Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 192 (2007) 179–187

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

# Photochemistry, photophysics and nonlinear optical parameters of phenoxy and *tert*-butylphenoxy substituted indium(III) phthalocyanines

Vongani Chauke [a], Mahmut Durmuş [a,b], Tebello Nyokong [a,*]

[a] *Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa*
[b] *Department of Chemistry, Gebze Institute of Technology, PO Box 141, Gebze 41400, Turkey*

Received 11 April 2007; received in revised form 20 May 2007; accepted 22 May 2007
Available online 25 May 2007

## Abstract

This work hereby presents the syntheses, photochemistry and photophysics of octaphenoxy ((Cl)InOPPc) and octakis(4-*tert*-butylphenoxy)chloroindium ((Cl)InOTBPPc) phthalocyanines. Calculated nonlinear parameters of these complexes are compared with those of the corresponding GaPc derivatives and tetrasubstituted GaPc and InPc complexes. Fluorescence quantum yields do not vary much between (Cl)InOPPc and (Cl)InOTBPPc complexes in different solvents. High quantum yields of triplet state ($\Phi_T$ ranging from 0.70 to 0.91 in dimethysulphoxide, DMSO) and singlet oxygen generation ($\Phi_\Delta$, ranging from 0.61 to 0.79 in DMSO) were obtained. Short triplet lifetimes 50–60 μs were obtained in DMSO). The optical limiting threshold intensity ($I_{\text{lim}}$) for the InPc derivatives were calculated and compared with those of corresponding tetrasubstituted InPc and GaPc complexes. The latter were found to be better optical limiters.

*Keywords:* Indium phthalocyanine; Galium phthalocyanine; Triplet quantum yield; Triplet lifetime; Fluorescence quantum yield; Singlet oxygen quantum yield; Nonlinear optical parameters

## 1. Introduction

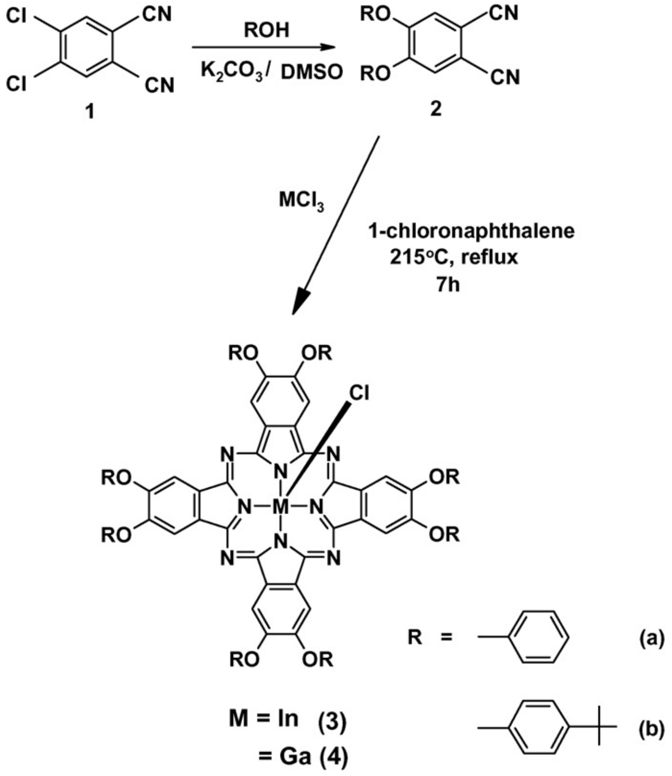
Metallophthalocyanines (MPcs), a family of aromatic macrocycles based on an extensive delocalized 18-π electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific research. There has been growing interest in the use of phthalocyanines in a variety of new technology fields including nonlinear optics [1] semiconductor devices [2], Langmuir–Blodgett films [3], electrochromic display devices [4], liquid crystals [5], and as photosensitizers in photodynamic therapy (PDT) [6]. For nonlinear optical applications MPcs have advantages over inorganic compounds currently in use due to their small dielectric constants [7], fast response times, ease of processibility into optical components and their economic feasibility [1,7]. The MPcs can be modulated in a plethora of ways by changing the peripheral and non-peripheral substituents on the ring in addition to changing the central metal and the axial ligands.

Heavy metals, especially diamagnetic metals, play a major role in photosensitising and optical limiting mechanisms because they enhance intersystem crossing through spin orbit coupling. This is desirable because it improves the chances of getting a large population in the triplet state. Axial ligands in MPcs are useful in preventing or minimizing intermolecular interactions which result in aggregation in solution. Aggregation can result in the fast decay of the excited states. Indium is a useful central metal in MPc complexes since it is diamagnetic and able to host axial ligands. Indium phthalocyanines have been reported to have good photosensitising and optical limiting properties [1,7–11]. Mainly tetrasubstituted InPc derivatives have been reported in the literature, since they have much higher solubility due to lower degree of order which facilitates salvation, compared to octasubstituted derivatives. Octasubstituted MPcs on the other hand have isomeric purity. In this work we study the photochemical (singlet oxygen and photodegradation quantum yields) properties and photophysical (triplet state lifetimes and quantum yields, and fluorescence quantum yields and lifetimes) behaviour of octasubstituted indium phthalocyanines in different solvents. These are substituted on the peripheral position with large ligands (phenoxy, (Cl)InOPPc, and *tert*-butyl phenoxy,

---

[*] Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.
*E-mail address:* t.nyokong@ru.ac.za (T. Nyokong).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2007.05.022



Scheme 1. Synthetic pathway to octa-substituted phenoxy and *tert*-butylphenoxy phthalocyaninato gallium and indium chloride on the peripheral positions.

(Cl)InOTBPPc, Scheme 1) to prevent aggregation. The synthesis of the (Cl)InOPPc complex has been reported before [12]. The nonlinear optical parameters are also calculated and compared with those of the corresponding GaPc derivatives reported before [13] and with those of the peripherally and non-peripherally tetrasubstituted GaPc and InPc derivatives [14], Fig. 1.

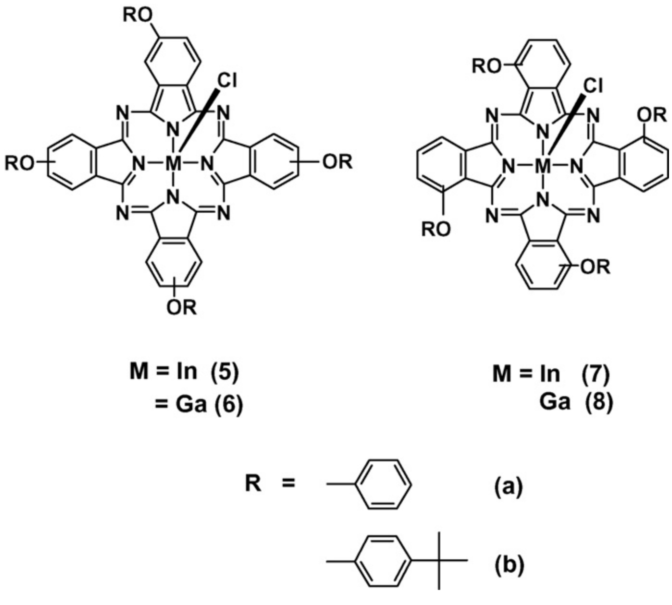


Fig. 1. Molecular structure of tetra substituted GaPc and InPc derivatives.

