

# The synthesis and photophysical properties of water soluble tetrasulfonated, octacarboxylated and quaternised 2,(3)-tetra-(2 pyridiloxy) Ga phthalocyanines

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## Abstract

The photophysical behaviour of chlorogallium 2,(3)-tetra-(2 pyridiloxy) phthalocyanine (ClGaT-2-PyPc) and its quaternised derivative were compared with that of the water soluble anionic tetrasulfonated gallium phthalocyanine ((OH)GaTSPc) and hydroxy gallium octacarboxy phthalocyanine ((OH)GaOCPc). Although both the quaternised compound and the tetrasulfonated gallium phthalocyanine aggregated in aq. solution at pH 11, resulting in low fluorescence and triplet yields, the presence of the surfactant *Cremophore EL* improved yields. Triplet quantum yields ranged from 0.52 to 0.70 and fluorescence quantum yields ranged from <0.01 to 0.21. The nature of substituent (sulfonate, carboxy and pyridiloxy) did not influence photophysical properties. Chlorogallium 2,(3)-tetra-(2 pyridiloxy) phthalocyanine and its quaternised derivative displayed longer triplet lifetime than both the tetrasulfonated gallium phthalocyanine ((OH)GaTSPc) and hydroxy gallium octacarboxy phthalocyanine in DMSO and in aq. media in both the presence and absence of surfactant.

## 1. Introduction

The synthesis of novel metallophthalocyanine (MPc) derivatives has become very important in recent years owing to their applications in various scientific, medicinal and nanotechnological areas. This family of aromatic macrocycles are important because of their extensive delocalized  $18\pi$  electron system and high stability and have been extensively studied [1] as nonlinear optical (NLO) devices [2], photosensitizers for dye sensitised solar cells (DSSC) [3] and [4], liquid crystals, Langmuir–Blodgett films, electrochromic devices [5], [6], [7], [8], [9], [10] and [11] and in fields such as photodynamic therapy of cancer (PDT) [12], [13] and [14]. Water soluble phthalocyanines exist as loosely associated aggregates that are not chemically bound in aqueous solution and which can be dissociated by surfactants or by non-aqueous solvents [15], [16] and [17]. Aggregation occurs as a result of solvent effects that alter the chemical properties of the MPc complexes leading to co-planar association of the aromatic rings [18], [19], [20], [21], [22] and [23]. MPc complexes that contain central metals (e.g. Ga(III)) and axial ligands may display reduced aggregation as the axial ligands act as spacers between the rings. Although the aggregation tendency of Pcs in aqueous medium is problematic, water solubility is an additional advantage for application in, for example, PDT, since they can be injected directly into the bloodstream.

This work concerns the synthesis of novel, cationic as well as anionic, gallium phthalocyanines tetrasubstituted at peripheral positions with 2-pyridiloxy groups and octasubstituted with carboxy groups, respectively. The complexes in question are chlorogallium 2,(3)-tetra-(2 pyridiloxy) phthalocyanine (ClGaT-2-PyPc), its quaternised derivative (QClGaT-2-PyPc) and hydroxy gallium octacarboxy phthalocyanine ((OH)GaOCPc), the latter two compounds being water soluble. The current authors have recently reported the synthesis and photophysical behaviour of chlorogallium 2,(3)-tetra-(3 pyridiloxy) phthalocyanine (ClGaT-3-PyPc), which differ in terms of the placement of the nitrogen of the pyridine group, and its quaternised (hence water soluble) derivative (QClGaT-3-PyPc) [24] and [25]. In this work the photophysical behaviour of the novel complexes ClGaT-2-PyPc and QClGaT-2-PyPc are compared with those of ClGaT-3-PyPc, QClGaT-3-PyPc. Although the synthesis of water soluble anionic tetrasulfonated gallium phthalocyanine ((OH)GaTSPc) has been previously reported [26] and [27], its photophysical properties are not known; similarly, whilst (OH)GaOCPc is also known [28] its photophysical behaviour is not.

## 2. Experimental and method

## 2.1. Materials

*Cremophore EL* (CEL), pyromellitic dianhydride, 4-sulfophthalic acid, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), urea, ammonium chloride and ammonium molybdate were obtained from Aldrich. Quinoline, dimethylsulphoxide (DMSO), methanol, n-hexane, chloroform (CHCl<sub>3</sub>), dichloromethane (DCM), tetrahydrofuran (THF), acetone, ethanol and dimethylformamide (DMF) were dried according to reported procedures [29] before use. 2-Tydropyridine, deuterated D<sub>2</sub>O, DMSO-*d*<sub>6</sub>, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), gallium(III) chloride, and dimethyl sulphate (DMS) were also obtained from Aldrich. Phosphate-buffered saline (PBS) solution pH 11 was prepared using appropriate amounts of Na<sub>2</sub>HPO<sub>4</sub> (0.005 mol) and NaOH (8.2 × 10<sup>-4</sup> mol) in 100 mL distilled water. All other reagents were obtained from commercial supplies and used as received. Zn tetrasulpho phthalocyanine (ZnTSPc) was synthesized according to well known procedures [30]. Zinc phthalocyanine was purchased from Aldrich.

