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# Synthesis, photophysical and photochemical properties of aryloxy tetra-substituted gallium and indium phthalocyanine derivatives

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**Abstract**—The synthesis, photophysical and photochemical properties of the tetra-substituted aryloxy gallium(III) and indium(III) phthalocyanines are reported for the first time. General trends are described for photodegradation, singlet oxygen, fluorescence, and triplet quantum yields and triplet lifetimes of these compounds. The introduction of phenoxy and *tert*-butylphenoxy substituents on the ring resulted in lowering of fluorescence quantum yields and lifetimes, and triplet quantum yields, and an increase of $k_{IC}$, $k_{ISC}$, and $k_F$. Photoreduction of the complexes was observed during laser flash photolysis. The singlet oxygen quantum yields ($\Phi_\Delta$), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.41 to 0.91. Thus, these complexes show potential as Type II photosensitizers.


## 1. Introduction

Phthalocyanines, which were first developed as industrial pigments, have been actively exploited in various technological applications such as optical recording photovoltaics, photocopying, gas sensing, liquid crystal, and photodynamic therapy.[1] Phthalocyanines are used in a number of applications due to their increased stability, architectural flexibility, diverse coordination properties, and improved spectroscopic characteristics. Applications in fields such as chemical sensors,[2] liquid crystals,[3] semiconductors,[2b] non-linear optics,[4] and photodynamic therapy (PDT)[5] have shown the increased importance of these macrocycles. Their physicochemical properties can be fine-tuned by changing the metal and/or nature of substituents.[1,6] Although metallophthalocyanine complexes have been extensively studied, their properties cannot be fully exploited as they have low solubility in most organic solvents and they aggregate. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework.[7] Tetra-substituted phthalocyanines are usually more soluble than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery.[7,8] According to their substituent positions, two types of tetra-substituted macrocycles, which show significant differences in their chemical and physical behaviors can be distinguished. Substitution at the more sterically crowded α (non-peripheral) position causes reduced aggregation tendencies more than substitution at β (peripheral) position.[9]

Metallophthalocyanine complexes have proved to be highly promising as photosensitizers for photodynamic therapy (PDT), due to their intense absorption in the red region of the visible light. High triplet state quantum yields and long triplet lifetimes are required for an efficient sensitization. The photophysical properties of the phthalocyanine dyes are strongly influenced by the presence and nature of the central metal ion. Complexation of phthalocyanine with transition metals gives dyes with short triplet lifetimes. Closed shell, diamagnetic ions, such as $Zn^{2+}$, $Al^{3+}$, and $Ga^{3+}$, give phthalocyanine complexes with both high triplet yields and long lifetimes.[5a]

Interestingly, there is a continuous effort to extend the chemistry of metallophthalocyanines. Nonetheless, gallium(III) and indium(III) phthalocyanine chemistry appears not to have been fully explored especially when compared to the development of aluminum (which is the other group IIIA metal) phthalocyanine complexes. Aluminum phthalocyanine complexes have been used as PDT agents. Gallium(III) and indium(III) phthalocyanine complexes

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show non-linear optical behavior. Ring unsubstituted gallium phthalocyanines with axial chloro, fluoro, or hydroxyl ligands were the first phthalocyanines to be investigated for their third-order non-linear behavior,[10] however there are only a few studies of the photochemical and photophysical properties of these compounds.[11]

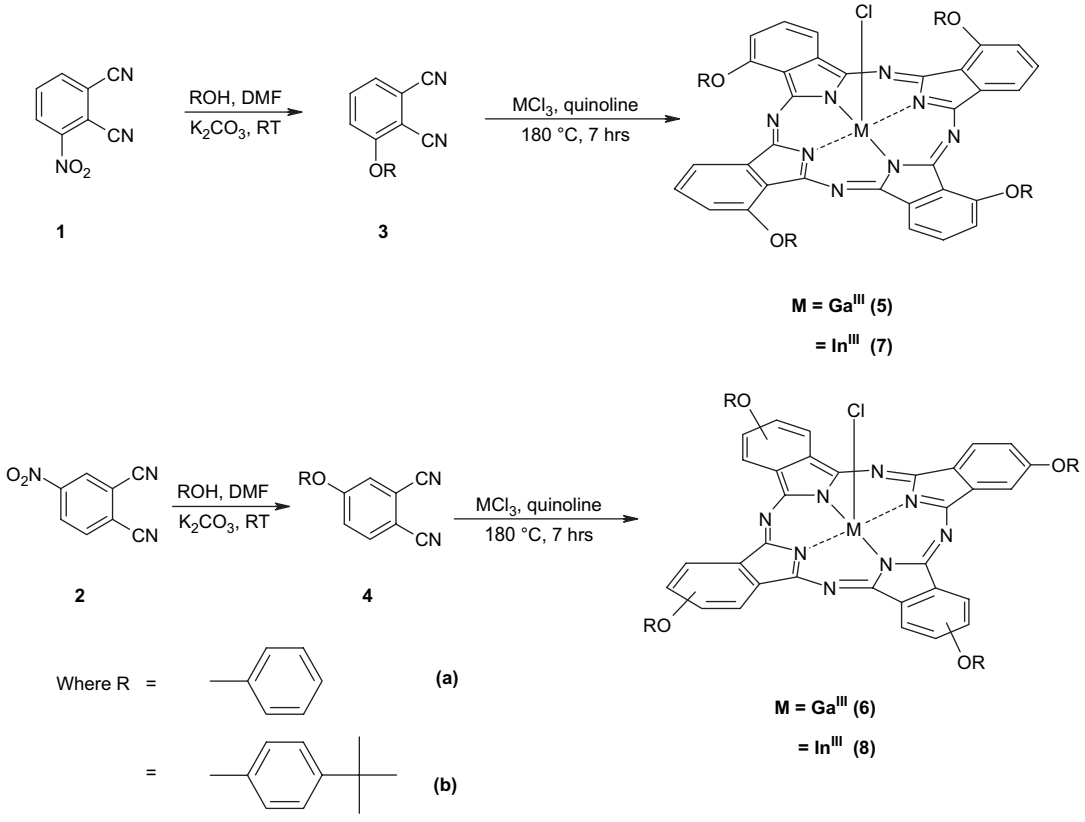
To our knowledge, aryloxy tetra-substitution on gallium and indium-based phthalocyanines has not been reported. The rarity of these phthalocyanines has thus prompted us to synthesize aryloxy-substituted gallium (ClGaPcs) and indium (ClInPcs) phthalocyanines because the development and elucidation of photophysical and photochemical properties of new phthalocyanine complexes are of fundamental importance. Specific phthalocyanines can thus be tailored such that they have certain properties, which are required for various applications, since the possibility of combining an unlimited number and type of substituents with a great number of central metals is infinite.

The aim of our ongoing research is to synthesize gallium and indium phthalocyanines as potential PDT agents. Photophysical and photochemical properties of ClGaPcs and ClInPcs are very useful in applications involving PDT, non-linear optics and optical limiters as these gallium and indium macrocycles are known to have remarkable properties.[10] Herein, we report the synthesis, spectroscopic, photophysical, and photochemical properties of ClGaPcs and ClInPcs tetra-substituted at the non-peripheral (complexes **5** and **7**) and peripheral (complexes **6** and **8**) positions with phenoxy and *tert*-butylphenoxy groups (Scheme 1).