## 2. Experimental

### 2.1. Materials

Acetic anhydride ($Ac_2O$), acetone, ammonia solution ($NH_4OH$), chloroform, methanol (MeOH), 1-chloronaphthalene, hexane and deuterated chloroform ($CDCl_3$) were obtained commercially and dried before use; formamide ($HCONH_2$), potassium carbonate ($K_2CO_3$), phthalonitrile, thionyl chloride ($SOCl_2$), phenol and 4-*tert*-butylphenol were purchased from Aldrich and used as received. 4,5-Dichloro-1,2-dicyanobenzene [15] and unsubstituted (chloro) indium phthalocyanine [16] were synthesized and purified according to literature procedure. Zinc(II) phthalocyanine (ZnPc) and 1,3-diphenylisobenzofuran (DPBF) were obtained from Aldrich. Dimethylsulphoxide (DMSO) was purchased from SAARCHEM, and dried in alumina before use.

### 2.2. Equipment

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 $F_{254}$. Ground state electronic absorption spectra were performed on a Varian Cary 500 UV–vis-NIR spectrophotometer; Infra-red spectra (KBr pellets) on Perkin-Elmer Spectrum 2000 FT-IR Spectrometer and $^1H$ nuclear magnetic resonance signals on a Bruker EMX 400 NMR spectrometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse Fluorescence spectrophotometer. Photo-irradiations were done using a General Electric Quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 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 MAX 5100 (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 Nd: YAG laser (Quanta-Ray, 1.5J/90 ns) pumped tunable dye laser (Lambda Physic FL 3002, Pyridin 1 dye in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube (PMT) was used as detector. Signals were recorded with a Tektronix TDS 360 two-channel digital real-time oscilloscope. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

### 2.3. Syntheses

*The substituted phthalonitriles*. 4,5-Bis(phenoxy)-1,2-dicyanobenzene (**2a**) and 4,5-bis(4-*tert*-butylphenoxy)-1,2-dicyanobenzene (**2b**) were synthesized from 4,5-dichloro-1,2-dicyanobenzene (**1**) and phenol (or 4-*tert*-butylphenol) in dry DMSO according to literature methods [15].

Complexes **3a** and **3b** (Scheme 1) were synthesized and characterised according the method reported before [12] with a slight modification (using corresponding phthalonitriles instead of diiminoisoindolines) as follows:

**3a** *((Cl)InOPPc).* A mixture of 4,5-bis(phenoxy)-1,2-dicyanobenzene **(2a)** (2.81 g, 10 mmol), anhydrous $InCl_3$ (0.99 g, 5 mmol) and 1-chloronaphthalene (~3.8 ml) were placed in a preheated oil bath (215 °C). The reaction mixture was stirred at this temperature for 7 h under dry nitrogen atmosphere. After cooling the green product was placed in a silica gel column, washed with hexane to remove the brownish layer of 1-chloronaphthalene. THF was then used to elute the green product from the column. THF solvent was then removed by evaporation. Preparative TLC (thin layer chromatography) silica gel plates were used for further purification with chloroform as the eluting solvent. The impurities (brown layers) were then cut from the plates leaving the pure green product. The silica gel/green product was placed in a beaker of chloroform to dissolve the product. The mixture was then filtered, and the solvent was removed by evaporation. Yield: 1.38 g (20%); UV/vis (DMSO): $\lambda_{max}$ (log $\varepsilon$); 691 (5.23), 622 (3.59), 368 (4.08); IR (KBr): $\nu_{max}$/cm$^{-1}$; 3034, 3052 (Ar–H), 1588 (C=C), 1460, 1452, 1407, 1339, 1275 1201 (C–O–C), 1162, 1089, 1089, 1037, 1003; $^1$H NMR: ($CDCl_3$,) $\delta$ ppm; 8.9 (s, 8H, Pc-H), 7.1–7.4 (m, 40H, phenyl-H). Calc. for $C_{80}H_{48}N_8O_8InCl$: C, 68.65; H, 3.45; N, 8.01. Found: C, 67.79; H, 3.37; N, 7.73.

**3b** *((Cl)InOTBPPc).* **3b** was synthesized as described above for **3a** except **2b** was used instead of **2a**. The amounts of the reagents employed were: **2b** (3.18 g, 8.00 mmol), anhydrous $InCl_3$ (0.88 g, 4.00 mmol) and 1-chloronaphthalene (4 ml); Yield: 1.11 g (35%); UV–vis (DMSO): $\lambda_{max}$ (log $\varepsilon$); 692 (5.10), 622 (3.59), 367 (4.22); IR (KBr): $\nu_{max}$/cm$^{-1}$; 3034–3052 (Ar–H), 2952–2866 (C–H), 1589 (C=C), 1506, 1489, 1454, 1411, 1338, 1274, 1205 (C–O–C), 1098, 1037, 891, 861, 741; $^1$H NMR: ($CDCl_3$) $\delta$ ppm; 8.7 (broad s, 8H, Pc-H), 7.0–7.4 (m, 32H, phenyl-H), 1.1–1.4 (m, 72H, $CH_3$); Calc. for $C_{112}H_{112}N_8O_8InCl.CHCl_3$: C, 68.97; H, 5.79; N, 5.69; Found: C, 69.42; H, 5.14; N, 5.29

The syntheses of (Cl)GaOPPc (**4a**) and (Cl)GaOTBPPc (**4b**) have been reported [13] before, as well as tetrasubstituted derivatives **5–8** [14] Fig. 1.

### 2.4. Photochemical and photophysical studies

#### 2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yields ($\Phi_\Delta$) were determined in air (no oxygen bubbled) using the relative method with ZnPc as reference and DPBF as chemical quencher for singlet oxygen, using the following equation:

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R_{DPBF} I_{abs}^{Std}}{R_{DPBF}^{Std} I_{abs}} \tag{1}$$

where $\Phi_\Delta^{Std}$ is the singlet oxygen quantum yield for the standard, ZnPc ($\Phi_\Delta = 0.67$ in DMSO [17], 0.56 in DMF [18], 0.58 in toluene [19] and 0.53 in THF [20]. $R_{DPBF}$ and $R_{DPBF}^{Std}$ are the DPBF photobleaching rates in the presence of the (Cl)InPc derivatives under investigation and the standard, respectively. $I_{abs}$ and $I_{abs}^{Std}$ are the rates of light absorption by the (Cl)InPc derivatives and the standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [18], the concentration of DPBF was lowered to ~$3 \times 10^{-5}$ mol dm$^{-3}$. Solutions of sensitizer (absorbance = 0.2 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the *Q* band region using the setup described above. DPBF degradation at 417 nm was monitored. The light intensity for singlet oxygen studies was $2 \times 10^{16}$ photons s$^{-1}$ cm$^{-2}$.