## 2.2. Equipment

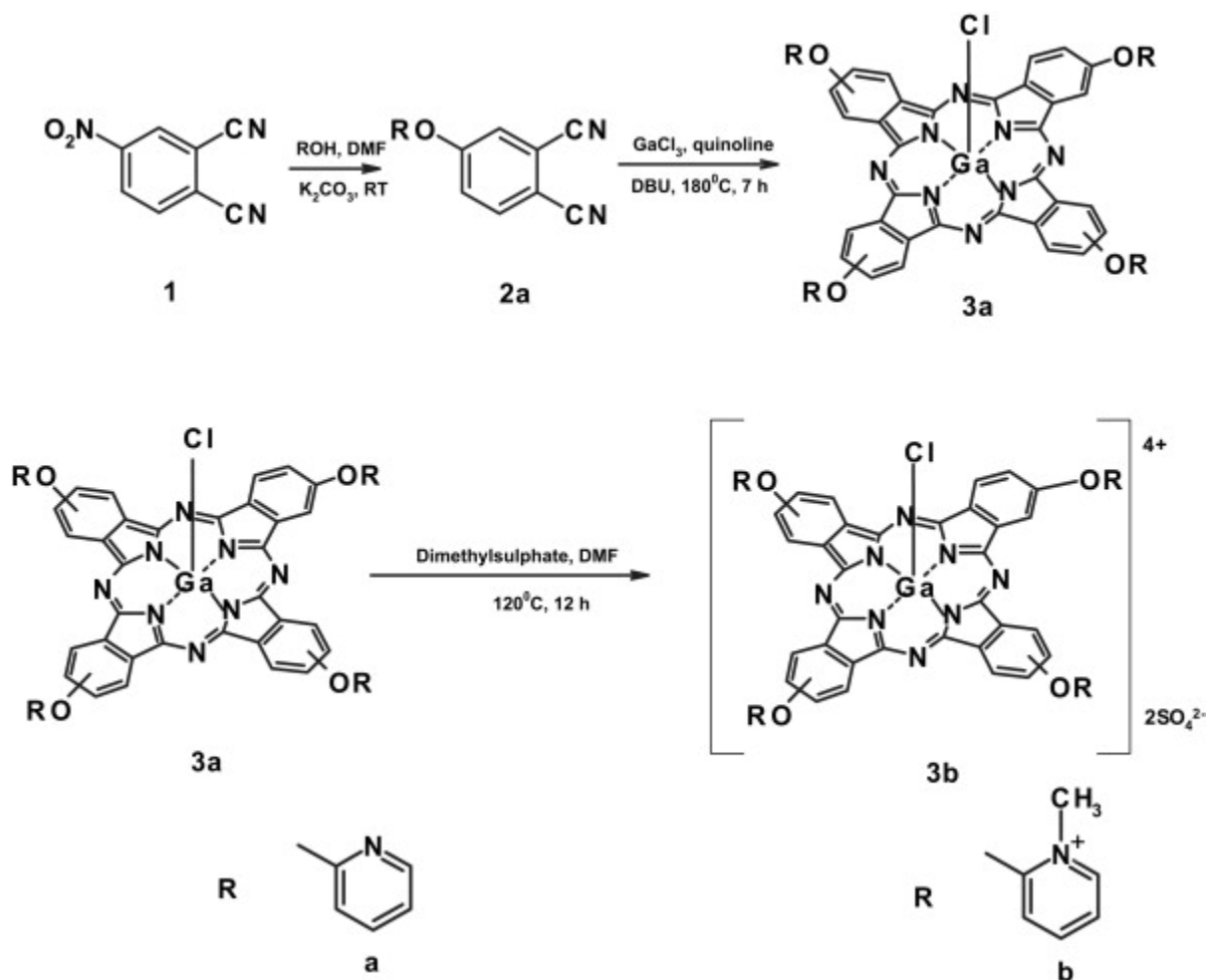
Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer. UV–visible spectra were recorded on a Varian 500 UV–Vis/NIR spectrophotometer. IR spectra (KBr pellets) were recorded on a Perkin–Elmer spectrum 2000 FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer. Laser flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd: YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda -Physik FL3002 dye (Pyridin 1 dye in methanol). Single pulse energy ranged from 2 to 7 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a digital real-time oscilloscope (Tektronix TDS 360). The triplet lifetimes were then determined by exponential fitting of the kinetic curves using the program OriginPro 7.5. Maldi-TOF mass spectrometry was carried out at the University of Stellenbosch using an ABI Voyager DE-STR Maldi-TOF instrument.

## 2.3. Synthesis

The synthesis of 4-(2-pyridyloxy)phthalonitrile (**2a**) has been reported before [31].

### 2.3.1. 2,(3)-(Tetra-2-pyridyloxyphthalocyaninato) gallium (III) chloride (Scheme 1, (ClGaT-2-PyPc, **3a**))

A mixture of anhydrous gallium (III) chloride (0.60 g, 3.4 mmol), 2-pyridyloxyphthalonitrile (**2a**) (1.50 g, 6.8 mmol) and quinoline (5 mL, doubly distilled over CaH<sub>2</sub>) was stirred at 180 °C for 7 h under nitrogen atmosphere. The solution was then cooled and dropped in n-hexane. The green solid product was precipitated and collected by centrifugation and washed with n-hexane. The crude product was dissolved in DMF. After concentrating, the dark green waxy product was precipitated with hot ethanol and washed according to reported procedure [31] with ethanol, acetone, THF, CHCl<sub>3</sub>, n-hexane and diethylether in a Soxhlet extraction apparatus.



Scheme 1. Synthesis of 2,3-(tetra-pyridyloxypthalocyaninato) gallium (III), (ClQGaT-2-PyPc) (**3a**) and water soluble quaternised 2,3-(tetra-pyridyloxypthalocyaninato)gallium (III), QClGaT-2-PyPc (**3b**).

Yield: (64%). IR (KBr,  $cm^{-1}$ ): 3439(O–H), 3102(C–H), 1564(C=C), 1474, 1235, 1092(C–O–C), 843, 748.  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$ , ppm 8.95–9.14 (4H, m, Pc-H), 9.25–9.38 (4H, d, Pc-H), 9.64–9.67 (4H, m, Pc-H), 8.21–8.29 (4H, br, Pyridyl-H), 8.10–8.14 (8H, m, Pyridyl-H), 7.83–7.95 (4H, br, Pyridyl-H). UV/Vis (DMF)  $\lambda_{max}$  nm (log  $\epsilon$ ): 340 (3.20), 686 (4.43). Calc. for  $C_{52}H_{28}ClN_{12}O_4Ga$ : C 63.08, H 2.83, N 16.98; Found: C 62.61, H 2.53 N 16.81.