## 2. Results and discussion

### 2.1. Synthesis and characterization

Generally, substituted phthalocyanines are prepared by cyclotetramerization of substituted phthalonitriles or 1,3-diimino-1*H*-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 3-substituted analogues.[12] 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 phthalocyanine compounds are obtained as isomer mixtures as expected. No attempt was made to separate the isomers of complexes **5**–**8**. 3-Nitro-1,2-dicyanobenzene (**1**) and 4-nitro-1,2-dicyanobenzene (**2**) were recently used to prepare 3-monosubstituted and 4-monosubstituted phthalonitrile derivatives, respectively, through base catalyzed nucleophilic aromatic displacement.[14] The same route was applied to prepare 3-phenoxyphthalonitrile (**3a**) from phenol and 3-nitro-1,2-dicyanobenzene (**1**) (Scheme 1). Similarly, the reaction of 4-*tert*-butylphenol under the same conditions with 4-nitro-1,2-dicyanobenzene (**2**) resulted in the expected compound **4** (Scheme 1). The reactions were carried out in dimethyl formamide at room temperature and gave yields of about 70–80%.




**Scheme 1**. Syntheses of tetra-substituted phenoxy and *tert*-butylphenoxy (phthalocyaninato)gallium(III) and indium(III) substituted at the α and β positions.

The preparation of phthalocyanine derivatives from the aromatic nitriles occurs under different reaction conditions. The syntheses of metallophthalocyanine complexes (**5**–**8**) were achieved by treatment of phthalonitriles **3** and **4** with $InCl_3$ or $GaCl_3$ in freshly distilled quinoline (Scheme 1). Because gallium and indium are large atoms, high energy is required to insert the metal ion into the phthalocyanine ring, thus a high-boiling solvent (such as quinoline) is used to achieve this purpose. Complexes **5** and **7** are non-peripherally (α) substituted, whereas complexes **6** and **8** are peripherally (β) substituted. Column 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 complexes (**5**–**8**) exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, toluene, and DMSO. For comparative purposes, the phenoxy and *tert*-butylphenoxy groups were tetra-substituted at the α and β positions of the ring. The new compounds were characterized by UV–vis, IR, and NMR spectroscopies, MALDI-TOF mass spectra and elemental analysis and these analyses are consistent with the predicted structures as shown in the Section 4. After conversion into gallium or indium phthalocyanine, the characteristic C≡N stretch at ~2300 $cm^{-1}$ of phthalonitriles **3** and **4** disappeared, indicative of metallophthalocyanine formation. The complexes showed characteristic vibrations due to ether groups (C–O–C) at 1077–1087 $cm^{-1}$, aromatic CH stretching at ca. 3040–3060 $cm^{-1}$ for complexes **5**–**8** and aliphatic CH stretching at ca. 2866–2962 $cm^{-1}$ for complexes **5b**, **6b**, **7b**, and **8b**.

The $^1H$ NMR spectra of tetra-substituted phthalocyanine derivatives (**5**–**8**) show complex patterns owing to the mixed isomer character of these compounds. The complexes were found to be pure by $^1H$ NMR spectra with all the substituents and ring protons observed in their respective regions. The phenoxy substituted complexes **5a**, **6a**, **7a**, and **8a** showed different behavior in that the peripherally substituted complexes (**6a** and **8a**) showed more resolved and split bands for the phthalocyanine ring. The resonances belonging to ring protons were observed in the range 7.71–8.86 ppm for **6a** and 7.64–8.93 ppm for **8a**, integrating for a total of 12 protons for both peripheral and non-peripheral protons. The phenoxy ring protons of **6a** were observed in the range 7.33–7.67 ppm, and 7.26–7.62 ppm for **8a**, integrating for a total of 20 protons as expected (Fig. 1). For the non-peripherally substituted complex (**5a** and **7a**) similar splitting of bands was not observed. The $^1H$ NMR spectra of **5a** and **7a** showed unresolved multiplets between 7.03 and 8.86 ppm, and 8.20 and 9.08 ppm, respectively, most likely due to the presence of isomers. Both complexes are expected to have positional isomers due to the presence of a single substituent on either the peripheral or non-peripheral positions.[15] Fewer positional isomers are expected for the non-peripherally substituted complexes (**5a** and **7a**) compared to the peripherally substituted complexes (**6a** and **8a**) due to steric effects in the former. Thus, the observed split in the $^1H$ NMR spectra could be due to lack of symmetry, which may result in unresolved (**5a** and **7a**) and split (**6a** and **8a**) spectra for the complexes. The resonances for the

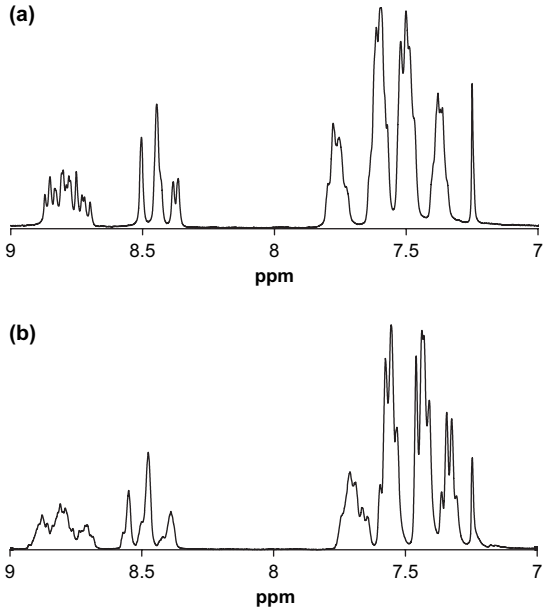



**Figure 1**. $^1H$ NMR spectra of: (a) complex **6a** and (b) **8a** in $CDCl_3$.

phenyl ring are also split for **6a** and **8a** and not for **5a** and **7a** for the same reasons. The phenyl ring substituents are observed between 7.03 and 7.47 ppm for **5a** and between 7.33 and 7.67 ppm for **6a**, and integrate for 20 protons for **5a** (but we obtained 24 protons because of the overlap of 4 phthalocyanine ring protons) and 20 protons for **6a**. The phenyl ring substituents are observed between 7.17 and 7.49 ppm for **7a** and between 7.26 and 7.62 ppm for **8a**, and integrate for 20 protons for **7a** (but we obtained 24 protons because of overlap of 4 phthalocyanine ring protons) and 20 protons for **8a**.