#### 2.4.2. Photodegradation quantum yields

To determine the stability of InPc derivatives ((Cl)InOPPc and (Cl)InOTBPPc) photodegradation quantum yields were calculated using the following equation:

$$\Phi_{Pd} = \frac{(C_0 - C_t) V N_A}{I_{abs} S t} \tag{2}$$

where $C_0$ and $C_t$ in mol dm$^{-3}$ are (Cl)InOPPc and (Cl)InOTBPPc concentrations before and after irradiation, respectively, $V$ the reaction volume, $S$ the irradiated cell area (2.0 cm$^2$), $t$ the irradiation time, $N_A$ the Avogadro's number and $I_{abs}$ is the overlap integral of the radiation source intensity and the absorption of the Pc (the action spectrum) in the region of the interference filter transmittance.

#### 2.4.3. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method, using the following equation [21,22]:

$$\Phi_F = \Phi_F(\text{Std}) \frac{F A_{Std} \eta^2}{F_{Std} A \eta_{Std}^2} \tag{3}$$

where $F$ and $F_{Std}$ are the areas under the fluorescence curves of the InPc derivatives and the standard, respectively. $A$ and $A_{Std}$ are the respective absorbances of the sample and standard at the excitation wavelengths (which was ~0.05 in all solvents used), and $\eta$ and $\eta_{Std}$ are the refractive indices of solvents used for the sample and standard, respectively. ZnPc was employed as a standard in DMSO ($\Phi_F = 0.18$ [23].

Natural radiative lifetimes ($\tau_0$) were determined using PhotochemCAD Program [24]. which uses the Strickler–Berg equation, and fluorescence life times ($\tau_F$) are given by the following equation:

$$\Phi_F = \frac{\tau_F}{\tau_0}. \tag{4}$$

#### 2.4.4. Triplet quantum yields and lifetimes

The triplet quantum yields were determined using the following equation [25]:

$$\Phi_T = \Phi_T^{Std} \frac{\Delta A_T \varepsilon_T^{Std}}{\Delta A_T^{Std} \varepsilon_T} \tag{5}$$

where $\Delta A_T$ and $\Delta A_T^{Std}$ are the changes in the triplet state absorbances of the InPc derivatives and the standard, respectively. $\varepsilon_T$ and $\varepsilon_T^{Std}$ are the triplet state molar extinction coefficients for the indium derivatives and the standard, respectively. $\Phi_T^{Std}$ is the triplet quantum yield for the standard, ZnPc

($\Phi_T = 0.65$ in DMSO [26], 0.58 in DMF [27] and 0.65 in toluene [28]).

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 a (Cl)InPc molecule.

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

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

### 2.5. Calculation of nonlinear optical parameters

#### 2.5.1. Limiting threshold intensity ($I_{lim}$)

Optical limiters show optical limiting effects when the intensity of a light beam is strongly attenuated, i.e. once the input exceeds a threshold limit intensity ($I_{lim}$). The limiting intensity values were calculated using the following equation [1,10]:

$$I_{lim} = \frac{h\omega^*}{2\pi\sigma_S\tau_T} \tag{7}$$

where $\omega^*$, $\sigma_S$ and $\tau_T$ are the frequency at which the system absorbs, singlet state absorption cross section and triplet lifetimes, respectively.

#### 2.5.2. Third order susceptibility $\chi^{(3)}$ and second hyperpolarizability, $\gamma$

The imaginary part of the third order susceptibility $\chi^{(3)}$ was calculated using the following equation [1]:

$$I_m[\chi^{(3)}] = \frac{2\eta^2 c^2 \beta}{\pi\omega^*} \times 10^{-22} \tag{8}$$

where $\eta$ ($\eta = 1.478$ for DMSO) and $c$ are, respectively, the linear refractive index, and the speed of light and $\omega^*$ is as defined above. $\beta = 5.3\varepsilon_S\varepsilon_T[C]\Phi_{ISC}$, where $\varepsilon_S$ and $\varepsilon_T$ are extinction coefficients for the ground and triplet state, respectively, $[C]$ is the concentration of active species in the triplet state and $\Phi_{ISC}$ is the intersystem crossing quantum yield.

At a molecular level, $\chi^{(3)}$ is directly related to the second hyperpolarizability, $\gamma$, through the following equation [1,5].

$$\gamma = \frac{I_m[\chi^{(3)}]}{f^4[C]N_a} \tag{9}$$

where $N_a$ is Avogadro's constant, $[C]$ the concentration of the active species in the triplet state and $f$ is Lorentz local field factor, $f = (\eta^2 + 2)/3$.

$I_m[\chi^{(3)}]$ and $\gamma$ were used to quantify the nonlinear absorption.

## 3. Results and discussion

### 3.1. Syntheses and characterization

Scheme 1 gives the synthetic pathways for the InPc complexes discussed in this work. 1,2-Dicyanobenzene was used to prepare 4,5-disubstituted phthalonitrile derivatives, through base-catalysed nucleophilic aromatic displacement. The same route was applied to prepare phenoxy and *tert*-butyl phenoxy substituted 1,2-dicyanobenzenes (**2a** and **2b**) from phenol and 4-*tert*-butylphenol, respectively (Scheme 1). The reactions were carried out in DMSO at room temperature and gave yields of 52% for **2a** and 48% for **2b**.

The syntheses of MPc complexes {(Cl)InOPPc and (Cl)InOTBPPc} were achieved by treatment of substituted 1,2-dicyanobenzenes **2a** and **2b** with anhydrous indium (III) chloride in 1-chloronaphthalene (Scheme 1). Indium is a large metal, it therefore requires high energy to insert it into the phthalocyanine ring. For this reason a high boiling solvent, 1-chloronaphthalene, was used to achieve this purpose. Complex **3a** is octaphenoxy substituted and **3b** is octa-*tert*-butylphenoxy substituted. Column and preparative thin layer chromatography with silica gel were employed to obtain the pure products from the reaction mixtures.