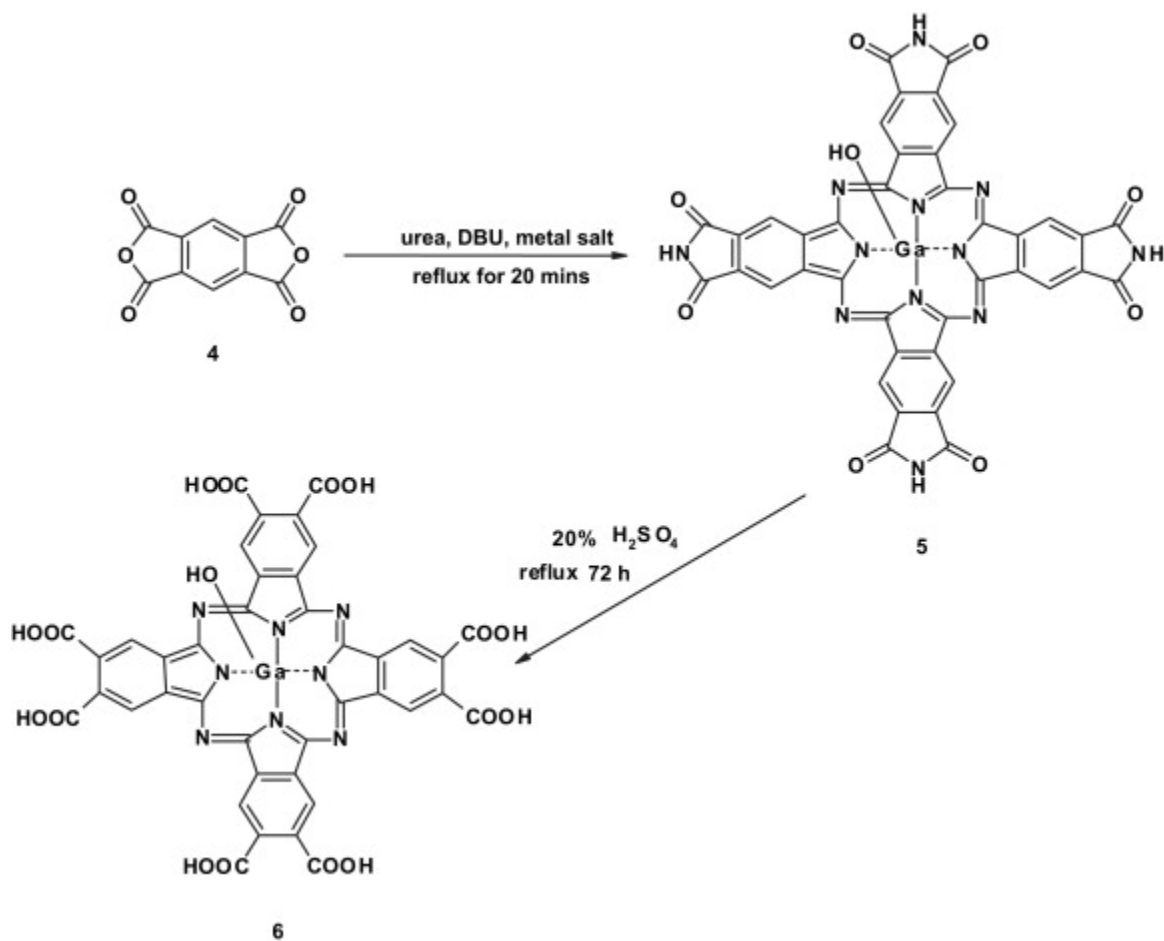
### 2.3.2. Quaternarized 2,3-(tetra-pyridyloxypthalocyaninato) gallium (III) chloride (Scheme 1, QClGaT-2-PyPc, **3b**)

This molecule was synthesized according to the reported literature procedure [32]. Complex **3a** (100 mg, 0.1 mmol) was heated to  $120^\circ C$  in freshly distilled DMF (0.5 ml) and dimethyl sulphate (0.2 ml) was added drop-wise. The mixture was stirred at  $120^\circ C$  for 12 h. After this time, the mixture was cooled to room temperature and the product was precipitated with hot acetone and collected by centrifugation. The green solid product was washed successively with hot ethanol, ethyl acetate, THF, chloroform, n-hexane and diethylether under Soxhlet extraction. The resulting hygroscopic product was dried over phosphorous pentoxide.

Yield: (75%). IR (KBr,  $\text{cm}^{-1}$ ): 3132(C-H), 1569(C=C), 1501, 1474, 1403, 1384, 1276(S=O), 1097(S=O), 1061(C-O-C), 1007, 749, 668,617.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$ , ppm 8.84–9.46 (28H, m, Pc-H and Pyridyl-H), 3.95–4.31 (12H, m,  $\text{CH}_3$ ): UV/Vis (pH 11/CEL)  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ ): 350 (4.10), 679(4.81): Calc. for  $\text{C}_{56}\text{H}_{46}\text{ClN}_{12}\text{O}_{14}\text{S}_2\text{Ga}$  ( $4\text{H}_2\text{O}$ ): C 50.93, H 3.48, N 12.73; Found: C 50.46, H 2.97, N 13.66. MALDI-TOF MS  $m/z$ : Calcd: 1014.4 amu. Found: (M - Cl) 1015.3 amu.