The *tert*-butylphenoxy substituted complexes (**5b**, **6b**, **7b**, and **8b**) both showed the phthalocyanine ring protons as unresolved multiplets integrating for a total of 12 protons each. The phthalocyanine ring protons were observed as follows: **5b**: 7.20–8.80 ppm; **6b**: 7.32–8.83; **7b**: 7.22–9.09 ppm; and **8b**: 7.51–8.90 ppm. In all cases there was an overlap with the phenyl protons. The phenyl ring protons were observed between 7.20 and 7.58 ppm for **5b**, 7.32 and 7.67 ppm for **6b**, 7.22 and 7.78 ppm for **7b**, 7.32 and 7.72 ppm for **8b** and integrated for 16 protons in each complex as expected. The methyl protons, which integrated for 36 protons were observed at 1.43 ppm for **5b**, 1.51 ppm for **6b**, 1.41 ppm for **7b**, and 1.46 ppm for **8b**. Although the presence of isomers as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals,[16] the observed spectra of all the complexes were relatively well-resolved.

The electronic absorption spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical of metalated phthalocyanine complexes, Figure 2.[17] In DMSO, the Q bands were observed at: 712 (**5a**), 717 (**5b**), 691 (**6a**), 697 (**6b**) and 712 (**7a**), 714 (**7b**), 696 (**8a**), 696 (**8b**), respectively, Tables 1 and 2. The Q bands of the α-substituted complexes (**5** and **7**) are red-shifted by 16–21 nm, when compared to the corresponding β-substituted complexes

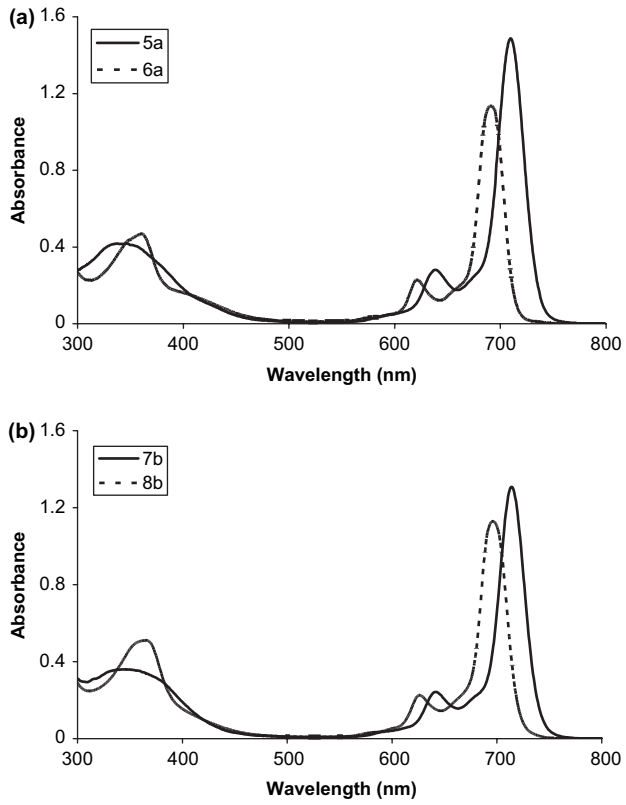



**Figure 2**. Absorption spectra of: (a) **5a** and **6a** and (b) **7b** and **8b** in DMSO. Concentration=$4\times10^{-6}$ mol dm$^{-3}$.

(**6** and **8**) in DMSO (Fig. 2 and Table 1). The observed red spectral shift is typical of phthalocyanines with substituents at the α positions.[18] 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 330–360 nm region.[19] In addition, the complexes exhibit a rarely observed N band arising from deeper π levels to LUMO

**Table 1**. UV–vis spectral data of complexes **5a**, **5b**, **6a**, and **6b** in toluene, DCM, $CHCl_3$, THF, and DMSO, respectively

| | Solvent | Q band/nm | B band/nm | N band/nm |
|---|---|---|---|---|
| **5a** | Toluene | 716 | 334 | — |
| | DCM | 717 | 336 | — |
| | THF | 707 | 330 | — |
| | $CHCl_3$ | 723 | 333 | — |
| | DMSO | 712 | 330 | — |
| **5b** | Toluene | 721 | 333 | — |
| | DCM | 723 | 338 | 264 |
| | THF | 714 | 334 | — |
| | $CHCl_3$ | 726 | 337 | — |
| | DMSO | 717 | 344 | — |
| **6a** | Toluene | 696 | 353 | — |
| | DCM | 698 | 353 | 290 |
| | THF | 691 | 364 | — |
| | $CHCl_3$ | 699 | 353 | 282 |
| | DMSO | 691 | 362 | — |
| **6b** | Toluene | 697 | 348 | — |
| | DCM | 698 | 352 | 292 |
| | THF | 691 | 363 | — |
| | $CHCl_3$ | 700 | 352 | 291 |
| | DMSO | 697 | 363 | — |

**Table 2**. Absorption, excitation, and emission spectral data for unsubstituted, peripherally and non-peripherally substituted indium phthalocyanine compounds in DMSO

| Compound | Q band $\lambda_{max}$ (nm) | Excitation $\lambda_{Ex}$ (nm) | Emission $\lambda_{Em}$ (nm) |
|---|---|---|---|
| ClInPc | 686 | 689 | 700 |
| **7a** | 712 | 721 | 732 |
| **7b** | 714 | 725 | 732 |
| **8a** | 696 | 706 | 715 |
| **8b** | 696 | 708 | 716 |

transitions,[20] in UV transparent solvents such as DCM and chloroform.

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.[21] In the aggregated state the electronic structure of the complexed phthalocyanine rings is perturbed resulting in alternation of the ground and excited state electronic structures.[22] In this study, the aggregation behavior of the phthalocyanines is investigated in different solvents (toluene, DCM, chloroform, THF, and DMSO) and at different concentrations; the phthalocyanine derivatives (**5**–**8**) did not show aggregation in these solvents. The Beer–Lambert law was obeyed for all of these compounds at concentrations ranging from $1.4\times10^{-5}$ to $4\times10^{-6}$ mol dm$^{-3}$.

## 2.2. Photophysical parameters

Complexes **5** and **6** showed similar fluorescence behavior. Figure 3a shows the fluorescence excitation and emission spectra for complex **6b** as an example. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra. The proximity of the wavelength for 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 are similar and not affected by excitation. The observed Stokes shift of ∼11 nm is typical for MPc complexes.

For the ClInPc complexes (**7** and **8**), the excitation spectra were different from the absorption spectra in that the Q band of the former showed splitting, Figure 3b, unlike the narrow Q band of the latter. This suggests that there are changes in the molecule following excitation, most likely due to loss of symmetry. The fluorescence spectra of complexes **7** and **8** were also broad. The Q band maxima of the excitation and absorption spectra were different (Table 2) due to the difference in the ground and excited state species. This was however not observed for the ClGaPc complexes. The difference in the behaviors of ClGaPc and ClInPc on excitation could be due to the larger In metal being more displaced from the core of the Pc ring, and the displacement being more pronounced on excitation, hence causing a loss of symmetry.