Phthalocyanines generally have poor solubility in most organic solvents; nevertheless introduction of phenoxy and 4-*tert*-butyl phenoxy substituents on the ring increases the solubility. The synthesized complexes {(Cl)InOPPc and (Cl)InOTBPPc)} show good solubility in organic solvents such as dichloromethane and DMSO. Indium derivatives were characterised by UV–vis, IR and NMR spectroscopies, and elemental analysis. The analyses are consistent with the predicted structures as shown in Section 2. After conversion into indium phthalocyanines, the characteristic C≡N stretch at 2237 and 2213 $\text{cm}^{-1}$ of 1,2-dicyanobenzenes **2a** and **2b** disappeared, indicative of metallophthalocyanine formation. The characteristic vibrations corresponding to ether groups (C–O–C) were observed at 1209 and 1219 $\text{cm}^{-1}$ for dinitrile compounds (**2a** and **2b**), 1201 and 1205 $\text{cm}^{-1}$ for phthalocyanine complexes (**3a** and **3b**). Aromatic CH stretching were observed from 3034 to 3052 $\text{cm}^{-1}$.

The substituted InPc derivatives were found to be pure by $^1$H NMR with all the substituents and ring protons observed in their respective regions. The phenoxy substituted complex **3a** showed the resonances belonging to ring protons as a singlet at 8.9 ppm, a multiplet between 7.1 and 7.4 ppm, integrating for 8 and 40 protons, respectively. The *tert*-butylphenoxy substituted complex **3b** showed the resonances belonging to ring protons as a singlet at 8.7 ppm and a multiplet between 7.0 and 7.4 ppm for aromatic protons integrating for 8 and 32 protons each, respectively, making a total of 40 protons as expected. The methyl protons appear as multiplets between 1.1 and 1.4 ppm integrating for 72 protons.

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

The ground state electronic absorption spectra of (Cl)InOPPc and (Cl)InOTBPPc show sharp Q bands (Figs. 2 and 3, Table 1), typical of unaggregated MPc complexes. The Q bands were observed at 686, 691 and 692 nm in DMSO for (Cl)InPc, (Cl)InOPPc and (Cl)InOTBPPc, respectively. The Q bands are slightly red shifted in the latter two complexes, suggesting a small electron donating ability of the substituents. Beer's law was obeyed for concentrations ranging from $1.85 \times 10^{-7}$ to $2.28 \times 10^{-5}$ mol $\text{dm}^{-3}$. For a particular MPc, ((Cl)InOPPc or

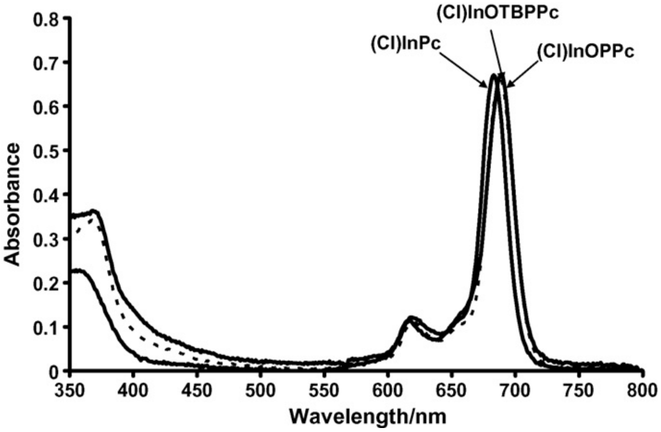


Fig. 2. Ground state absorption spectra of (Cl)InPc, (Cl)InOPPc and (Cl)InOTBPPc in DMF. Concentration: ~$2.5 \times 10^{-5}$ mol dm$^{-3}$.

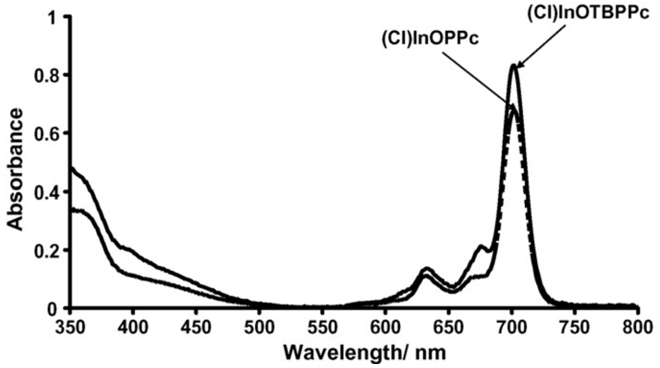


Fig. 3. Ground state absorption spectra of (Cl)InOPPc and (Cl)InOTBPPc in $CHCl_3$. Concentration: ~$2.2 \times 10^{-5}$ mol dm$^{-3}$.

(Cl)InOTBPPc) in different solvents, it can be observed that the longest Q band absorption wavelengths are obtained in chloroform while the shortest are obtained in DMF, Table 1. This observation could, to some extent, be explained by considering the refractive indices of the solvents. It is known that red-shifting of absorption spectra is a function of the solvent's refractive index [19]. For the substituted derivatives, (Cl)InOPPc and (Cl)InOTBPPc, new absorption bands are observed at ~430 nm (Figs. 2 and 3). Since these bands are observed only for the substituted derivatives, they must be due to charge transfer transitions involving the substituents.

### 3.3. Photophysical studies

#### 3.3.1. Fluorescence quantum yields and lifetimes

The octasubstituted InPc complexes studied in this work showed similar fluorescence behaviour in all the solvents. Fig. 4 shows the absorbance and fluorescence spectra of (Cl)InOPPc in chloroform. The fluorescence spectra are mirror images of absorption spectra. The small Stokes shifts suggest that the structural change between the ground and excited states are small. However, the fluorescence spectra is slightly more broadened

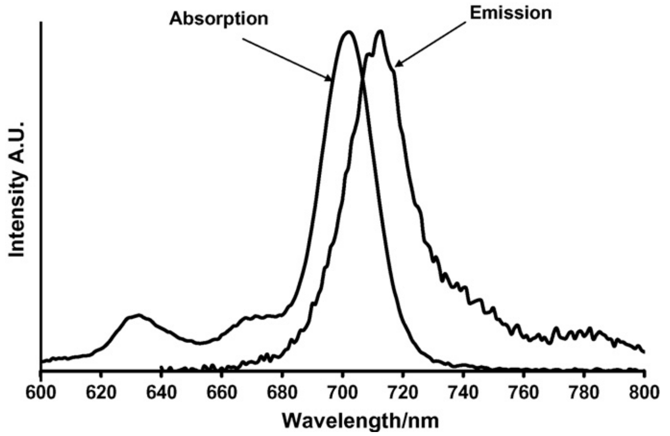


Fig. 4. Fluorescence emission ($\lambda_{exc}$ = 640 nm) and absorbance spectra of (Cl)InOPPc in $CHCl_3$.