### 2.3.3. Hydroxy gallium octacarboxy phthalocyanine (Scheme 2, (OH)GaOCPC, 6)

(OH)GaOCPC was synthesized, purified and characterized according to the established literature methods for similar complexes [33]. Benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride (**4**); (caution: flammable, hazardous) 2.50 g 11.5 mmol), urea (13.0 g, 0.22 mol),  $\text{GaCl}_3$  (0.72 g, 4.1 mmol) and DBU (0.1 g, 0.7 mmol) were heated to  $250^\circ\text{C}$  in a flask until the reaction mixture was fused. The reaction products were washed with water, acetone and 6 M hydrochloric acid (HCl), forming the solid product **5**, which was not purified any further following literature [33]. To form the final product **6**, complex **5** was dried and hydrolyzed in 20%  $\text{H}_2\text{SO}_4$  for a period of 72 h. Then the product was purified as explained in literature [33].

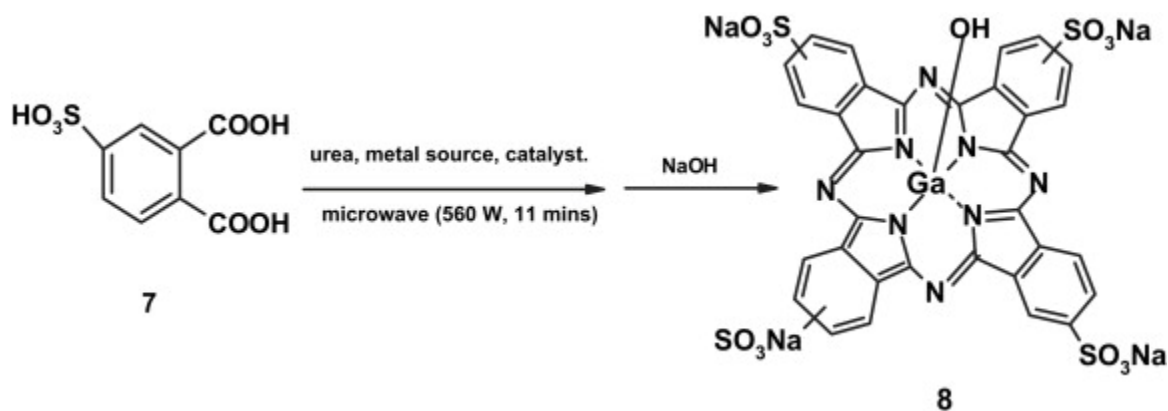


Scheme 2. Synthesis of gallium octacarboxy phthalocyanine, ((OH)GaOCPC) (6).

Yield: (34%). IR (KBr,  $\text{cm}^{-1}$ ): 3423(OH), 3029 (C–H), 2781, 1724(C=O), 1466, 1398, 1399, 1283, 1186(C–O or O–H) 1054, 772, 536.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ): 8.73–8.78 (8H, s, Pc-H), 4.81–4.86 (8H, s, Carboxylic-H). UV/Vis (pH 11):  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ ) 360 (3.41), 688(4.52) nm. Calc. for  $\text{C}_{40}\text{H}_{17}\text{N}_8\text{O}_{17}\text{Ga}$  ( $18\text{H}_2\text{O}$ ): C 37.67, H 4.16, N 8.79; Found: C 37.03, H 3.71, N 8.55. MALDI-TOF MS  $m/z$ : Calcd: 951.2 amu. Found: (M + 1) 952.4 amu.

#### 2.3.4. Hydroxy gallium tetrasulfo phthalocyanine (Scheme 3, (OH)GaTSPc, 8)

The (OH)GaTSPc was synthesized and purified according to the microwave procedure for SnTSPc [34]. Briefly, a mixture of commercially available 50% aqueous 4-sulfophthalic acid solution (7) (4 g, 8.12 mmol), urea (1.95 g, 32 mmol), and  $\text{GaCl}_3$  (0.72 g, 4.1 mmol) in the presence of ammonium chloride (1.56 g, 29 mmol) and ammonium molybdate (0.17 g, 0.14 mmol) as catalysts, was irradiated in a microwave oven at 560 W for 15 min. The mixture was then added to aqueous sodium hydroxide solution (100 ml, 10 wt.%), heated until it boiled, and cooled to the room temperature. The solution was then poured into methanol (50 ml), and then *i*-propyl alcohol (100 ml) was added to precipitate the product. The complex was purified by following literature methods [34] in addition to Soxhlet extraction of impurities using methanol and ethanol.



Scheme 3. Microwave synthesis of gallium tetrasulfonated phthalocyanine, ((OH)GaTSPc) (8).

Yield: (47%). IR (KBr,  $\text{cm}^{-1}$ ): 3432(OH), 2046, 1669, 1631(C=C), 1401, 1195, 1136(S=O), 904, 686, 584.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ): 8.31–8.33(4H, s, Pc-H), 8.01–8.06 (8H, d, Pc-H), 6.60–6.63(1H s-br.O–H). UV/Vis  $\lambda_{\text{max}}$ (nm) ( $\log \epsilon$ ) (pH 11/CEL): 380 (3.74), 678 (4.96) nm. Calc. for  $\text{C}_{32}\text{H}_{13}\text{N}_8\text{O}_{13}\text{S}_4\text{Na}_8\text{Ga}$  ( $2\text{H}_2\text{O}$ ): C 33.85, H 1.50, N 9.87; Found: C 34.13, H 2.06, N 9.68. MALDI-TOF MS  $m/z$ : Calcd: 898.4 amu. Found: (M – OH) 898.9 amu.