The fluorescence quantum yields ($\Phi_F$) of ClGaPc complexes **5** and **6** are typical of MPc complexes, but are lower than that of the unsubstituted ClGaPc, Table 3. This suggests that the

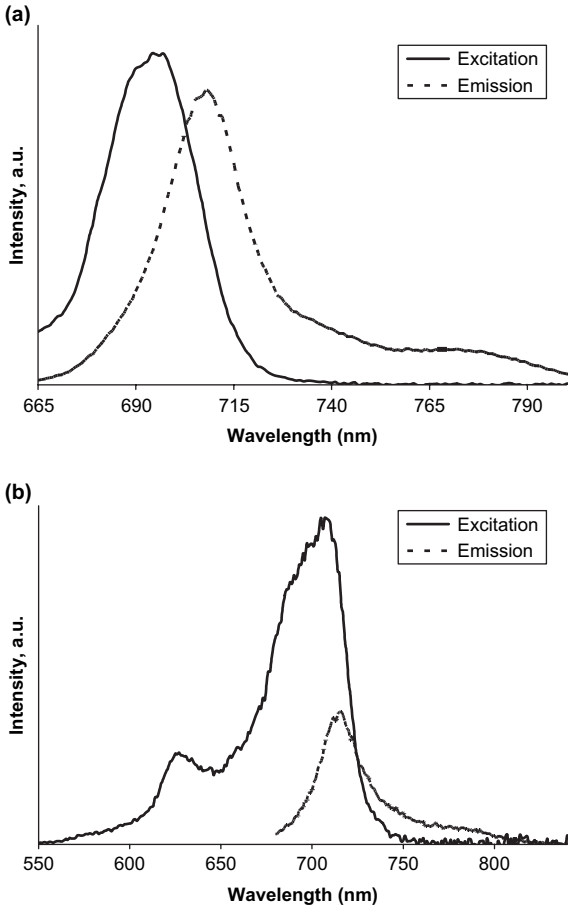



**Figure 3**. Fluorescence excitation and emission spectra of (a) **6b** and (b) **8b** in DMSO. Excitation wavelength=655 nm for **6b** and 670 nm for **8b**.

substituents quench the excited singlet state. The peripherally substituted complexes **6a** and **6b** show marginally larger $\Phi_F$ values, suggesting less quenching of the excited singlet state by peripheral substitution compared to non-peripheral. For the ClInPc complexes (**7** and **8**), the $\Phi_F$ values were very low due to enhancement of intersystem crossing (ISC) by the presence of a heavier In atom in these complexes. The enhanced ISC will also result in increased triplet quantum yields and decreased triplet lifetimes as will be discussed below.

Lifetimes of fluorescence ($\tau_F$, Table 4) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been[23a] found for the experimentally determined fluorescence lifetimes and the theoretically determined lifetimes for the unaggregated molecules as is the case in this work. Thus we believe that the values obtained using this equation are a good measure of fluorescence lifetimes. The $\tau_F$ values were within the range reported for MPc complexes.[23a] The $\tau_F$ values were lower for complexes **5–8** when compared to unsubstituted derivatives Table 4, suggesting quenching of fluorescence by the ring substituents. For the ClGaPc complexes, longer $\tau_F$ values were obtained for the peripherally substituted complexes **6** compared to **5**, suggesting more quenching by peripheral substitution when compared to non-peripheral substitution. This, however, was not the case for ClInPc complexes (**7** and **8**). The $\tau_F$ values for ClInPc complexes were lower than that of the ClGaPc complexes. The rate constants for fluorescence ($k_F$) however increased on going from unsubstituted ClGaPc (or ClInPc) to the corresponding substituted complexes **5–8**, Table 4. There was no clear trend observed on comparing $k_F$ for peripherally (**6**) to non-peripherally (**5**) substituted ClGaPc complexes. But for ClInPc complexes, peripherally substituted complexes **8** showed lower $k_F$ values than corresponding non-peripherally substituted complexes **7**. Complexes **5–8** also showed larger rate constants ($k_{IC}$, Table 4) and quantum yields for internal conversion ($\Phi_{IC}$, Table 3) when compared to the respective unsubstituted ClGaPc and ClInPc complexes. In addition, larger rate constants for intersystem crossing ($k_{ISC}$) for complexes **5–8** compared

**Table 4**. Rate constants for various excited state deactivation processes of gallium and indium phthalocyanine complexes in DMSO

| Compound | $\tau_F$ (ns) | $k_F$ ($s^{-1}$)[a] | $k_{ISC}$ ($s^{-1}$)[b] | $k_{IC}$ ($s^{-1}$)[c] | $k_d$ ($s^{-1}$)[d] |
|---|---|---|---|---|---|
| ClGaPc | 3.71 | $0.83\times10^8$ | $1.85\times10^8$ | $2.69\times10^6$ | 1.37 |
| **5a** | 0.92 | $1.51\times10^8$ | $6.73\times10^8$ | $2.60\times10^8$ | 0.51 |
| **5b** | 1.01 | $1.48\times10^8$ | $5.34\times10^8$ | $3.06\times10^8$ | 0.58 |
| **6a** | 1.29 | $1.47\times10^8$ | $4.72\times10^8$ | $1.55\times10^8$ | 1.04 |
| **6b** | 1.19 | $1.67\times10^8$ | $3.78\times10^8$ | $2.94\times10^8$ | 0.68 |
| ClInPc | 0.90 | $1.99\times10^8$ | $10.11\times10^8$ | $0.77\times10^8$ | 19.8 |
| **7a** | 0.51 | $9.36\times10^8$ | $15.29\times10^8$ | $3.33\times10^8$ | 2.3 |
| **7b** | 0.14 | $10.52\times10^8$ | $42.14\times10^8$ | $27.80\times10^8$ | 3.47 |
| **8a** | 0.37 | $8.51\times10^8$ | $18.64\times10^8$ | $7.56\times10^8$ | 4.88 |
| **8b** | 0.20 | $9.33\times10^8$ | $38.50\times10^8$ | $10.50\times10^8$ | 4.28 |

[a] $k_F$ is the rate constant for fluorescence. Values calculated using $k_F=\Phi_F/\tau_F$.
[b] $k_{ISC}$ is the rate constant for intersystem crossing. Values calculated using $k_{ISC}=\Phi_T/\tau_F$.
[c] $k_{IC}$ is the rate constant for internal conversion. Values calculated using $k_{IC}=\Phi_{IC}/\tau_F$.
[d] $k_d$ is the rate constant for photodegradation. Values calculated using $k_d=\Phi_d/\tau_T$.

