\rm F}({\rm Std}) \frac{{\rm F} \cdot {\rm A}_{\rm Std} \cdot {\rm n}^2}{{\rm F}_{\rm Std} \cdot {\rm A} \cdot {\rm n}_{\rm Std}^2}$$
(1)

where F and F<sub>Std</sub> are the areas under the fluorescence emission curves of the Ga(III)Pcs (**5a,b** and **6a**) and the standard, respectively. A and A<sub>Std</sub> are the relative absorbance of the sample and standard at the excitation wavelength, respectively. n and n<sub>Std</sub> are the refractive indices of solvents for the sample and standard, respectively ( $n_{toluene} = 1.50$ ,  $n_{DMSO} = 1.48$ ). Unsubstituted ZnPc (in DMSO) ( $\Phi_F = 0.20$ ) [35] was employed as the standard. Both the sample and standard were excited at the same wavelength. The absorbance of the solutions ranged between 0.04 and 0.05 at the excitation wavelength.

Natural radiative  $(\tau_0)$  lifetimes were determined using Photochem CAD program which uses the Strickler–Berg equation [36]. The fluorescence lifetimes  $(\tau_F)$  were evaluated using Equation (2).

$$\Phi_{\rm F} = \frac{\tau_{\rm F}}{\tau_0} \tag{2}$$

Using the  $\tau_F$  values, rate constants for fluorescence  $(k_f)$ , intersystem crossing  $(k_{ISC})$ , internal conversion  $(k_{IC})$  and photodegradation  $(k_d)$  were estimated.

## 2.4. Photochemical parameters

#### 2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) determinations were carried out by using the experimental set-up described in literature [37–39]. Typically a 3 mL portion of the respective unsubstituted (ZnPc) and substituted Ga(III)Pcs (**5a,b** and **6a,b**) solutions (concentration = 1 × 10<sup>-5</sup> M) containing the singlet oxygen quencher was irradiated in the Q band region with the photoirradiation set-up described in references [37–39].  $\Phi_{\Delta}$  was determined in air using the relative method with ZnPc (in toluene) as a reference. DPBF was used as chemical quenchers for singlet oxygen in toluene. Equation (3) was employed for the calculations of  $\Phi_{\Delta}$ :

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{R \cdot l_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot l_{\text{abs}}} \tag{3}$$

where  $\Phi_{\Delta}^{\text{Std}}$  is the singlet oxygen quantum yield for the standard ZnPc ( $\Phi_{\Delta}^{\text{Std}} = 0.58$  in toluene) [40]. R and R<sub>Std</sub> are the DPBF photobleaching rates in the presence of the respective Ga(III)Pcs (**5a,b** and **Ga,b**) and standard, respectively. I<sub>abs</sub> and I<sub>abs</sub><sup>Std</sup> are the rates of light absorption by the Ga(III)Pcs (**5a,b** and **Ga,b**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [41] the concentration of quencher was

lowered to ~3 × 10<sup>-5</sup> mol dm<sup>-3</sup>. Solutions of sensitizer containing DPBF was prepared in the dark and irradiated in the Q band region using the above set-up. DPBF degradation at 417 nm was monitored. The light intensity was 6.66 × 10<sup>15</sup> photons s<sup>-1</sup> cm<sup>-2</sup> for  $\Phi_{\Delta}$  determinations.

## 2.4.2. Photodegradation quantum yields

Determinations of photodegradation quantum yield ( $\Phi_d$ ) were carried out previously described in the literature [37–39].  $\Phi_d$  was determined using Equation (4),

$$\Phi_{d} = \frac{(C_{0} - C_{t}) \cdot V \cdot N_{A}}{I_{abs} \cdot S \cdot t}$$
(4)

where  $C_0$  and  $C_t$  are the Ga(III)Pcs (**5a,b** and **6a,b**) concentrations before and after irradiation respectively, V, N<sub>A</sub>, S, t and I<sub>abs</sub> are reaction volume, the Avogadro's constant, irradiated cell area, irradiation time and the overlap integral of the radiation source light intensity, respectively. A light intensity of 2.22  $\times$  10<sup>16</sup> photons s<sup>-1</sup> cm<sup>-2</sup> was employed for  $\Phi_d$  determinations.