#### 2.4. Fluorescence and photophysical studies

Fluorescence quantum yields ( $\Phi_F$ ) were determined by comparative method [35] (Equation (1)),

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

where  $F$  and  $F_{\text{Std}}$  are the areas under the fluorescence curves of the MPc derivatives and the used standard.  $A$  and  $A_{\text{Std}}$  are the absorbances of the sample and reference at the excitation wavelength, and  $n$  and  $n_{\text{Std}}$  are the refractive indices of solvents used for the sample and standard, respectively. ZnPc in DMSO was used as a standard,  $\Phi_F = 0.2$  [36]. For each study at least two independent experiments were performed for the quantum yield determinations. Both the sample and the standard were excited at the same relevant wavelength.

Triplet quantum yields were determined using a comparative method based on triplet decay, using Equation (2):

(2)

$$\Phi_T^{\text{Sample}} = \Phi_T^{\text{Std}} \frac{\Delta A_{\text{Sample}}^{\text{Std}}}{\Delta A_{\text{Std}}^{\text{Sample}}}$$

where  $\Delta A_{\text{T}}^{\text{Sample}}$  and  $\Delta A_{\text{T}}^{\text{Std}}$  are the changes in the triplet state absorbance of the sample and the standard, respectively.  $\epsilon_{\text{T}}^{\text{Sample}}$  and  $\epsilon_{\text{T}}^{\text{Std}}$  are the triplet state extinction coefficients for the sample and standard, respectively.  $\Phi_T^{\text{Std}}$  is the triplet state quantum yield for the standard. ZnTSPc in aqueous solution,  $\Phi_T^{\text{Std}} = 0.56$  [37], unsubstituted ZnPc in DMSO,  $\Phi_T^{\text{Std}} = 0.65$  [37] and unsubstituted ZnPc in DMF  $\Phi_T^{\text{Std}} = 0.58$  [38] were used as standards. Quantum yields of internal conversion were obtained from Equation (3) which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet states of the complexes.

(3)

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T)$$

### 3. Results and discussion

#### 3.1. Synthesis and characterisation

Scheme 1, Scheme 2 and Scheme 3 show the synthetic pathways for the compounds used in this work. Substituted phthalocyanines are normally prepared by cyclotetramerization of substituted phthalonitriles. 4-Tetra-substituted phthalocyanines can be synthesized from 4-substituted phthalonitriles (**2a**) Scheme 1 or from commercially available starting materials (**7**) Scheme 3. Octacarboxy phthalocyanines can be synthesized from commercially available pyromellitic dianhydride (**4**) as shown Scheme 2. Sulfonated phthalocyanines can also be obtained from commercially available 4-sulfophthalic acid through microwave synthesis as shown in Scheme 3. The syntheses of all these complexes gave satisfactory spectroscopic analyses. The 2-pyridiloxy substituents on complex **3a** Scheme 1 are suitable for conversion into quaternary ammonium groups and this results in solubility in water. Unquaternised and quaternised metallophthalocyanines (Scheme 1) were obtained in the presence of metal salts and substituted phthalonitriles. Complex **3b** was obtained by methylation of **3a** in DMF in the presence of dimethylsulfate and good yields were obtained. The non-ionic complex **3a** in this study was soluble in organic solvents such as DCM, DMF and DMSO and the ionic complex **3b** was highly soluble in polar solvents like water, methanol and DMSO. Octacarboxy phthalocyanine ((OH)GaOCPC) Scheme 2 was highly soluble and monomeric in alkaline medium and gave similar spectroscopic results to the previously reported metalloctacarboxy complexes [39]. The synthesis of tetrasulfonated gallium phthalocyanines Scheme 3 has been reported before as stated previously and gave satisfactory spectroscopic results. The OH axial ligand for (OH)GaOCPC and (OH)GaTSPc is a result of work-up procedure. The complexes were characterized by various spectroscopic methods: IR, UV-vis, <sup>1</sup>H NMR and elemental analysis and are consistent with predicted structures. The characteristic of a nitrile stretch at  $\sim 2225 \text{ cm}^{-1}$  (**2a**) disappears upon formation of the phthalocyanine (**3a**), Scheme 1. The <sup>1</sup>H NMR spectra of all the complexes showed aromatic ring protons between 8 and 10 ppm. The presence of isomers as well as phthalocyanine aggregation at the concentrations used for the <sup>1</sup>H NMR measurements leads to broadening of the aromatic signals [40]. However, the peaks integrated correctly giving the expected total number of protons for each complex, confirming the relative purity of the complexes. Mass spectral data was additionally employed to characterise the water soluble complexes, and the data was consistent with the structure of the complexes.

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

The ground state electronic spectra of the QClGaT-2-PyPc Fig. 1a shows that this complex is aggregated in aqueous solution (pH 11), with the presence of two main bands one at  $\sim 678 \text{ nm}$  due to the monomeric species and the other at  $\sim 645 \text{ nm}$  due to the aggregated species. This pH was chosen to allow for the solubility of both

QClGaT-2-PyPc, (OH)GaTSPc and (OH)GaOCPC. The latter is only soluble in highly basic media. Addition of a surfactant, CEL, resulted in a decrease in the intensity of the band due to the aggregates with a slight increase in the intensity and narrowing of the band due to the monomeric species, which confirms that the complexes were aggregated in aqueous solution of pH 11. There was incomplete disaggregation of QClGaT-2-PyPc even after the addition of CEL, as judged by the observation of some broadening in the 640 nm region after addition of CEL in Fig. 1a. In contrast, (OH)GaTSPc was weakly aggregated, Fig. 1b, as judged by less pronounced absorption in the 640 nm region. There was a decrease in absorption in the 640 nm region on addition of CEL, Fig. 1b. There was also a 4 nm red shift of the Q band of the (OH)GaTSPc after addition of CEL, Fig. 1b, Table 1, probably due to change in media.