Table 1
Spectral, photophysical and photochemical parameters of InPc derivatives in various solvents

| Solvent | MPc | $\lambda_{max} Q_{abs}$ (nm) | $\lambda_{max} Q_{emm}$ (nm) | $\tau_T$ (µs) | $\Phi_F$ | $\Phi_T$[a] | $\Phi_{IC}$[a] | $\Phi_{pd}$ ($\times 10^5$) | $\Phi_\Delta$ | $S_\Delta$[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| DMSO | (Cl)InPc[c] | 686 | 700 | 50 | 0.018 | 0.91 | 0.01 | 9.90 | 0.61 | 0.67 |
| | (Cl)InOPPc | 691 | 705 | 60 | 0.025 | 0.84 | 0.14 | 1.39 | 0.79 | 0.94 |
| | (Cl)InOTBPPc | 692 | 702 | 50 | 0.020 | 0.70 | 0.28 | 2.35 | 0.72 | 1.03 |
| DMF | (Cl)InPc | 681 | 696 | 10 | 0.017 | 0.83 | 0.15 | 1.05 | 0.70 | 0.94 |
| | (Cl)InOPPc | 686 | 700 | 20 | 0.018 | 0.76 | 0.22 | 5.64 | 0.60 | 0,79 |
| | (Cl)InOTBPPc | 686 | 697 | 9.5 | 0.022 | 0.61 | 0.37 | 4.83 | 0.50 | 0.82 |
| Toluene[d] | (Cl)InOPPc | 698 | 707 | 20 | 0.023 | 0.55 | 0.43 | 2.75 | 0.31 | 0.56 |
| | (Cl)InOTBPPc | 698 | 708 | 10 | 0.021 | 0.41 | 0.60 | 3.19 | 0.30 | 0.71 |
| THF | (Cl)InPc | 687 | 698 | 8.8 | 0.076 | – | – | 1.15 | – | – |
| | (Cl)InOPPc | 696 | 708 | 7.8 | 0.020 | – | – | 0.82 | – | – |
| | (Cl)InOTBPPc | 697 | 707 | 30 | 0.020 | – | – | 1.87 | – | – |
| $CHCl_3$[d] | (Cl)InOPPc | 700 | 710 | 8.1 | 0.056 | – | – | 5.96 | – | – |
| | (Cl)InOTBPPc | 701 | 710 | 7.8 | 0.059 | – | – | 6.09 | – | – |

[a] Values not obtained in THF and $CHCl_3$ due to lack of reference standards.
[b] $S_\Delta = \Phi_\Delta / \Phi_T$.
[c] Values were from literature, Ref. [13].
[d] (Cl)InPc is not soluble in $CHCl_3$ and toluene.

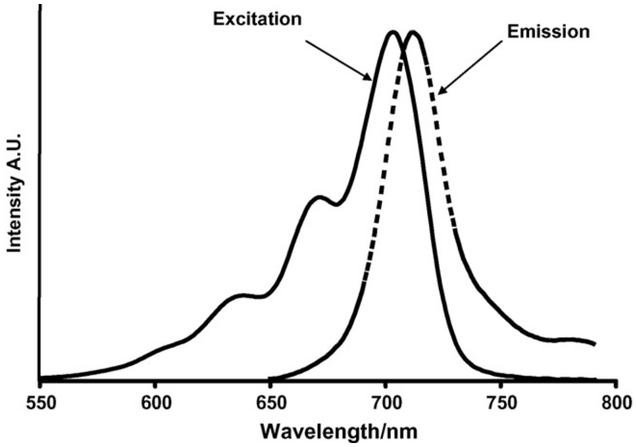


Fig. 5. Excitation and fluorescence emission ($\lambda_{exc} = 640$ nm) spectra of (Cl)InOPPc in $CHCl_3$.

compared to the absorption spectra. The excitation spectra are different from absorbance spectra, Fig. 5. The Q bands of all the excitation spectra suggests that following excitation, there were some changes in the molecule, presumably due to loss of symmetry. This loss of symmetry may be the cause of the slight broadening of the fluorescence spectra stated above. This behaviour was not observed in the corresponding GaPc complexes (complexes **4** in Scheme 1) reported before [13]. This could be due to the fact that indium is a rather large metal, hence more likely to lose symmetry due to the metal which does not fit well in the ring. Fluorescence quantum yield ($\Phi_F$) values can be affected by a number of factors that include temperature, molecular structure and solvent parameters, such as polarity, viscosity, refractive index, and the presence of heavy atoms in the solvent molecule. Table 1 shows $\Phi_F$ values of InPc derivatives studied in this work. The differences of $\Phi_F$ values among the InPc derivatives is not significant, for example in DMF, $\Phi_F$ values for (Cl)InPc, (Cl)InOPPc and (Cl)InOPTBPPc are 0.017, 0.018 and 0.022, respectively. The $\Phi_F$ values for these InPc derivatives are low relative to their corresponding gallium counterparts, which ranged from 012 to 0.22 [13]. The low values were expected and are due to the heavy indium atom which enhances intersystem crossing (through spin orbit coupling) which then affords large triplet quantum yields, Table 1, see discussion below.

Chloroform, unexpectedly, yielded the highest $\Phi_F$ values of 0.056 and 0.059 for (Cl)InOPPc and (Cl)InOTBPPc, respectively. Because chloroform contains a heavy Cl atom which promotes intersystem crossing, lower $\Phi_F$ values were expected. This could be proof that it is not only the heavy atom effect that affects $\Phi_F$ values. $\Phi_F$ values in THF showed interesting behaviour in that the unsubstituted InPc ($\Phi_F = 0.076$) yielded the largest $\Phi_F$ value. High values of $\Phi_F$ in THF have been reported before [19].

Table 2 shows that the fluorescence lifetimes ($\tau_F$) of the complexes were within the accepted range for phthalocyanines. In highly viscous solvents such as DMF and DMSO, the rate constant of fluorescence ($k_F$) decreases with increasing size of substituents as follows: (Cl)InPc > (Cl)InOPPc > (Cl)InOTBPPc. The opposite was observed in toluene and chloroform, i.e. the rates increased with increasing size of substituents, (Cl)InOTBPPc > (Cl)InOPPc. $k_F$ values in THF did not conform to any pattern.

### *3.3.2. Triplet quantum yields and lifetimes*

Table 1 gives the triplet state parameters, $\Phi_T$ and $\tau_T$. The triplet quantum yields ($\Phi_T$) which are a measure of molecules that undergo intersystem crossing to occupy the triplet state, were calculated using Eq. (5). From the results in Table 1, it seems both solvent and the introduction of phenoxy and *t*-butylphenoxy onto the (Cl)InPc ring had an effect on the $\Phi_T$ values. Larger $\Phi_T$ values were obtained in highly viscous and coordinating solvents, for example in DMSO values of 0.91, 0.84 and 0.70 were obtained for (Cl)InPc, (Cl)InOPPc and (Cl)InOTBPPc, respectively. $\Phi_T$ values in toluene were the smallest. The small values in toluene could be due poor intersystem crossing as a result of loss through internal conversion, large quantum yields of internal conversion ($\Phi_{IC}$) were observed in toluene, Table 1.

