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

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The synthesis, liquid crystalline, photophysical and photochemical properties of the *peripheral*- and *non-peripheral-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 $^1$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.

## 1. Introduction

Phthalocyanines (Pcs) are highly delocalized π-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 $(CnS)_8PcH_2$, $n = 8$, 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

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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, $K_2CO_3$, 1,3-diphenylisobenzofuran (DPBF), 1,5-diazabicyclo[4.3.0]non-5-ene (DBU), deuterated $CDCl_3$, 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 $F_{254}$.

### 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. $^1$H NMR spectra were recorded in $CDCl_3$ 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$^e$ Thermal Analysis System/DSC 822$^e$ with scan rate of 10 °C min$^{-1}$. 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]

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

where F and $F_{Std}$ are the areas under the fluorescence emission curves of the Ga(III)Pcs (**5a,b** and **6a**) and the standard, respectively. A and $A_{Std}$ are the relative absorbance of the sample and standard at the excitation wavelength, respectively. n and $n_{Std}$ 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 PhotochemCAD program which uses the Strickler–Berg equation [36]. The fluorescence lifetimes ($\tau_F$) were evaluated using Equation (2).

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

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$^{-5}$ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation 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 $\Phi_\Delta$:

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

where $\Phi_\Delta^{Std}$ is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{Std} = 0.58$ in toluene) [40]. R and $R_{Std}$ are the DPBF photobleaching rates in the presence of the respective Ga(III)Pcs (**5a,b** and **6a,b**) and standard, respectively. $I_{abs}$ and $I_{abs}^{Std}$ are the rates of light absorption by the Ga(III)Pcs (**5a,b** and **6a,b**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [41] the concentration of quencher was