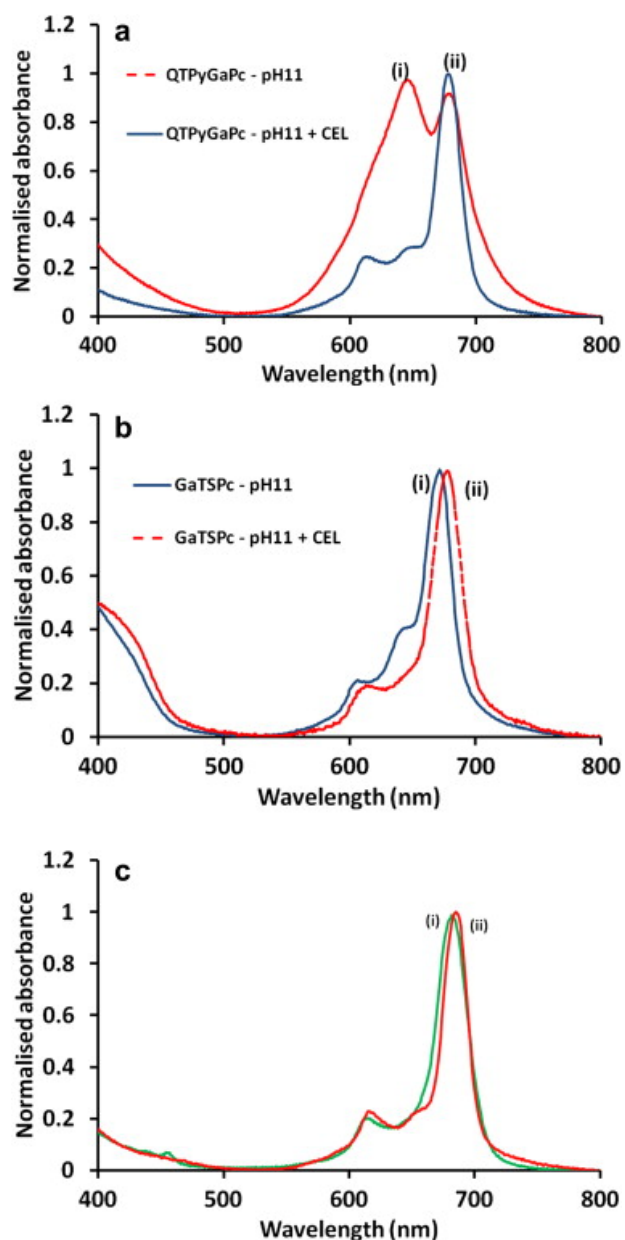


Fig. 1. Ground state electronic absorption spectra of (a) QClGaT-2-PyPc and (b) ClGaTSPc in the absence (i) and presence of (ii) CEL, both in pH 11. (c) ground state electronic absorption spectra of ClGaT-2-PyPc in DMF (i) and (OH)GaOCPC in pH 11 buffer (ii).

Table 1.

Ground state absorption, fluorescence emission and excitation spectral parameters for various MPc complexes.

Complex	Solvent	Q band $\lambda_{\text{abs}}$ (nm)	Excitation $\lambda_{\text{ex}}$ (nm)	Emission $\lambda_{\text{em}}$ (nm)	Stokes shift $\Delta_{\text{stokes}}$
OHGaOCPC	pH 11	688	687	699	17
OHGaTSPc	pH 11	674	674	679	5
OHGaTSPc	pH 11 + CEL	678	675	681	6
QClGaT-2-PyPc	pH 11	645, 678	680	683	3
QClGaT-2-PyPc	pH 11 + CEL	678	675	682	7
ClGaT-2-PyPc	DMF	686	683	700	17
ClGaT-2-PyPc	DMSO	690	689	701	12
<sup>a</sup> ClGaT-3-PyPc	DMSO	687	686	702	15
<sup>a</sup> QClGaT-3-PyPc	Water	681	681	694	13

<sup>a</sup> Values from Ref. [25].

Unlike the tetrasulfonated and the quaternised complexes, the ground state electronic absorption spectra (Fig. 1c, ii) of (OH)GaOCPC in pH 11 was monomeric  $\sim$ 688 nm which was evident by a single narrow Q band typical of metallated phthalocyanine complexes [16] in aqueous solution. The spectrum of ClGaT-2-PyPc (Fig. 1c, i) in DMF shows characteristic monomeric absorption in the Q band region at 686 nm. The absorption spectra of the monomers in pH 11 (with CEL where needed) varied from 674 for (OH)GaTSPc to 688 nm for (OH)GaOCPC, showing red shifting for the latter. In DMSO, QClGaT-2-PyPc showed blue shifting compared to ClGaT-2-PyPc due to the lowering of the electron donating ability of the nitrogen groups on quaternization as was the case for the corresponding QClGaT-3-PyPc and ClGaT-3-PyPc complexes [24].

Fig. 2 shows that as the concentration was increased for (OH)GaOCPC in pH 11, the intensity of the absorption of the Q band also increased and there were no new bands normally blue shifted due to the aggregated species. Same trend was also observed with the ClGaT-2-PyPc derivatives which did not show aggregation in DMF. Beer-Lambert's law was obeyed for both of these compounds in the concentrations ranging from  $2 \times 10^{-6}$  to  $12 \times 10^{-6}$  mol dm<sup>-3</sup>.