## 2.4.3. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the Ga(III)Pcs (**5a,b** and **6a,b**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complexes, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence spectra of Ga(III)Pcs (**5a,b** and **6a**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation [42] was shown in Equation (5):

$$\frac{\mathbf{I}_0}{\mathbf{I}} = 1 + \mathbf{K}_{\mathrm{SV}}[\mathbf{B}\mathbf{Q}] \tag{5}$$

where  $I_0$  and I are the fluorescence intensities of fluorophore where  $I_0$  and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and  $K_{SV}$  is the Stern–Volmer constant which is the product of the bimolecular quenching constant ( $k_q$ ) and the  $\tau_F$  and is expressed in Equation (6).

$$K_{SV} = k_q \cdot \tau_F \tag{6}$$

The ratios of  $I_o/I$  were calculated and plotted against [BQ] according to Equation (5), and  $K_{SV}$  is determined from the slope.

## 2.5. Syntheses

4-Nitrophthalonitrile [43] (1), 3-nitrophthalonitrile [44] (2), 4-(1-mercaptododecyl) phthalonitrile [45] (3a), 4-(1-mercapto hexadecyl) phthalonitrile [45] (3b), and 3-(1-mercaptododecyl) phthalonitrile [44] (4a) were synthesized and purified according to published procedures.

#### 2.5.1. 3-(1-mercaptohexadecyl) phthalonitrile (4b)

The 3-nitrophthalonitrile (2.0 g, 11.6 mmol) was dissolved in dimethyl sulfoxide (20 mL) under argon atmosphere and hexadecane-1-thiol (3.2 g, 12.4 mmol) was added to this solution. After 30 min anhydrous potassium carbonate (2.4 g, 17.4 mmol) was added in portions during 3 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at ambient temperature. After 24 h, the reaction mixture was added to 100 g ice. The resulting pale yellow solid was filtered then washed with cold distilled water. Colorless crystals were obtained by re-crystallization from hot ethanol. Yield: 3.56 g, 80%. mp: 90 °C. FT-IR  $v_{max}/cm^{-1}$  (KBr pellet): 3055 (CH<sub>ar</sub>), 2916–2849 (CH), 2230 (C=N), 1566 (C=C), 1469, 1196,

796, 719. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm: 7.59 (m, 2H, CH<sub>ar</sub>), 7.55 (d, H, CH<sub>ar</sub>), 3.06 (t, 2H, SCH<sub>2</sub>), 1.71 (m, 2H, CH<sub>2</sub>), 1.46 (m, 2H, CH<sub>2</sub>), 1.26 (m, 24H, CH<sub>2</sub>), 0.88 (t, 3H, CH<sub>3</sub>). MS (ESI-MS) *m/z*: Calc. 384; Found: 407 [M + Na]<sup>+</sup>.

# 2.5.2. 2(3),9(10),16(17),23(24)-tetrakis[(1-mercaptododecyl) phthalocyaninato] chlorogallium(III) (5a)

A mixture of anhydrous gallium(III) chloride (0.27 g. 1.52 mmol). 4-(1-mercaptododecyl) phthalonitrile (3a) (1.00 g, 3.04 mmol), DBU (0,2 mL) and quinoline (3 mL, doubly distilled over CaH<sub>2</sub>) was stirred at 180 °C for 7 h under a nitrogen atmosphere. After cooling, the solution was dropped into the ethanol. The green solid product that precipitated was collected by filtration and washed with ethanol. The crude product was dissolved in CHCl<sub>3</sub> and then filtered. After filtering and concentrating, the green product was purified by passing through a silica gel column, using THF as the eluting solvent. Furthermore this product was purified with preparative thin layer chromatography (silica gel) using CHCl<sub>3</sub> as solvent. Yield: 0.42 g, 39%. FT-IR v<sub>max</sub>/cm<sup>-1</sup> (KBr pellet): 3060 (CH<sub>ar</sub>), 2955–2852 (CH), 1600 (C=C), 1494, 1459, 1395, 1335, 1316, 1254, 1144, 1079, 1040, 920, 815, 743. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 8.78–7.46 (m, 12H, Ar–CH), 3.41-3.02 (br, 8H, -SCH<sub>2</sub>), 1.95 (br, 8H, -SCH<sub>2</sub>CH<sub>2</sub>), 1.62 (br, 8H, CH<sub>2</sub>), 1.50–1.25 (m, 64H, CH<sub>2</sub>), 0.92 (t, 12H, CH<sub>3</sub>). Calc for C80H112ClGaN8S4: %C 67.70, %H 7.95, %N 7.90; Found: %C 67.80, %H 8.05, %N 7.80. MS (MALDI) *m*/*z*: Calc. 1419; Found: 1383 [M - Cl]<sup>+</sup>, 1419 [M]<sup>+</sup>, 1536 [M - Cl + DHB]<sup>+</sup>.