Table 2
Rate consatants for the excited singlet state deactivation processes

| Solvent | MPc | $\tau_F$ (ns) | $k_F$ ($10^{-7}$ $s^{-1}$)[a] | $k_{ISC}$ ($10^{-8}$ $s^{-1}$)[a] | $k_{IC}$ ($10^{-7}$ $s^{-1}$)[a] | $k_d$ ($s^{-1}$)[a] |
|---|---|---|---|---|---|---|
| DMSO | (Cl)InPc | 0.18 | 8.74 | 0.36 | 0.016 | 2.44 |
| | (Cl)InOPPc | 0.32 | 7.81 | 26.3 | 43.8 | 2.05 |
| | (Cl)InOTBPPc | 0.26 | 7.70 | 27.0 | 107.7 | 3.54 |
| DMF | (Cl)InPc | 0.11 | 15.5 | 75.4 | 136.4 | 10.5 |
| | (Cl)InOPPc | 0.16 | 11.3 | 47.5 | 137.5 | 28.3 |
| | (Cl)InOTBPPc | 0.21 | 10.5 | 29.0 | 176.2 | 50.8 |
| Toluene | (Cl)InOPPc | 0.19 | 12.1 | 28.9 | 22.6 | 10.5 |
| | (Cl)InOTBPPc | 0.10 | 21.0 | 42.0 | 600.0 | 6.23 |
| THF | (Cl)InPc | 0.62 | 1.22 | – | – | 13.8 |
| | (Cl)InOPPc | 0.05 | 40.0 | – | – | 31.9 |
| | (Cl)InOTBPPc | 0.05 | 30.2 | – | – | 13.0 |
| $CHCl_3$ | (Cl)InOPPc | 0.61 | 9.18 | – | – | 73.2 |
| | (Cl)InOTBPPc | 0.57 | 10.3 | – | – | 78.0 |

[a] $k_F = \frac{\Phi_F}{\tau_F}$; $k_{ISC} = \frac{\Phi_T}{\tau_F}$; $k_{IC} = \frac{\Phi_{IC}}{\tau_F}$; $k_d = \frac{\Phi_{pd}}{\tau_T}$.

It is interesting to note that the quantum yields of triplet state ($\Phi_T$) decrease with increase in size of substituents, in the order (Cl)InPc > (Cl)InOPPc > (Cl)InOTBPPc. This could be due to a concept called the "loose bolt" effect [29] for the *tert*-butyl phenoxy substituted (Cl)InOTBPPc. The effect is associated with the vibrations of the bonds set off by the parent molecule in a similar way as a loose bolt in a moving part of the machine, which tends to be set in motion by the other moving parts of the machine. It seems the $\sigma$ C–H bonds of the *t*-butyl substituents may show this effect. The effect increases the rate of internal conversion as electronic energy is lost through C–H vibrations [29]. The "loose bolt" effect is expected to be less pronounced in the (Cl)InOPPc complex since it has less C–H bonds than (Cl)InOTBPPc. The triplet lifetimes $\tau_T$ Table 1, were relatively small. The short triplet lifetimes could be due to their large triplet state quantum yields. Table 1 gives the rate constants for internal conversion and intersystem crossing. There were no well-defined trends in these values.

### 3.4. *Photochemical studies*

#### 3.4.1. *Singlet oxygen quantum yields ($\Phi_\Delta$)*

Table 1 lists singlet oxygen quantum yield ($\Phi_\Delta$) values. $\Phi_\Delta$ measures the photosensitizer's ability to generate singlet oxygen. Singlet oxygen is formed through energy transfer from an energy rich photosensitizer in the triplet excited state to ground state molecular oxygen. The generation of singlet oxygen depends on a number of factors such as the triplet quantum yield, triplet state lifetime, the effectiveness of energy transfer, the ability of the subsituents to quench the triplet state and the triplet energy. The largest $\Phi_\Delta$ values of 0.79 and 0.72 was for obtained (Cl)InOTPPc and (Cl)InOTBPPc in DMSO, respectively. In DMSO, DMF and THF, (Cl)InOPPc yielded larger $\Phi_\Delta$ values than (Cl)InOTBPPc. The values were similar in toluene.

$S_\Delta$ measures the efficiency of the excited energy transfer from the triplet photosensitizer to the molecular oxygen in its triplet state. The results for most of the InPc derivatives in different solvents were near unity (except for (Cl)InOPPc in toluene) which reflects that there's an efficient quenching of the triplet state by the molecular oxygen in its triplet state.

#### 3.4.2. *Photodegradation quantum yields ($\Phi_{pd}$)*

Photodegradation is a process where a phthalocyanine ring is degraded under irradiation. $\Phi_{pd}$ are affected by several factors, such as the nature of the solvent and of the ring substiuents. Some susbtituents are known to stabilize the ring against photodegradation and others make it more vulnerable to oxidative attack. Although there is no defined trend to the $\Phi_{pd}$ values in Table 1, all the MPcs studied in this work fall within the reported [19,30,31] stability range ($\times 10^{-5}$) for phthalocyanines. The rate constants for photodegradation were within the normal range for MPcs.

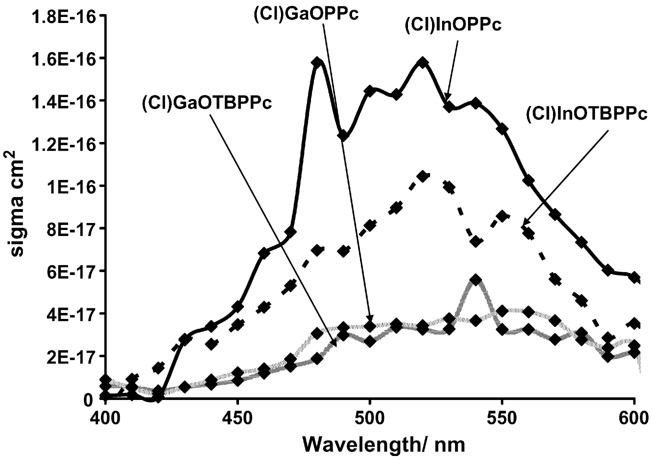


Fig. 6. Absorption cross sections for the excitet triplet state for gallium and indium phthalocyanine derivatives.