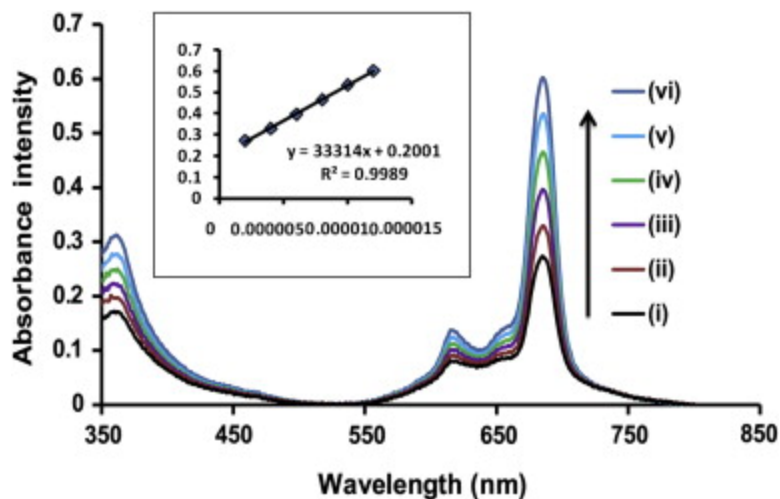


Fig. 2. Ground state absorption spectra of (OH)GaOCPC at various concentrations: (i) =  $2 \times 10^{-6}$ , (ii) =  $4 \times 10^{-6}$ , (iii) =  $6 \times 10^{-6}$ , (iv) =  $8 \times 10^{-6}$ , (v) =  $10 \times 10^{-6}$ , and (vi) =  $12 \times 10^{-6}$  mol dm<sup>-3</sup>.

Fluorescence excitation spectra of (OH)GaTSPc complexes showed a lack of agreement between the absorbance and excitation spectra as shown in Fig. 3a. The band around 640 nm, associated with the dimer is not seen in the fluorescence excitation spectrum since only the monomer fluoresces but there was improvement upon addition of CEL, Fig. 3b. It has been documented before in literature that dimers are non-photoactive [15]. However the absorption spectra was mirror image of the emission spectra for the ClGaT-2-PyPc in (DMF and DMSO) and of the (OH)GaOCPC in pH 11 which is usual for MPc complexes. The Stokes' shifts shown in Table 1 ranged from 3 nm to 17 nm, typical of MPc complexes.

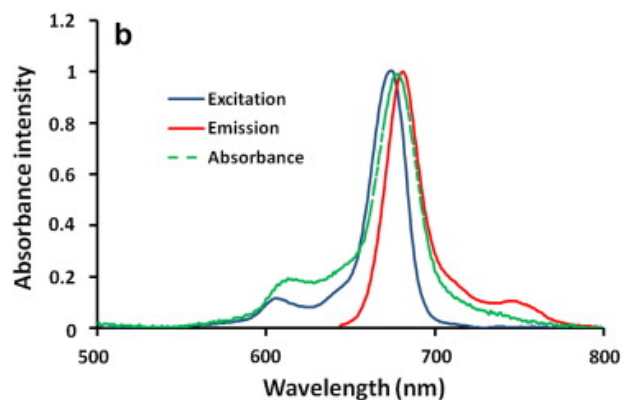
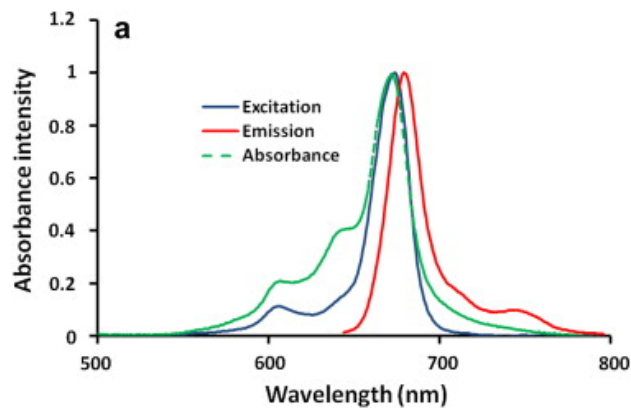


Fig. 3. Absorption, fluorescence emission and excitation spectra of (OH)GaTSPc in pH 11 (a) and in pH 11 + CEL (b), excitation wavelength = 630 nm.

### 3.3. Photophysical parameters

Fig. 4 shows the transient absorption spectrum of (OH)GaOCPc in pH 11. The absorption of the triplet state is at  $\sim 460\text{--}550\text{ nm}$ . The triplet absorption curve of (OH)GaOCPc in pH 11 is shown in Fig. 4 (inset), and it obeyed second order kinetics. This is typical of MPC complexes at high concentrations [41] due to triplet–triplet recombination.

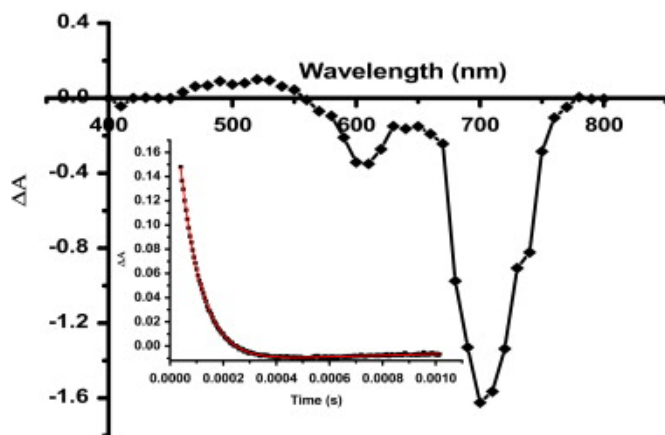


Fig. 4. Transient differential curve for (OH)GaOCPc in pH 11, excitation wavelength = 687 nm and triplet decay curve insert.