# 2.5.3. 2(3),9(10),16(17),23(24)-tetrakis[(1-mercaptohexadecyl) phthalocyaninato] chlorogallium(III) (**5b**)

Synthesis and purification was outlined as for **5a** except **3b** was employed instead of **3a**. The amount of the reagents employed were: **3b** (1.00 g, 2.60 mmol), gallium(III) chloride (0.22 g, 1.30 mmol) and DBU (0.2 mL) in quinoline (3 mL). Yield: 0.33 g, 31%. FT-IR  $\nu_{max}/cm^{-1}$  (KBr pellet): 3061 (CH<sub>ar</sub>), 2958–2850 (CH), 1600 (C=C), 1498, 1448, 1397, 1335, 1312, 1255, 1148, 1075, 1036, 915, 815, 744. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm: 8.75–7.50 (m, 12H, Ar–CH), 3.45–3.06 (br, 8H, –SCH<sub>2</sub>), 1.97 (br, 8H, –SCH<sub>2</sub>CH<sub>2</sub>), 1.69 (br, 8H, CH<sub>2</sub>), 1.52–1.29 (m, 96H, CH<sub>2</sub>), 0.93 (t, 12H, CH<sub>3</sub>). Calc. for C<sub>96</sub>H<sub>144</sub>ClGaN<sub>8</sub>S<sub>4</sub>: %C 70.15, %H 8.83, %N 6.82; Found: %C 70.01, %H 9.02, %N 6.70. MS (MALDI) *m/z*: Calc. 1643; Found: 1606 [M – Cl + 2H]<sup>+</sup>, 1760 [M – Cl + 2H + DHB]<sup>+</sup>.

## 2.5.4. 1(4),8(11),15(18),22(25)-tetrakis[(1-mercaptododecyl) phthalocyaninato] chlorogallium(III) (**6a**)

Synthesis and purification was outlined as for **5a** except **4a** was employed instead of **3a**. The amount of the reagents employed were: **4a** (1.00 g, 3.04 mmol), gallium(III) chloride (0.27 g, 1.52 mmol) and DBU (0.2 mL) in quinoline (3 mL). Yield: 0.38 g, 35%. FT-IR  $\nu_{max}/cm^{-1}$  (KBr pellet): 3060 (CH<sub>ar</sub>), 2960–2850 (CH), 1588 (C=C), 1500, 1465, 1327, 1238, 1190, 1159, 1113, 1080, 909, 794, 740. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm: 8.95–7.40 (m, Ar–CH, 12H), 3.46–2.98 (t, 8H, –SCH<sub>2</sub>), 2.05 (m, 8H, –SCH<sub>2</sub>CH<sub>2</sub>), 1.77 (m, 8H, CH<sub>2</sub>), 1.63–1.26 (m, 64H, CH<sub>2</sub>), 0.92 (t, 12H, CH<sub>3</sub>). Calc. for C<sub>80</sub>H<sub>112</sub>ClGaN<sub>8</sub>S<sub>4</sub>: %C 67.70, %H 7.95, %N 7.90; Found: %C 67.82, %H 8.11, %N 7.75. MS (MALDI) *m/z*: Calc. 1419; Found: 1383 [M – Cl]<sup>+</sup>, 1536 [M – Cl + DHB]<sup>+</sup>.

## 2.5.5. 1(4),8(11),15(18),22(25)-tetrakis[(1-mercaptohexadecyl) phthalocyaninato] chlorogallium(III) (**6b**)

Synthesis and purification was outlined as for **5a** except **4b** was employed instead of **3a**. The amount of the reagents employed were: **4b** (1.00 g, 2.60 mmol), gallium(III) chloride (0.22 g, 1.30 mmol) and DBU (0,2 mL) in quinoline (3 mL). Yield: 0.35 g, 33%. FT-IR  $\nu_{max}/cm^{-1}$  (KBr pellet): 3060 (CH<sub>ar</sub>), 2960–2850 (CH), 1590 (C=C), 1468, 1325, 1242, 1190, 1153, 1113, 1082, 908, 794, 740. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm: 8.97–7.40 (m, 12H, Ar–CH), 3.47–2.97 (t, 8H, –SCH<sub>2</sub>), 2.06 (m, 8H, –SCH<sub>2</sub>CH<sub>2</sub>), 1.78 (m, 8H, CH<sub>2</sub>), 1.60–1.29 (m, 96H, CH<sub>2</sub>), 0.89

(t, 12H, CH<sub>3</sub>). Calc. for C<sub>96</sub>H<sub>144</sub>ClGaN<sub>8</sub>S<sub>4</sub>: %C 70,15, %H 8,83, %N 6,82; Found: %C 70.05, %H 9.05, %N 6,75. MS (MALDI) m/z: Calc. 1643; Found: 1609 [M – Cl]<sup>+</sup>, 1762 [M – Cl + DHB]<sup>+</sup>.