**Table 3**. Photophysical and photochemical parameters of peripherally and non-peripherally substituted Ga(III) and In(III) phthalocyanines in DMSO

| Compound | $\tau_T$ (μs) | $\Phi_F$ | $\Phi_T$ | $\Phi_{IC}$ | $\Phi_d$ ($\times10^{-4}$) | $\Phi_\Delta$ | $S_\Delta$ |
|---|---|---|---|---|---|---|---|
| ClGaPc | 200 | 0.30 | 0.69 | 0.01 | 2.75 | 0.41 | 0.59 |
| **5a** | 230 | 0.14 | 0.62 | 0.24 | 1.19 | 0.64 | 1.03 |
| **5b** | 350 | 0.15 | 0.54 | 0.31 | 2.03 | 0.62 | 1.14 |
| **6a** | 270 | 0.19 | 0.61 | 0.20 | 2.82 | 0.64 | 1.04 |
| **6b** | 340 | 0.20 | 0.45 | 0.35 | 2.32 | 0.58 | 1.28 |
| ClInPc | 50 | 0.018 (0.031)[a] | 0.91 (0.9)[a] | 0.07 (0.07)[a] | 9.90 | 0.61 | 0.67 |
| **7a** | 40 | 0.048 | 0.78 | 0.17 | 0.92 | 0.88 | 1.12 |
| **7b** | 40 | 0.015 | 0.59 | 0.39 | 1.39 | 0.92 | 1.55 |
| **8a** | 50 | 0.032 | 0.69 | 0.28 | 2.44 | 0.87 | 1.26 |
| **8b** | 50 | 0.019 | 0.60 | 0.38 | 2.14 | 0.88 | 1.46 |

[a] The data in brackets are for literature values in 1-chloronaphthalene, Ref. 11a.

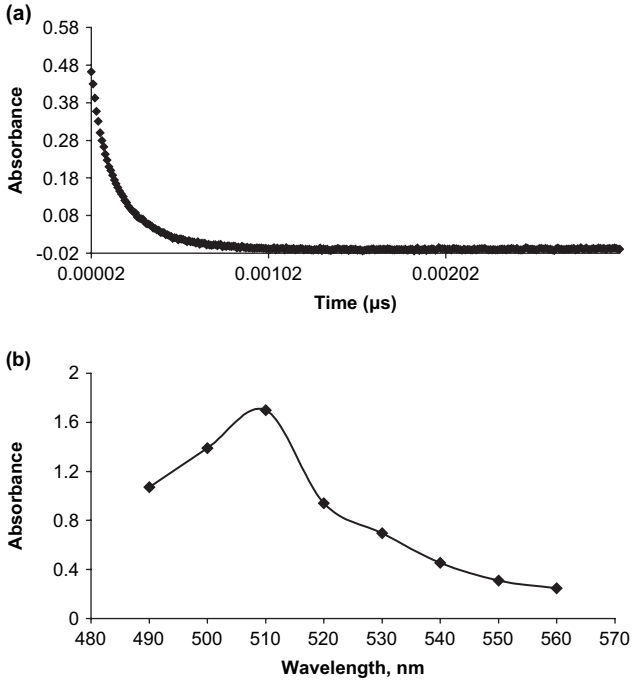



**Figure 4**. (a) Triplet decay curve of ClGaPc in DMSO. Excitation wavelength=680 nm. (b) The triplet absorption spectrum for ClInPc in DMSO. Excitation wavelength=686 nm. Concentrations $\sim 1\times10^{-5}$ mol dm$^{-3}$.

to the respective unsubstituted ClGaPc and ClInPc complexes show improved intersystem crossing to the triplet state.

Figure 4a shows the triplet decay curve for unsubstituted ClGaPc in DMSO, and Figure 4b the triplet absorption curve for unsubstituted ClInPc. Table 3 shows that the triplet lifetimes for the ClGaPc complexes ranged from 200 to 350 μs, with unsubstituted ClGaPc showing the shortest lifetime and having a correspondingly larger triplet quantum yield ($\Phi_T$) when compared to complexes **5** and **6**. Due to enhanced ISC, ClInPc complexes (**7** and **8**) showed much higher quantum yields of triplet state and shorter triplet lifetimes when compared to the corresponding ClGaPc complexes.

Figure 5a shows that for complexes **5–8** and unsubstituted derivatives, there was a change in spectra following laser irradiation (or irradiation with white light for that matter in nitrogen saturated solutions, for **5–8** only). The spectral changes involved a decrease in the Q band and an increase in the absorption near 580 nm. However, on exposure of the solution to air, the Q band increased in intensity and the band around 580 nm decreased (Fig. 5b) suggesting that this band is due to reduction products of the complexes. These spectral changes were only observed in DMSO. The first ring reduction in MPc complexes is characterized by a decrease in the Q band and the formation of weak bands between 500 and 600 nm.[24] Thus, we propose that during laser irradiation, the ClGaPc and ClInPc derivatives were partly transformed to an anion ($Pc^{-3}$) species. This type of transformation has been observed before during photodegradation of pyridinoporphyrazines[23b] using visible light. The suggested mechanism for the formation of $Pc^{-3}$ in the presence of H donors is shown by Eqs. 1–3:

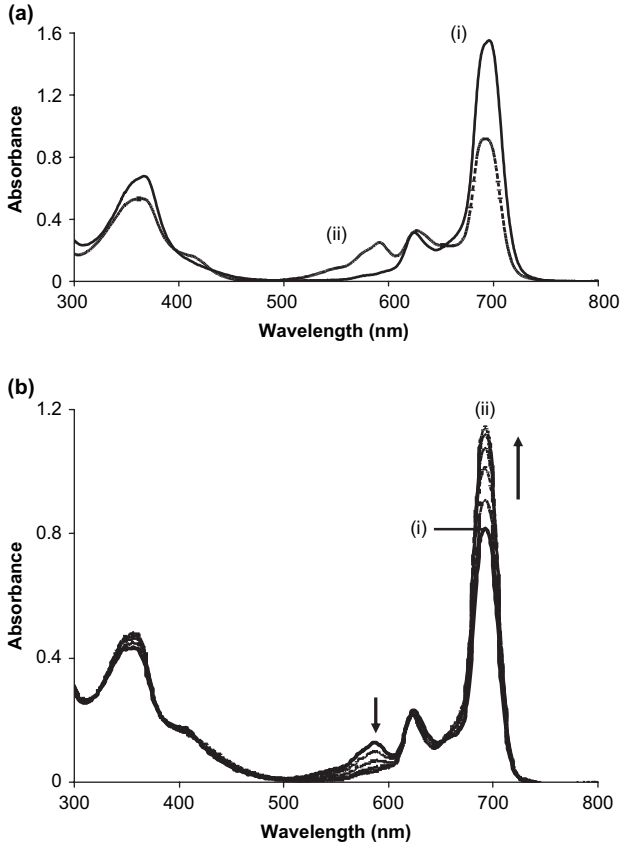



**Figure 5**. (a) Absorption spectral changes of compound **8a** before (i) and after (ii) laser irradiation. (b) Absorption spectral changes of compound **6b** after irradiation with white light (100 V) for 10 min, and exposing the irradiated solution to air and recording spectra at the times shown; exposure to air increasing from (i) 0 to (ii) 250 s in steps of 50 s.

$$MPc + h\nu \rightarrow {}^3MPc^* \quad (1)$$

$$^3MPc^* + S{-}H \rightarrow MPc^{\bullet -} + S{-}H^{\bullet +} \quad (2)$$

$$MPc^{\bullet -} + O_2 \rightarrow MPc + O_2{}^{\bullet -} \quad (3)$$

S=solvent.

This photoreduction could be the reason for lower $\Phi_T$ values for complexes **5–8** when compared to respective unsubstituted ClGaPc and ClInPc complexes. The $\Phi_T$ values were slightly lower than $\Phi_\Delta$ as discussed below due to this photoreduction.