### 3.5. *Nonlinear optical parameters*

These parameters were calculated for (Cl)InOPPc (**3a**) and (Cl)InOTBPPc (**3b**) and compared with the corresponding (Cl)GaOPPc (**4a**) and (Cl)GaOTBPPc (**4b**) and to the peripherally and non-peripherally tetrasubstituted InPc (**5**,**7**) and GaPc (**6**,**8**) derivatives. Triplet absorption cross sections for indium and gallium derivatives occurred in the region between 400 and 600 nm, Fig. 6 for all four complexes. An ideal optical limiter should have a low threshold limit value ($I_{lim}$) because if it is too high, it becomes less reliable in terms of protection of optical elements. The $I_{lim}$ values give an indication of the saturation energy density values, $F_{sat}$, which are commonly employed in nonlinear optical studies. Table 3, gives the $I_{lim}$ values for the octasubstituted InPc derivatives and compares them with the corresponding octasubstituted GaPc complexes. (Cl)GaOPPc has the lowest value of 0.15 W cm$^{-2}$, followed by (Cl)GaOTBPPc with 0.20 W cm$^{-2}$. The value of $10^2$ W cm$^{-2}$ is generally taken as the standard value for the minimum intensity using the human eye as the reference light-sensing element [1]. Thus the $I_{lim}$ values obtained in Table 3 for octasubstituted GaPc and InPc derivatives show that the derivatives

Table 3
Optical limiting parameters for octa substituted GaPc and InPc derivatives in DMSO

| MPc (in DMSO) | λ (nm) | $\tau_T$ (μs) | Im[$\chi^{(3)}$] (esu) | $\gamma$ (esu) | $(k)\sigma_{ex}/\sigma_g$ | $I_{lim}$ (W cm$^{-2}$) |
|---|---|---|---|---|---|---|
| (Cl)GaOPPc | 530 | 370 | $7.99 \times 10^{-11}$ | $3.49 \times 10^{-35}$ | 9.96 | 0.15 |
| (Cl)GaOTBPPc | 540 | 290 | $1.12 \times 10^{-10}$ | $4.88 \times 10^{-35}$ | 3.13 | 0.20 |
| (Cl)InOPPc | 520 | 60 | $4.59 \times 10^{-11}$ | $2.00 \times 10^{-35}$ | 41.4 | 1.16 |
| (Cl)InOTBPPc | 520 | 50 | $2.87 \times 10^{-11}$ | $3.07 \times 10^{-35}$ | 53.4 | 1.92 |

Table 4
Optical limiting parameters for tetra substituted GaPc and InPc derivatives in DMSO

| MPc (in DMSO) | λ (nm) | $\tau_T$ (μs) | Im[$\chi^{(3)}$] (esu) | $\gamma$ (esu) | $(k)\sigma_{ex}/\sigma_g$ | $I_{lim}$ (W cm$^{-2}$) |
|---|---|---|---|---|---|---|
| α-(Cl)GaTPPc | 520 | 230 | $6.44 \times 10^{-11}$ | $2.81 \times 10^{-35}$ | 1.11 | 0.22 |
| α-(Cl)GaTBPPc | 540 | 350 | $4.67 \times 10^{-10}$ | $2.04 \times 10^{-35}$ | 3.76 | 0.26 |
| β-(Cl)GaTBPPc | 520 | 340 | $4.85 \times 10^{-11}$ | $2.12 \times 10^{-35}$ | 3.19 | 0.20 |
| α-(Cl)InTPPc | 550 | 40 | $1.12 \times 10^{-10}$ | $4.83 \times 10^{-35}$ | 2.12 | 2.11 |
| α-(Cl)InTBPPc | 540 | 40 | $8.40 \times 10^{-11}$ | $3.66 \times 10^{-35}$ | 5.24 | 1.81 |
| β-(Cl)InTPPc | 510 | 50 | $9.19 \times 10^{-11}$ | $4.01 \times 10^{-35}$ | 2.58 | 1.93 |
| β-(Cl)InTBPPc | 510 | 50 | $3.23 \times 10^{-11}$ | $1.41 \times 10^{-35}$ | 1.24 | 1.71 |

are good optical limiters, with OPPc derivatives showing better nonlinear optical behaviour that the OTBPPc complexes. The smaller the limiting intensity, the better, hence the octa-substituted GaPc derivatives are better than the corresponding octasubstituted InPc derivatives discussed in this work as optical limiters.

Among the tetra substituted the GaPc derivatives show better optical limiting behaviour than InPc derivatives. Peripheral ($\beta$) substitution show better optical behaviour than non-peripheral ($\alpha$) substitution in Table 4. Comparing octa with tetra substitution, shows that the former are better optical limiters than the latter.

The excited state ($\sigma_{ex}$) to ground state ($\sigma_g$) absorption cross-section ratio ($k = \sigma_{ex}/\sigma_g$) is also an excellent indicator of limiting power. The values of $k$ are listed in Tables 3 and 4. As with $I_{lim}$ values, the $k$ values are highest for InPc derivatives, showing that these complexes are good optical limiters. The $k$ values for GaPc derivatives ((Cl)GaOPPc and (Cl)GaOTBPPc) are within the range of the values reported in the literature for MPc containing metals including Ga, Zn, Co, Cu, Ni, Si and In [32–36] ranging between 3 and 15. The $k$ values for InPc peripherally substituted with *tert*-butyl groups were however found be much high $k \sim 30$ [32]. The values obtained for (Cl)InOPPc and (Cl)InOTBPPc in this work are 41.4 and 53.4, respectively, hence are slightly larger than reported in the literature. Compared to octa-substituted derivatives, the tetra-substituted counterparts gave lower $k$ values (Table 4) suggesting that octa-substitution improves optical limiting characteristics.

The values of third order susceptibility ($I_m[\chi^{(3)}]$) and second hyperpolarizability ($\gamma$) for InPc and GaPc derivatives are listed in Tables 3 and 4. The $I_m[\chi^{(3)}]$ values were well within expected ranges for phthalocyanines ($\sim 10^{-11}$ to $10^{-9}$) [1,7,37]. The $I_m[\chi^{(3)}]$ are larger for octasubstituted GaPc derivatives compared to corresponding InPc complexes. There is a general increase in $I_m[\chi^{(3)}]$ of the tetra substituted derivatives compared to the corresponding octasubstituted ones, Tables 3 and 4, with the exception of (Cl)GaOPPc and (Cl)GaTBPPc. In general, peripheral substitution decreases the $I_m[\chi^{(3)}]$ values.

The $\gamma$ values are listed in Tables 3 and 4. Of the octa-substituted derivatives, smaller $\gamma$ were obtained for phenoxy substituted GaPc and InPc derivatives, compared to TBPPc derivatives. In general, tetra substitution increases $\gamma$ values for InPc derivatives and decreases the values for GaPc complexes, whereas peripheral ($\beta$) substitution decreases the values. The $\gamma$ values are within the range reported for MPc complexes [1,7].