## 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthesis route is given in Scheme 1. Alkylthiophthalonitriles **3a,b** and **4a,b** were used as starting compounds for alkylthio *tetra*-substituted Ga(III)Pcs. Compounds **3a,b** and **4a** have been prepared by nucleophilic substitution of the nitro group in 4nitrophthalonitrile [43] (1) or 3-nitrophthalonitrile [44] (2) with 1mercaptododecane or 1-mercaptohexadecane according to published procedures [44,45]. 3-(1-Mercaptohexadecyl) phthalonitrile (**4b**) was synthesized for the first time by the same method and analysis results were given in Experimental section.

Generally, substituted phthalocyanines are prepared bv cyclotetramerization of substituted phthalonitriles or 1,3-diimino-1H-isoindoles. 2(3),9(10),16(17),23(24)-Tetra-substituted phthalocyanines can be synthesized from 4-substituted phthalonitriles while 1(4),8(11),15(18),22(25)-*tetra*-substituted phthalocyanines are obtained from the 3-substituted analogs (Scheme 1). The synthesis of Ga(III) phthalocyanine complexes (5a,b and 6a,b) were achieved by treatment of alkylthio substituted phthalonitriles **3a,b** and **4a,b** with anhydrous GaCl<sub>3</sub> in freshly distilled quinoline. Complexes **5a** and **5b** are *peripherally* substituted, whereas complexes **6a** and **6b** are *non*peripherally substituted (Scheme 1). Generally high-boiling alcohols such as 1-hexanol or 1-pentanol are used as solvents in these types of reactions. Nevertheless a large central atom requires high energy to insert into the phthalocyanine core thus the use of higher-boiling solvents such as quinoline is preferred to obtain higher yield in the gallium based Pcs [29-32]. In both peripheral- and non-peripheraltetra-substituted phthalocyanines, four possible structural isomers can be designed from their molecular symmetry as  $C_{4h}$ ,  $C_{2v}$ ,  $C_{s}$ , and  $D_{2h}$ [46]. In this study, the synthesized tetra-substituted phthalocyanines have been obtained as an isomer mixture as expected and no attempt was made to separate the isomers. Novel Ga(III)Pcs (**5a,b** and **6a,b**) were purified by column and preparative thin layer chromatography with silica gel. All these complexes were soluble in dichloromethane, chloroform and toluene but they were insoluble in polar solvents e.g. DMF and DMSO.

The novel Ga(III)Pcs (**5a,b** and **6a,b**) have been characterized by elemental analysis, IR, <sup>1</sup>H NMR, UV–Vis and mass spectrometry and the results were given in Experimental section. The mass spectra which were obtained by MALDI-TOF (2,5-dihydroxybenzoic acid was used as matrix) were consistent with assigned formulations without axially substituted chlorine atoms [31,32].

The <sup>1</sup>H NMR spectra of novel Ga(III)Pcs (**5a,b** and **6a,b**) were recorded in CDCl<sub>3</sub>. The expected signals were observed in accord with the proposed structures. However, the aromatic ring protons and SCH<sub>2</sub> protons showed complex patterns because of the isomeric character of the *tetra*-substituted Pc compounds [30,46]. Both complexes types are expected to have isomers due to the presence of a single substituent on either the peripheral or nonperipheral positions. However, the non-peripherally substituted Ga (III)Pcs (6a,b) were present as a major isomer which can be attributed to 1,8,15,22-tetra-substituted compound with C4h symmetry, as a consequence of the steric demands of the large alkyl chains. Thus the <sup>1</sup>H NMR signals belonging to the aromatic rings protons were observed as unresolved doublets for peripheral substituted Ga(III)Pcs (5a,b) in the range of 8.78-7.45 ppm and doublets and triplets for non-peripheral substituted Ga(III)Pcs (**6a,b**) in the range of 8.95–7.40 ppm. The -SCH<sub>2</sub> protons gave triplet signals in the range of 3.45–3.00 ppm for all compounds. The other CH<sub>2</sub> protons of alkyl chains showed complex multiplets in their respective regions (in the range of 2.10-1.25 ppm) and the CH<sub>3</sub> protons were observed as a triplet at ca. 0.90 ppm.

## 3.2. The mesogenic properties

#### 3.2.1. Thermotropic phase behavior

The phase transition behavior of Ga(III)Pcs (**5a,b** and **6a,b**) was determined by differential scanning calorimetry (DSC) and



Scheme 1. Synthesis routes of alkylthio substituted Ga(III)phthalocyanine complexes.