There was no clear general trend on the effect of peripheral (complexes **6** and **8**) versus non-peripheral (complexes **5** and **7**) substitution on the triplet lifetimes or quantum yields. However when comparing ClGaPc complexes **5a** with **6a**, both containing phenoxy substituents, there was a marginal increase in triplet lifetimes on going from the former to the latter (Table 3). However when comparing **5b** with **6b**, both containing *tert*-butylphenoxy substituents, there was a marginal decrease in triplet lifetimes and a substantial decrease in $\Phi_T$ values on going from the former to the latter. When comparing phenoxy with *tert*-butylphenoxy substitution,

that is, comparing **5a** with **5b** or **6a** with **6b**, **7a** with **7b** or **8a** with **8b**, we observed a large decrease in $\Phi_T$ values on going from the phenoxy to the *tert*-butylphenoxy substitution (Table 3).

### 2.3. Photochemical studies

Because of the presence of oxygen during the determination of singlet oxygen quantum yields ($\Phi_\Delta$) the photoreduction of complexes **5–8** was not observed during singlet oxygen studies as shown in Figure 6. There was no decrease in the Q band or formation of new bands. The values of $\Phi_\Delta$ were higher for complexes **5–8** when compared to respective unsubstituted ClGaPc or ClInPc complexes. The magnitude of the $S_\Delta$ ($=\Phi_\Delta/\Phi_T$) represents the efficiency of quenching of the triplet excited state by singlet oxygen. Most of the complexes showed $S_\Delta$ near unity (Table 3), suggesting efficient quenching of the triplet state by singlet oxygen. In some cases (e.g., **7b**), the $S_\Delta$ values are slightly larger than unity. This is due to low $\Phi_T$ values as a result of the phototransformation by laser light discussed above. The $S_\Delta$ values were less than unity for unsubstituted ClGaPc and ClInPc complexes, suggesting inefficient quenching of the triplet state by singlet oxygen.

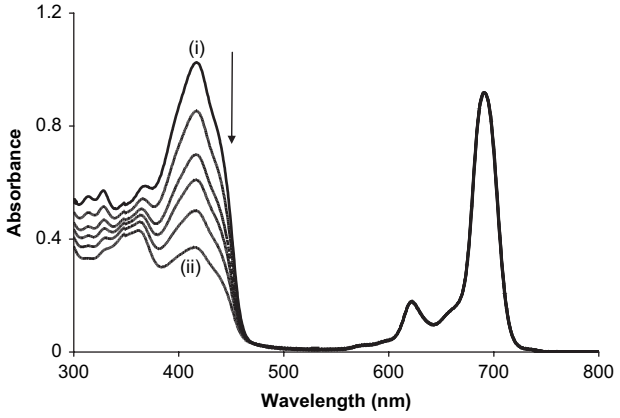



**Figure 6**. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **6b** in DMSO at a concentration of $3\times10^{-5}$ M. Photolysis times increasing from (i) 0 s to (ii) 25 s in steps of 5 s.

All the complexes showed about the same stability with $\Phi_d$ in the order of $10^{-4}$. These complexes are less stable than the corresponding ZnPc derivatives.[25] Again there was no photoreduction of the complexes during photodegradation studies in the presence of oxygen, hence the magnitudes of the observed $\Phi_d$ are not due to phototransformation. The rate constant for photodegradation ($k_d$) was lower for complexes **5–8** when compared to respective unsubstituted ClGaPc and ClInPc complexes.

## 3. Conclusions

In conclusion, we have shown in this work that unsubstituted ClGaPc and ClInPc complexes and their phenoxy and *tert*-butylphenoxy substituted derivatives are monomeric in solution. The introduction of these substituents on the ring resulted in lowering of fluorescence quantum yields and lifetimes, and triplet quantum yields, and an increase of $k_{IC}$, $k_{ISC}$, and $k_F$. Photoreduction of the complexes was observed during laser flash photolysis. The singlet oxygen quantum yields ($\Phi_\Delta$), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.41 to 0.91. Thus, these complexes show potential as Type II photosensitizers.

## 4. Experimental

### 4.1. Materials

Quinoline, dimethylsulfoxide (DMSO), methanol, hexane, chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), acetone, ethanol, and dimethyl formamide (DMF) were dried as described by Perrin and Armarego[26] before use. Gallium(III) chloride, indium(III) chloride, deuterated $CDCl_3$, 4-*tert*-butylphenol, and phenol were purchased from Aldrich. 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 $F_{254}$. 3-Nitrophthalonitrile (**1**),[27] 4-nitrophthalonitrile (**2**),[28] 3-phenoxyphthalonitrile (**3a**),[29] 3-*tert*-butylphenoxyphthalonitrile (**3b**),[29] 4-phenoxyphthalonitrile (**4a**),[29] 4-*tert*-butylphenoxyphthalonitrile (**4b**),[29] unsubstituted gallium(III) phthalocyanine[30] and unsubstituted indium(III) phthalocyanine[30] were synthesized and purified according to literature procedures.

### 4.2. Equipments

UV–vis spectra were recorded on a Cary 500 UV–vis/NIR spectrophotometer. Fluorescence excitation and emission spectra, were recorded on a Varian Eclipse spectrofluoremeter using 1-cm pathlength cuvettes at room temperature. IR spectra (KBr pellets) were recorded on a Perkin–Elmer spectrum 2000 FTIR spectrometer. $^1$H NMR spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer. MALDI-TOF spectra were recorded with Perseptive Biosystems Voyager DE-PRO Biospectrometry Workstation and Processing Delayed Extraction Technology at the University of Cape Town. Elemental Analyses were also performed at the University of Cape Town.

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 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. Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were 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 was 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 two-channel digital real-time

oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 16 laser pulses.

### 4.3. Photophysical parameters

**4.3.1. Fluorescence quantum yields.** Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method (Eq. 4),[31]

$$\Phi_F = \Phi_F(\text{Std})\frac{FA_{\text{Std}}\eta^2}{F_{\text{Std}}A\eta^2_{\text{Std}}} \quad (4)$$

where $F$ and $F_{\text{Std}}$ are the areas under the fluorescence emission curves of the samples (**5–8**) and the standard, respectively. $A$ and $A_{\text{Std}}$ are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. The refractive indices of the solvents were employed in calculating fluorescence quantum yields in different solvents. Unsubstituted ZnPc (in DMSO) ($\Phi_F$=0.18)[32] 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.