## 4. Conclusion

From the results obtained in this work, it can be concluded that the substituted InPc derivatives ((Cl)InOPPc and (Cl)InOTBPPc) gave large triplet state ($\Phi_T$) and singlet oxygen quantum yields ($\Phi_\Delta$) due to the heavy atom effect of the In central metal, which also resulted in short triplet lifetimes ($\tau_T$). The $\Phi_T$ values ranged from 0.70 to 0.91 and $\Phi_\Delta$ from 0.61 to 0.79 in DMSO. The lowest $\Phi_\Delta$ were obtained in toluene. The good performance of these complexes in producing singlet oxygen radicals shows that they are suitable candidates as PDT agents. The photodegradation studies showed that they are stable. The optical limiting threshold intensity ($I_{lim}$) for the InPc derivatives were calculated and compared with those of corresponding GaPc complexes. The latter were found to be better optical limiters. The $I_{lim}$ values obtained were far less than of $10^2$ W cm$^{-2}$ which is generally taken as the standard value for the minimum intensity using the human eye as the reference light sensing element.

## Acknowledgements

This work has been supported by the National Research Foundation (NRF GUN = 2053657) of South Africa, CSIR, as well as Rhodes University.

## References

[1] D. Dini, M. Hanack, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook: Physical Properties of Phthalocyanine-based Materials, vol. 17, Academic Press, USA, 2003, p. 22.
[2] J. Simon, P. Bassoul, Design of Molecular Materials: Supramolecular Engineering, VCH, Weinheim, 2000.
[3] M.J. Cook, N.B. McKeown, J.M. Simmons, A.J. Thomson, M.F. Daniel, K.J. Harrison, R.M. Richardson, S.J. Roser, J. Mater. Chem. 1 (1991) 121.
[4] D. Schlettwein, D. Wöhrle, N.I. Jaeger, J. Electrochem. Soc. 136 (1989) 2882.
[5] J. Simon, C. Sirlin, Pure Appl. Chem. 61 (1989) 1625.
[6] J.E. van Lier, in: D. Kessel (Ed.), Photodynamic Theraphy of Neoplastic Diseases, vol. 1, CRC Press, Boca Raton, FL, 1990.
[7] Y. Chen, M. Hanack, Y. Araki, O. Ito, Chem. Soc. Rev. 34 (2005) 517.
[8] H. Bartagnolli, W.J. Blau, Y. Chen, D. Dini, S.M. O'Flaherty, M. Hanack, V. Kishnan, J. Mater. Chem. 15 (2005) 683.
[9] M. Hanack, T. Schneider, M. Barthel, J.S. Shirk, S.R. Flom, R.G.S. Pong, Coord. Chem. Rev. 219 (2001) 235.
[10] D. Dini, M. Barthel, M. Hanack, Eur. J. Org. Chem. (2000) 3759.
[11] M. Calvete, G.Y. Yang, M. Hanack, Synth. Met. 141 (2004) 231.

[12] M.J. Plater, A. Jeremiah, G. Bourhill, J. Chem Soc., Perkin Trans. 1 (2002) 91.
[13] V. Chauke, A. Ogunsipe, M. Durmuş, T. Nyokong, Polyhedron 26 (2007) 2663.
[14] M. Durmuş, T. Nyokong, Tetrahedron 63 (2007) 1385.
[15] D. Wőhrle, M. Eskes, Shigeharak, A. Yamada, Synthesis (1993) 194.
[16] J.P. Linsky, T.R. Paul, R.S. Norh, M.E. Kenney, Inorg. Chem. 19 (1980) 3131.
[17] N. Kuznetsova, N. Gretsova, E. Kalmykova, E. Makarova, S. Dashkevich, V. Negrimovskii, O. Kaliya, E. Luk'yanets, Russ. J. Gen. Chem. 70 (2000) 133.
[18] W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Roder, G. Schnurpfeil, J. Porphyr. Phthalocya. 2 (1998) 145.
[19] A. Ogunsipe, D. Maree, T. Nyokong, J. Mol. Struct. 650 (2003) 131.
[20] L. Kaestner, M. Cesson, K. Kassab, T. Christensen, P.D. Edminson, M.J. Cook, I. Chambrier, G. Jori, Photochem. Photobiol. Sci. 2 (2003) 660.
[21] S. Fery-Forgues, D. Lavabre, J. Chem. Ed. 76 (1999) 1260.
[22] J. Fu, X.Y. Li, D.K.P. Ng, C. Wu, Langmuir 18 (2002) 3843.
[23] P. Jacques, A.M. Braun, Helv. Chim. Acta 64 (1981) 1800.
[24] H. Du, R.A. Fuh, J. Li, A. Corkan, J.S. Lindsey, Photochem. Photobiol. 68 (1998) 141.
[25] P. Kubát, J. Mosinger, J. Photochem. Photobiol. A: Chem. 96 (1996) 93.
[26] T.H. Tran-Thi, C. Desforge, C. Thiec, J. Phys. Chem. 93 (1989) 1226.
[27] Kossanyi, O. Chahraoui, Int. J. Photoenergy 2 (2000) 9.
[28] S.M. Bishop, A. Beeby, A.W. Parker, M.S.C. Foley, D. Phillips, J. Photochem. Photobiol. A: Chem. 90 (1995) 29.
[29] N.J. Turro, Modern Molecular Photochemistry, The Benjamin/Cummings Publishing Co., Inc., California, 1978 (Chapter 6).
[30] A. Ogunsipe, J. Chen, T. Nyokong, New J. Chem. 28 (2004) 882.
[31] T. Nyokong, Coord. Chem. Rev. 251 (2007) 1707.
[32] Y. Liu, S.M. O'Flaherty, Y. Chen, Y. Araki, J. Bai, J. Doyle, W.J. Blau, O. Ito, Dyes Pigments 75 (2007) 88.
[33] E.M. García-Frutos, S.M. O'Flaherty, S.V. Hold, G. de la Torre, S. Maier, P. Vázquez, W. Blau, T. Torres, Synth. Met. 137 (2003) 1479.
[34] E.M. García-Frutos, S.M. O'Flaherty, E.M. Maya, G. de la Torre, W. Blau, P. Vázquez, T. Torres, J. Mater. Chem. 13 (2003) 749.
[35] A. Auger, W.J. Blau, P.M. Burnham, I. Chambrier, M.J. Cook, B. Isare, F. Nekelson, S.M. O'Flaherty, J. Mater. Chem. 13 (2003) 1042.
[36] S.M. O'Flaherty, S.V. Hold, M.J. Cook, T. Torres, Y. Chen, M. Hanack, W.J. Blau, Adv. Mater. 15 (2003) 19.
[37] G. de la Torre, P. Vázquez, F. Agulló-López, T. Torres, Chem. Rev. 104 (2004) 3723.