Fig. 1. Photomicrograph of the texture of 6b at 50 °C.

polarized optical microscopy (POM) observations. In the microscopic investigations, Ga(III)Pcs (**5a,b** and **6a,b**) showed isotropic transitions at about 160, 145, 182, and 160 °C, respectively. All compounds exhibited one mesogenic phase over a wide temperature range including room temperature. The same behavior was obtained in repeated heating and cooling cycles. Thus, the first clearing behavior of Ga(III)Pcs (**5a,b** and **6a,b**) were observed using a DSC. The microscopic observations of these compounds demonstrate the textures. Fig. 1 shows the photomicrograph of the mesophase for **6b** at 50 °C. These textures were typical of that of a columnar mesophase, showing both large cylindrical domains and a large homeotrophic area, strongly suggesting a hexagonal columnar mesophase, Col<sub>h</sub> [19,20,22,47–49].

The thermal stabilities of the Ga(III)Pcs (5a,b and 6a,b) have been investigated by thermal gravimetric analysis (TGA). All compounds started to decompose at ca. 300 °C. The main decomposition points were about 360 °C. Thus, the heating cycles were limited between the -40 and  $\sim 230$  °C to avoid decomposition of the compounds in the DSC measurement. Phase transition temperatures and the corresponding enthalpy changes were determined by DSC and they are summarized in Table 1. The DSC measurements of the compounds **6a** and **6b** showed that a weak peak which relates to clearing at 96 and 82 °C, respectively. A linear decrease in these temperatures with increasing the length of alkyl chain was detected for compounds 6a and 6b. Compounds 5a also showed a weak melting peak around 124 °C on heating but no peaks were observed in the cooling. No such peak is observed for compound **5b**. Thus, comparing the phase transition temperatures with difference in the length and/or position of alkyl chain was not accomplished.



Fig. 2. Photomicrograph of the texture of the lyotropic mesophase of 6b formed from tetrachloroethane at 25  $^\circ\text{C}.$ 

#### 3.2.2. Lyotropic mesophase behavior

The lyotropic mesophase behavior of all Ga(III)Pcs (**5a,b** and **6a,b**) has been investigated in chloroform, tetrachloroethane, toluene and n-hexanol at ambient temperature. The samples were prepared as described in the literature [16,50,51]: compounds were dissolved in a minimum amount of solvent (one or two drops) and placed between two microscope slides then allowed time for a partial evaporation of the solvent from the edge of the slide. The slow evaporation of solvent achieved the higher concentration of compounds at the edge of slide. Eventually, the lyotropic mesophase which formed at this more concentrated part of all compounds solutions were very similar to the thermotropic textures. Fig. 2 shows the texture of **6b** in tetrachloroethane as an example. The best textures which are probably formed as a result of the formation of columnar aggregates [16,50,51] were found in chloroform and tetrachloroethane.

#### 3.2.3. X-ray diffraction

The mesophase determinations of Ga(III)Pcs (**5a,b** and **6a,b**) were carried out by microscopic observation and X-ray diffraction measurements at 30 °C. The X-ray data were summarized in Table 2. Powder diffraction patterns of four Ga(III)Pcs (**5a,b** and **6a,b**) contain the typical reflections of a columnar mesophase of substituted phthalocyanines [52]. The five Bragg reflections having reciprocal spacings of  $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ , which are characteristic of

Table 1

Phase transition temperatures and enthalpy changes for the liquid-crystalline Ga(III)Pcs (**5a,b** and **6a,b**) determined by DSC (heating and cooling rates are 10 °C min<sup>-1</sup>, heating range is from -40 to 250 °C).

Compound	Heating		Cooling		
	C> C	ol <sub>h</sub> ──► I	I> Co	$ol_h \longrightarrow C$	
5a	_	124.93 (6.61)	_	_	
5b	12.81 (34.26)	_	_	8.03 (22.28)	
6a	_	96.63 (0.54)	92.37 (0.94)	_	
6b	11.80 (35.92)	82 31 (0 59)	78.69 (0.84)	8.69 (21.38)	