Fluorescence lifetimes were determined using PhotochemCAD program, which uses the Strickler–Berg equation.[33]

**4.3.2. Triplet quantum yields and lifetimes.** The deaerated solutions of the respective peripheral and non-peripheral tetra-substituted gallium(III) and indium(III) phthalocyanine complexes (**5–8**) were introduced into a 1-cm pathlength spectrophotometric cell and irradiated at the Q band maxima with the laser system described above. Triplet quantum yields ($\Phi_T$) were determined by a comparative method using triplet decay,[11a] Eq. 5:

$$\Phi_T^{\text{Sample}} = \Phi_T^{\text{Std}}\frac{\Delta A_T^{\text{Sample}}\varepsilon_T^{\text{Std}}}{\Delta A_T^{\text{Std}}\varepsilon_T^{\text{Sample}}} \quad (5)$$

where $\Delta A_T^{\text{Sample}}$ and $\Delta A_T^{\text{Std}}$are the changes in the triplet state absorbances of the samples (**5–8**) and standard, respectively; $\varepsilon_T^{\text{Sample}}$ and $\varepsilon_T^{\text{Std}}$, the triplet state extinction coefficients for the samples (**5–8**) and standard, respectively. The standard employed was zinc phthalocyanine (ZnPc) in DMSO. The triplet quantum yield ($\Phi_T^{\text{Std}}$) for the standard is $\Phi_T^{\text{Std}} = 0.65$ for ZnPc[34] in DMSO.

Quantum yields of internal conversion ($\Phi_{IC}$) were obtained from Eq. 6, which assumes that only three processes (fluorescence, intersystem crossing, and internal conversion), jointly deactivate the excited singlet state of peripherally and non-peripherally tetra-substituted gallium(III) and indium(III) phthalocyanine complexes.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \quad (6)$$

Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

**4.3.3. Singlet oxygen and photodegradation quantum yields.** Singlet oxygen ($\Phi_\Delta$) and photodegradation ($\Phi_d$) quantum yield determinations were carried out using the experimental set-up described above.[23] Typically, a 2 ml portion of the respective peripheral and non-peripheral tetra-substituted gallium(III) and indium(III) phthalocyanine (**5–8**) solutions containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described above.[23] The $\Phi_\Delta$ values were determined in air using the relative method with DPBF as singlet oxygen chemical quencher in DMSO (Eq. 7):

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}}\frac{RI_{\text{abs}}^{\text{Std}}}{R^{\text{Std}}I_{\text{abs}}} \quad (7)$$

where $\Phi_\Delta^{\text{Std}}$ is the singlet oxygen quantum yield for the standard (ZnPc in DMSO ($\Phi_\Delta^{\text{ZnPc}} = 0.67$)),[35] $R$ and $R^{\text{Std}}$ are the DPBF photobleaching rates in the presence of the respective (**5–8**) and standard, respectively; $I_{\text{abs}}$ and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples (**5–8**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen,[36] the concentration of DPBF was lowered to $\sim 3\times10^{-5}$ mol $l^{-1}$. Solution of sensitizer (absorbance ~1.5 at the irradiation wavelength) containing DPBF was 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 used for $\Phi_\Delta$ determinations was found to be $8.6\times10^{16}$ photons $s^{-1}$ $cm^{-2}$. The error in the determination of $\Phi_\Delta$ was ~10% (determined from several $\Phi_\Delta$ values). Photodegradation quantum yields were determined using Eq. 8,

$$\Phi_d = \frac{(C_0 - C_t)VN_A}{I_{\text{abs}}St} \quad (8)$$

where $C_0$ and $C_t$ are the sample (**5–8**) concentrations before and after irradiation, respectively, $V$ is the reaction volume, $N_A$ the Avogadro's constant, $S$ the irradiated cell area and $t$ the irradiation time. $I_{\text{abs}}$ is the overlap integral of the radiation source light intensity and the absorption of the samples (**5–8**). A light intensity of $2.78\times10^{17}$ photons $s^{-1}$ $cm^{-2}$ was employed for $\Phi_d$ determinations.

### 4.4. Synthesis

**4.4.1. 1(4),8(11),15(18),22(25)-(Tetraphenoxyphthalocyaninato)gallium(III) (5a).** A mixture of anhydrous gallium(III) chloride (0.60 g, 3.4 mmol), 3-phenoxyphthalonitrile (**3a**) (1.50 g, 6.8 mmol), and quinoline (5 ml, doubly distilled over $CaH_2$) was stirred at 180 °C for 7 h under nitrogen atmosphere. After cooling, the solution was dropped in the *n*-hexane. The green solid product was precipitated and collected by filtration and washed with *n*-hexane. The crude product was dissolved in $CH_2Cl_2$ and then filtered. After filtering and concentrating, the dark green waxy product was purified by passing through a silica gel column, using THF as an eluting solvent. Furthermore this product was purified with preparative thin layer chromatography (TLC and silica gel) using $CHCl_3$ solvent system ($R_f$=0.53). Yield: 0.50 g (30%). UV–vis (DMSO): $\lambda_{\text{max}}$ nm (log $\varepsilon$) 344 (4.80), 639 (4.69), 712 (5.34). IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3036 (Ar–CH), 1582 (C=C), 1077 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.18–8.86 (4H, m, Pc–H), 7.53–7.92 (4H, m, Pc–H), 7.03–7.47 (24H, m, Phenyl–H, Pc–H). Calcd for $C_{56}H_{32}ClGaN_8O_4$: C 68.21, H 3.27, N 11.36; Found: C

68.20, H 3.35, N 10.88. MALDI-TOF-MS *m/z*: Calcd 986.08; Found (M) 985.77.

**4.4.2. 1(4),8(11),15(18),22(25)-(Tetra-*tert*-butylphenoxyphthalocyaninato)gallium(III) (5b).** Synthesis and purification was as outlined for **5a** except **3b** was employed instead of **3a**. The amount of the reagents employed were: **3b** (1.50 g, 5.4 mmol), gallium(III) chloride (0.47 g, 2.7 mmol) in quinoline (5 ml). TLC: $R_f$=0.61. Yield: 0.65 g (39%). UV–vis (DMSO): $\lambda_{max}$ nm ($\log \varepsilon$) 348 (4.72), 644 (4.60), 717 (5.31). IR [(KBr) $\nu_{max}/cm^{-1}$]: 3036 (Ar–CH), 2960 and 2866 (C–H), 1586 (C=C), 1079 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.12–8.80 (4H, m, Pc–H), 7.61–7.89 (4H, m, Pc–H), 7.20–7.58 (20H, m, Phenyl–H, Pc–H), 1.43 (36H, s, *t*-Bu). Calcd for $C_{72}H_{64}ClGaN_8O_4$: C 71.44, H 5.33, N 9.26; Found: C 70.80, H 5.23, N 8.94. MALDI-TOF-MS *m/z*: Calcd 1210.5; Found ($M^{2+}$) 1212.0.

**4.4.3. 2(3),9(10),16(17),23(24)-(Tetraphenoxyphthalocyaninato)gallium(III) (6a).** Synthesis and purification was as outlined for **5a** except **4a** was employed instead of **3a**. The amount of the reagents employed were: **4a** (1.5 g, 6.8 mmol), gallium(III) chloride (0.60 g, 3.4 mmol) in quinoline (5 ml). TLC: $R_f$=0.59. Yield: 0.70 g (42%). UV–vis (DMSO): $\lambda_{max}$ nm ($\log \varepsilon$) 361 (4.89), 621 (4.61), 691 (5.29). IR [(KBr) $\nu_{max}/cm^{-1}$]: 3039 (Ar–CH), 1588 (C=C), 1084 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.68–8.86 (4H, m, Pc–H), 8.32–8.50 (4H, s, s, d, Pc–H), 7.71–7.82 (4H, m, Pc–H), 7.56–7.67 (8H, d, Phenyl–H), 7.46–7.55 (8H, t, Phenyl–H), 7.33–7.43 (4H, t, Phenyl–H). Calcd for $C_{56}H_{32}ClGaN_8O_4$: C 68.40, H 3.27, N 11.36; Found: C 68.10, H 3.31, N 10.82. MALDI-TOF-MS *m/z*: Calcd 986.1; Found ($M^+$) 987.8.