Triplet quantum yield  $\Phi_T$  is the measure of the fraction of absorbing molecules that undergo intersystem crossing (isc) to the triplet state. The efficiency of a phthalocyanine as a photosensitizer is determined by its triplet state quantum yield ( $\Phi_T$ ) and lifetime ( $\tau_T$ ). All the complexes showed relatively high triplet yields (Table 2). It has been documented in literature that gallium phthalocyanines give good photochemical and photophysical properties that make them useful for PDT [42]. Unquaternised ClGaT-2-PyPc showed the highest triplet yield in DMSO followed by the (OH)GaOCPc in pH 11 and QClGaT-2-PyPc in pH 11 + CEL. All the three complexes are monomeric in their respective solutions, and monomers have greater tendencies to undergo intersystem crossing because less energy is lost through internal conversion [43]. (OH)GaTSPc, in pH 11 without CEL, showed the lowest triplet yield followed by QClGaT-2-PyPc in pH 11 (without CEL) due to aggregation, but there was a high improvement after addition of CEL for both complexes. The  $\Phi_T$  value for QClGaT-2-PyPc is lower than that reported for QClGaT-3-PyPc in aqueous media [25], Table 2. However the effect of different pH cannot be ignored. The reported data [25] for QClGaT-3-PyPc were in non-buffered water. The determination of triplet yield and lifetime values for QClGaT-2-PyPc in unbuffered water did not make much difference in the values. The  $\Phi_T$  value of unquaternised ClGaT-2-PyPc in DMSO is larger than that of the corresponding ClGaT-3-PyPc [25], Table 2. Since for these complexes, the same media was employed, the differences do suggest that the position of the nitrogen atom on the substituents affects the photophysical behaviour of the complexes.

Table 2.

Photophysical parameters for various excited state deactivation processes of the MPc complexes.

Complex	Solvent	$\Phi_T$	$\tau_T$ ( $\mu$ s)	$\Phi_F$	$\Phi_{IC}$
(OH)GaOCPC	pH 11	0.67	80	0.21	0.12
(OH)GaTSPc	pH 11	0.52	60	0.09	0.39
(OH)GaTSPc	pH 11 + CEL	0.63	80	0.15	0.22
QClGaT-2-PyPc	pH 11	0.55	60	<0.01	0.45
<sup>a</sup> QClGaT-3-PyPc	Water	0.61	50	0.12	0.27
QClGaT-2-PyPc	pH 11 + CEL	0.68	170	0.04	0.28
ClGaT-2-PyPc	DMF	0.59	120	0.16	0.25
ClGaT-2-PyPc	DMSO	0.70	170	0.20	0.10
<sup>a</sup> ClGaT-3-PyPc	DMSO	0.57	160	0.19	0.24

<sup>a</sup> Values from Ref. [25].

The triplet lifetime,  $\tau_T$  values range from 60 to 170  $\mu$ s, for complexes under discussion in this work, which is a usual range for MPc complexes containing heavy metals. (OH)GaOCPC in pH 11 alone gave the same lifetime as (OH)GaTSPc in the presence of CEL, and ClGa-2-PyPc in DMSO gave the same lifetime as QClGa-2-PyPc in the presence of CEL. The triplet lifetimes are highly influenced by the presence of oxygen, however in the work the solutions for triplet lifetimes determinations were deaerated sufficiently before recording of flash photolysis traces. The  $\tau_T$  values for ClGaT-2-PyPc reported in this work in DMSO were marginally higher than those reported for the corresponding ClGaT-3-PyPc [25], Table 2. Similarly for QClGaT-2-PyPc,  $\tau_T$  values are slightly higher than the corresponding QClGaT-3-PyPc in aqueous media [25]. As stated above, pH 11 is employed in this work in order to ensure solubility of all complexes (MOCPC complexes in particular are soluble in basic media). The reported data [25] for QClGaT-3-PyPc were in non-buffered water. Lifetimes were longer in the presence of CEL compared to pH 11 alone for the aggregated complexes ((OH)GaTSPc and QClGaT-2-PyPc), which may be due to the reduction in the exposure of the phthalocyanine in the aqueous medium because of the presence of the CEL and due to monomerization.

The fluorescence quantum yields  $\Phi_F$  of the complexes are also listed in Table 2. The aggregated ((OH)GaTSPc and QClGaT-2-PyPc) complexes showed relatively low yields of fluorescence in pH 11, but there was an improvement on addition of CEL. Aggregation is known to dissipate the electronic energy of the excited singlet state, thereby lowering fluorescence. Thus monomerization of the aggregates enhances fluorescence and this is noticed in the  $\Phi_F$  of the complexes in the presence of CEL. Some of the  $\Phi_F$  values are however low compared to MPcs in general [44].  $\Phi_F$  values were relatively higher for the (OH)GaOCPC and ClGaT-2-PyPc probably due to their monomeric nature. The values of intersystem quantum yields were highest for ClGaT-2-PyPc in pH 11 buffer, Table 2.  $\Phi_F$  values in DMSO are almost the same for ClGaT-3-PyPc and ClGaT-2-PyPc.

#### 4. Conclusion

New peripherally tetrasubstituted unquaternised gallium phthalocyanine (ClGaT-2-PyPc) and its quaternised derivative (QClGaT-2-PyPc), have been synthesized and characterized. Their photophysical properties have been studied and compared with each other and with those of gallium tetrasulfo phthalocyanine ((OH)GaTSPc) and gallium octacarboxy phthalocyanines ((OH)GaOCPC). All these complexes gave good photophysical properties with ClGaT-2-PyPc in DMSO giving the highest triplet quantum yield. QClGaT-2-PyPc and (OH)GaTSPc were aggregated in aqueous solution of pH 11 which resulted in low triplet and fluorescence yield. There was an improvement on the photophysical properties of these molecules when they were studied in the presence of a surfactant (CEL) resulting in increased photoactivity and improved photosensitizing ability. (OH)GaOCPC in pH 11 and (OH)GaTSPc in pH 11 + CEL showed the same trend of triplet lifetimes. High triplet yield for this molecules and their solubility in aqueous solvents showed a potential to be further studied for applications in areas such as photodynamic therapy (PDT).

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