Table 2

Compound	Lattice constants/Å	Observed spacing/Å	Calculated spacing/Å	Ratio	Miller indices
5a	a = 31.69	27.42	27.41	1	(100)
		15.72	15.71	√3	(110)
		13.68	13.67	$\sqrt{4}$	(200)
		10.35	10.34	√7	(210)
		4.36	4.36		
		3.54	3.54		
5b	a = 38.07	32.93	32.91	1	(100)
		19.02	19.01	√3	(110)
		16.50	16.49	$\sqrt{4}$	(200)
		12.48	12.47	√7	(210)
		10.97	10.97	√9	(300)
		4.26	4.26		
		3.53	3.53		
		3.46	3.46		
6a	a = 28.82	24.93	24.92	1	(100)
		14.47	14.46	√3	(110)
		12.52	12.51	$\sqrt{4}$	(200)
		9.48	9.48	√7	(210)
		8.35	8.34	√9	(300)
		4.13	4.13		
		3.72	3.72		
6b	a = 34.48	29.83	29.81	1	(100)
		17.08	17.06	√3	(110)
		14.81	14.81	$\sqrt{4}$	(200)
		11.37	11.37	√7	(210)
		4.33	4.33		
		3.62	3.62		

X-ray diffraction data of liquid-crystalline Ga(III)Pcs (**5a,b** and **6a,b**).

a two-dimensional hexagonal lattice as in the columnar mesophase were observed. The mesophase could be established as a discotic hexagonal columnar (Col<sub>h</sub>) mesophase in the low angle region of the XRD pattern. In the wide angle region the compounds show a diffused halo around 4.30 Å ( $2\theta \approx 20^{\circ}$ ) which is compatible with the disorder of paraffinic tails in the side chains. Another reflection around 3.55 Å ( $2\theta \approx 25^{\circ}$ ) which is attributed to the stacking distance of phthalocyanine cores within the columns [16,22,53].

The lattice constant (**a**) was calculated with d-spacing and miller indices,  $hkl[1/d^2 = 4/3(h^2 + hk + k^2/a^2)]$  (Table 2). The lattice constant corresponds to the distance between the axes of two neighboring columns. The diameter of the aromatic core can be estimated as 15 Å and the alkyl chains extended the diameter of columns to 31.69 Å (for **5a**), 38.07 Å (for **5b**), 28.82 Å (for **6a**), and 34.48 Å (for **6b**). The linear increase of lattice constant with increasing the length of chain was folded as expected. The *peripheral tetra*-substituted complexes (**5a**,**b**) have a large value than *non-peripheral tetra*-substituted complex (**6a**,**b**). This result suggests that the side chains require more space in compound **5a**,**b** because of the positions of substitution and causes an increase in inter-columnar distance.

#### 3.3. Ground state electronic absorption and fluorescence spectra

The ground state electronic absorption spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical of metalated phthalocyanine complexes [54], Fig. 3. In toluene, the Q bands were observed at: 708 for **5a**, 711 for **5b**, 733 for **6a** and 734 for **6b**. The Q bands of the *non-peripheral tetra*-substituted Ga(III)Pc complexes **6a** and **6b** are red-shifted 25 and 23 nm, respectively when compared to the corresponding *peripheral tetra*-substituted Ga(III)Pc complexes **5a** and **5b** in toluene. The observed red spectral shift is typical of phthalocyanines with substituents at the *nonperipheral* positions and has been explained [55,56] to be due to linear combinations of the atomic orbital (LCAO) coefficients at the



Fig. 3. Absorption spectra of tetra-substituted Ga(III)Pcs in toluene. Concentration  $\sim 1.2\,\times\,10^{-5}$  M.

*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 ( $\Delta E$ ) between the HOMO and Lowest Unoccupied Molecular Orbital (LUMO) becomes smaller, resulting in a bathochromic shift. The shoulder between 400 and 500 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<sub>1</sub> and B<sub>2</sub> bands in the 340–360 nm region [55].

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 behavior of the *tetra*-substituted Ga(III)Pc complexes (**5a,b** and **6a,b**) were investigated in different solvents (chloroform, dichloromethane, THF and toluene), (Fig. 4 for complex 6a as an example). While the all synthesized Ga(III)Pc complexes did not showed aggregation in chloroform, THF and toluene, they showed a little aggregation in dichloromethane. The aggregation behavior of the *tetra*-substituted Ga(III)Pc complexes (**5a,b** and **6a,b**) were also investigated at different concentrations in toluene. In toluene, 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 studied Ga(III)Pc complexes (5a,b and 6a,b), (Fig. 5 for complex 5a as an example). Beer–Lambert law was obeyed for all of the compounds in the concentrations ranging from  $1.8 \times 10^{-5}$  to  $8 \times 10^{-6}$  M.



**Fig. 4.** UV–Vis spectra of **6a** in different solvents. Concentration =  $1.2 \times 10^{-5}$  M.



Fig. 5. Aggregation behavior of 5a in toluene at different concentrations:  $18 \times 10^{-6}$  (A),  $16 \times 10^{-6}$  (B),  $14 \times 10^{-6}$  (C),  $12 \times 10^{-6}$  (D),  $10 \times 10^{-6}$  (E),  $8 \times 10^{-6}$  (F) M. (Inset: Plot of absorbance versus concentration).