**4.4.4. 2(3),9(10),16(17),23(24)-(Tetra-*tert*-butylphenoxyphthalocyaninato)gallium(III) (6b).** Synthesis and purification was as outlined for **5a** except **4b** was employed instead of **3a**. The amount of the reagents employed were: **4b** (1.5 g, 5.4 mmol), gallium(III) chloride (0.47 g, 2.7 mmol) in quinoline (5 ml). TLC: $R_f$=0.63. Yield: 0.78 g (48%). UV–vis (DMSO): $\lambda_{max}$ nm ($\log \varepsilon$) 358 (4.90), 623 (4.65), 697 (5.32). IR [(KBr) $\nu_{max}/cm^{-1}$]: 3038 (Ar–CH), 2962 and 2868 (C–H), 1601 (C=C), 1085 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.12–8.83 (8H, m, Pc–H), 7.32–7.67 (20H, m, Pc–H, Phenyl–H), 1.51 (36H, s, *t*-Bu). Calcd for $C_{72}H_{64}ClGaN_8O_4$: Calcd C 71.44, H 5.33, N 9.26; Found: C 71.58, H 5.28, N 8.95. MALDI-TOF-MS *m/z*: Calcd 1210.5; Found ($M^{2+}$) 1212.0.

**4.4.5. 1(4),8(11),15(18),22(25)-(Tetraphenoxyphthalocyaninato)indium(III) (7a).** Synthesis and purification was as outlined for **5a** except indium chloride instead of gallium chloride was employed. The amount of the reagents employed were: **3a** (1.5 g, 6.8 mmol), indium(III) chloride (0.75 g, 3.4 mmol) in quinoline (5 ml). TLC: $R_f$=0.47. Yield: 0.66 g (37%). UV–vis (DMSO): $\lambda_{max}$ nm ($\log \varepsilon$) 331 (4.89), 639 (4.69), 712 (5.13). IR [(KBr) $\nu_{max}/cm^{-1}$]: 3063 (Ar–CH), 1588 (C=C), 1077 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.20–9.08 (4H, m, Pc–H), 7.57–8.02 (4H, m, Pc–H), 7.17–7.49 (24H, m, Phenyl–H and Pc–H). Calcd for $C_{56}H_{32}ClN_8O_4In$: C 65.23, H 3.13, N 10.87; Found: C 65.78, H 3.19, N 10.56. MALDI-TOF-MS *m/z*: Calcd 1031.18; Found (M) 1031.06.

**4.4.6. 1(4),8(11),15(18),22(25)-(Tetra-*tert*-butylphenoxyphthalocyaninato)indium(III) (7b).** Synthesis and purification was as outlined for **5a** except **3b** instead of **3a** and indium chloride instead of gallium chloride were employed. The amount of the reagents employed were: **3b** (1.50 g, 5.4 mmol), indium(III) chloride (0.59 g, 2.7 mmol) in quinoline (5 ml). TLC: $R_f$=0.51. Yield: 0.79 g (47%). UV–vis (DMSO): $\lambda_{max}$ nm ($\log \varepsilon$) 340 (4.77), 641 (4.60), 714 (5.20). IR [(KBr) $\nu_{max}/cm^{-1}$]: 3064 (Ar–CH), 2961 and 2867 (C–H), 1582 (C=C), 1078 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.42–9.04 (4H, m, Pc–H), 7.78–8.11 (4H, m, Pc–H), 7.22–7.78 (20H, m, Phenyl–H and Pc–H), 1.41 (36H, s, *t*-Bu). Calcd for $C_{72}H_{64}ClN_8O_4In$: C 68.87, H 5.14, N 8.92; Found: C 69.42, H 5.16, N 8.98. MALDI-TOF-MS *m/z*: Calcd 1255.6; Found ($M^{2+}$) 1257.3.

**4.4.7. 2(3),9(10),16(17),23(24)-(Tetraphenoxyphthalocyaninato)indium(III) (8a).** Synthesis and purification was as outlined for **5a** except **4a** instead of **3a** and indium chloride instead of gallium chloride were employed. The amount of the reagents employed were: **4a** (1.5 g, 6.8 mmol), indium(III) chloride (0.75 g, 3.4 mmol) in quinoline (5 ml). TLC: $R_f$=0.63. Yield: 0.92 g (52%). UV–vis (DMSO): $\lambda_{max}$ nm ($\log \varepsilon$) 364 (5.02), 625 (4.65), 696 (5.09). IR [(KBr) $\nu_{max}/cm^{-1}$]: 3065 (Ar–CH), 1589 (C=C), 1086 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.67–8.93 (1H, 2H, 1H, m, Pc–H), 8.33–8.59 (1H, 2H, 1H, s, s, s, Pc–H), 7.64–7.79 (4H, m, Pc–H), 7.48–7.62 (8H, dd, Phenyl–H), 7.38–7.46 (8H, dd, Phenyl–H), 7.26–7.37 (4H, dd, Phenyl–H). Calcd for $C_{56}H_{32}ClN_8O_4In$: C 65.23, H 3.13, N 10.87; Found: C 65.46, H 3.18, N 10.96. MALDI-TOF-MS *m/z*: Calcd 1031.18; Found (M) 1031.01.

**4.4.8. 2(3),9(10),16(17),23(24)-(Tetra-*tert*-butylphenoxyphthalocyaninato)indium(III) (8b).** Synthesis and purification was as outlined for **5a** except **4b** instead of **3a** and indium chloride instead of gallium chloride were employed. The amount of the reagents employed were: **4b** (1.5 g, 5.4 mmol), indium(III) chloride (0.59 g, 2.7 mmol) in quinoline (5 ml). TLC: $R_f$=0.69. Yield: 0.81 g (48%). UV–vis (DMSO): $\lambda_{max}$ nm ($\log \varepsilon$) 363 (4.99), 626 (4.64), 696 (5.14). IR [(KBr) $\nu_{max}/cm^{-1}$]: 3063 (Ar–CH), 2961 and 2867 (C–H), 1601 (C=C), 1087 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$, ppm 8.31–8.90 (8H, m, Pc–H), 7.51–7.72 (12H, m, Pc–H and Phenyl–H), 7.32–7.43 (8H, m, Phenyl–H), 1.46 (36H, s, *t*-Bu). Calcd for $C_{72}H_{64}ClN_8O_4In$: Calcd C 68.87, H 5.14, N 8.92; Found: C 68.29, H 5.11, N 8.79. MALDI-TOF-MS *m/z*: Calcd 1255.6; Found ($M^+$) 1256.7.

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