The *tetra*-substituted Ga(III)Pc complexes (**5a,b** and **6a,b**) showed the same fluorescence behavior in toluene. Fig. 6 shows fluorescence emission, absorption and excitation spectra for complex **5b** as an example in toluene. Fluorescence emission peaks were observed at: 720 nm for **5a**, 722 nm for **5b**, 741 nm for **6a** and 745 nm for **6b** in toluene (Table 3). The observed Stokes shifts were typical of MPc complexes in toluene (Table 3).

The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra in toluene (Fig. 6 for complex **5b** as an example) for all substituted Ga(III)Pc complexes (**5a,b** and **6a,b**). The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for all complexes suggests that the nuclear configurations of the ground and excited states were similar and not affected by excitation in toluene.

## 3.4. Photophysical and photochemical properties

Photophysical and photochemical properties of phthalocyanine complexes are very useful for photocatalytic application such as



Fig. 6. Absorption, excitation and emission spectra for compound 5b in toluene. Excitation wavelength = 680 nm.

PDT agents for cancer treatments. In particular, the singlet oxygen quantum yields give an indication of the efficiency of the potential of these photosensitizers in PDT applications.

### 3.4.1. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields ( $\Phi_F$ ) of *tetra*-substituted Ga(III) Pcs (**5a,b** and **6a,b**) are typical of MPc complexes, Table 4. The *peripheral tetra*-substituted Ga(III)Pc complex **5b** shows marginally larger  $\Phi_F$  values among the investigated Ga(III)Pcs.

Fluorescence lifetimes  $(\tau_F)$  were calculated using the Strickler– Berg equation. Using this equation, a good correlation has been [33] 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 an appropriate measure of fluorescence lifetimes. The  $\tau_F$  values were within the range reported for MPc complexes [33]. The *peripheral* 

Table 3

Absorption, excitation and emission spectral data for alkylthio substituted Ga(III)Pcs  $({\bf 5a,b} \ {\rm and} \ {\bf 6a,b})$  in toluene.

Compound	Q band λ <sub>max</sub> , (nm)	$(\log \epsilon)$	Excitation λ <sub>Ex</sub> , (nm)	Emission λ <sub>Em</sub> , (nm)	Stokes shift $\Delta_{\text{Stokes}}$ , (nm)
5a	708	5.01	709	720	12
5b	711	5.05	713	722	11
6a	733	5.22	734	741	8
6b	734	5.30	735	745	11

#### Table 4

Photophysical and photochemical parameters of alkylthio substituted Ga(III)Pcs (**5a,b** and **6a,b**) in toluene.

Compound	$\Phi_{\text{F}}$	$\tau_F(ns)$	$\tau_{0}\left(ns\right)$	$^{a}k_{F}\left( s^{-1}\right) (\times 10^{7})$	$\Phi_d~(\times 10^{-5})$	$\Phi_{\Delta}$
5a	0.14	1.82	12.89	7.70	0.24	0.40
5b	0.16	2.08	13.02	7.67	0.89	0.43
6a	0.12	1.24	10.34	9.67	3.43	0.50
6b	0.10	0.94	8.17	12.21	1.58	0.65

<sup>a</sup> k<sub>F</sub> is the rate constant for fluorescence. Values calculated using  $k_F = \Phi_F/\tau_F$ .



Fig. 7. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **6a** in toluene at a concentration of 1 × 10<sup>-5</sup> M (Inset: Plots of DPBF absorbance versus time).

*tetra*-substituted Ga(III)Pc complexes (**5a,b**) show larger  $\tau_F$  values than the *non-peripheral tetra*-substituted Ga(III)Pc complexes (**6a,b**).

The non-peripheral substituted complexes showed larger rate constants for fluorescence ( $k_F$ ) values than the peripheral tetrasubstituted complexes in toluene (Table 4). The peripheral tetrasubstituted complexes showed larger natural radiative lifetime ( $\tau_0$ ) values, compared to peripheral tetra-substituted complexes in toluene (Table 4). Fluorescence quantum yield ( $\Phi_F$ ) and lifetime ( $\tau_F$ ) values of employed Ga(III)Pc complexes (**5a,b** and **6a,b**) resemble those of substituted Pcs in the literature [29–32,57].

#### 3.4.2. Singlet oxygen quantum yields

Singlet oxygen quantum yields ( $\Phi_{\Delta}$ ) were determined in toluene using 1,3-diphenylisobenzofuran (DBPF) as a chemical quencher. The disappearance of DPBF 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 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 ( $\Phi_{\Delta}$ ) the photodegradation of complexes was not observed during singlet oxygen studies as shown by Fig. 7 for complex **6a** (as an example) in toluene. There was no decrease in the Q band or formation of new bands. The  $\Phi_{\Delta}$  values of the *non-peripheral tetra*-substituted Ga(III)Pc complexes were higher than those of the *peripheral tetra*-substituted Ga(III)Pc complexes in toluene. This suggests that the higher  $\Phi_{\Delta}$  values of *non-peripheral tetra*-substituted Pc complexes (**6a,b**) could be due to the red-shift of the Q bands for these complexes when compared to the *peripheral tetra*-substituted phthalocyanine complexes



Fig. 8. Fluorescence emission spectral changes of 6a (1.00 × 10<sup>-5</sup> M) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.



**Fig. 9.** Stern–Volmer plots for benzoquinone (BQ) quenching of *tetra*-substituted gallium(III) phthalocyanines (**5a–b** and **6a–b**). [MPc]  $\sim 1.00 \times 10^{-5}$  M in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

(**5a,b**). The  $\Phi_{\Delta}$  values, found in this study, are similar to Ga(III)Pc derivatives having different substituents on the phthalocyanine ring reported in the literature [29–32,57].

#### 3.4.3. 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 their absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation. The spectral changes observed for all the Ga(III)Pc complexes (**5a,b** and **6a,b**) during irradiation confirm photodegradation occurred without phototransformation. All the complexes showed about the same stability with  $\Phi_d$  of the order of  $10^{-5}$ . Stable phthalocyanine molecules show  $\Phi_d$  values as low as  $10^{-6}$  and for unstable molecules, values of the order of  $10^{-3}$  have been reported [58]. It seems gallium metal and alkyl chains decreases the  $\Phi_d$  values and increases the stability of phthalocyanine complexes. The  $\Phi_d$  values of the *peripheral tetra*-substituted Ga(III)Pc complexes (**5a,b**) are higher than those of the *non-peripheral tetra*-substituted Ga(III)Pc complexes (**6a,b**) in toluene.

## 3.4.4. Fluorescence quenching studies by 1,4-benzoquinone [BQ]

The fluorescence quenching of *tetra*-substituted Ga(III)Pc complexes by 1,4-benzoquinone (BQ) in toluene was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 8 shows the quenching of complex **6a** by BQ in toluene as an example. The slope of the plots shown in Fig. 9 gave K<sub>SV</sub> values, listed in Table 5. The increase of the length of the alkyl chain (from C12 to C16) decreased the K<sub>SV</sub> values of the complexes. When compared **5a** showed the highest K<sub>SV</sub> value in toluene, while complex **5b** showed the lowest K<sub>SV</sub>. The order in the bimolecular quenching constant (k<sub>q</sub>) values among the substituted complexes was as follows: **6b** > **6a** > **5a** > **5b** in toluene.

#### Table 5

Fluorescence quenching data for unsubstituted ZnPc and alkylthio substituted Ga (III)Pcs (**5a,b** and **6a,b**) in toluene.

Compound	$K_{SV} (M^{-1})$	$k_q/10^{10}$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
5a	21.82	1.19
5b	15.63	0.75
6a	19.69	1.59
6b	18.22	1.93

#### 4. Conclusions

In this work, we have synthesized and characterized the first examples of C12 or C16 alkylthio substituted liquid-crystalline Ga (III)Pcs. The mesogenic properties of these Ga(III)Pcs have been investigated and these compounds showed Col<sub>h</sub> liquid-crystalline properties over a wide temperature range encompassing room temperature. The photophysical and photochemical properties of the synthesized Ga(III)Pc have also been investigated in toluene. In toluene solution, the spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical of metalated phthalocyanine complexes for all studied Ga(III)Pc complexes (5a,b and **6a,b**) in this study. We have studied the aggregation behavior of these new Ga(III)Pc complexes (5a,b and 6a,b) in different solvents and different concentration in toluene. The substituted Ga(III)Pc complexes have showed similar and typical fluorescence behavior in toluene. The substituted Ga(III)Pc complexes (5a-b and 6a-b) have got good singlet oxygen quantum yields. It seems gallium metal and alkyl chains decreases the  $\Phi_d$  values and increases the stability of phthalocyanine complexes in toluene. The main aim of this study is to develop new liquid-crystalline phthalocyanine complexes using gallium(III) atom as the central metal. The future work of this study will focus on the investigation of the non-linear optical (NLO) and the optical limiting properties of these compounds considering the effects of the orientation of Pc molecules on optical limiting and NLO properties in liquid-crystalline phase.

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