

**SYNTHESIS, PHOTOCHEMICAL AND
PHOTOPHYSICAL PROPERTIES OF GALLIUM AND
INDIUM PHTHALOCYANINE DERIVATIVES**

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“When I said ‘my foot is slipping’ your love, O Lord, supported me. When anxiety was great within me, your consolation brought joy to my soul”. Psalm 94: 18-19.

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***"I can no other answer make, but, thanks, and thanks".
- William Shakespeare***

Much love to all...

ABSTRACT

The syntheses of octasubstituted and unsubstituted gallium(III) chloride and indium(III) chloride phthalocyanines (GaPc and InPc), their photophysical, photochemical and nonlinear optical parameters are hereby presented. The photocatalytic oxidation of 1-hexene using the synthesized GaPc and InPc complexes as well as electrochemical characterization is also presented in this thesis. Fluorescence quantum yields do not vary much among the four Ga complexes, except for complex 21c; therefore it was concluded that the effect of substituents is not significant among them.

Solvents however, had an effect on the results. Lower Φ_F values were obtained in low viscosity solvents like toluene, relative to highly viscous solvents, such as DMSO. The triplet quantum yields were found to be lower in DMSO than in DMF and toluene. The rate constants for fluorescence, intersystem crossing and internal conversion as well as fluorescence and triplet lifetimes are reported. Photodegradation and singlet oxygen quantum yields have also been reported. There was no clear correlation between the latter parameters. It was however established that the four gallium MPcs were stable, within the allowed stability range for phthalocyanines.

High quantum yields of triplet state (Φ_T ranging from 0.70 to 0.91 in dimethylsulfoxide, DMSO) and singlet oxygen generation (Φ_Δ , ranging from 0.61 to 0.79 in DMSO) were obtained. Short triplet lifetimes 50 to 60 μ s were obtained in DMSO).

Abstract

Calculated non-linear parameters of these complexes are compared with those of the corresponding GaPc derivatives and tetrasubstituted GaPc and InPc complexes. The optical limiting threshold intensity (I_{lim}) values for the InPc and GaPc derivatives were calculated and compared with those of corresponding tetrasubstituted InPc and GaPc complexes. The octasubstituted were found to be better optical limiters.

Photocatalytic oxidation of 1-hexene by GaPc (21a-c) and InPc (22a-c) derivatives is also presented. The photocatalytic oxidation products for 1-hexene were 1,2-epoxyhexane and 1-hexen-3-ol. The % conversion values of 1-hexene and % selectivity of 1,2-epoxyhexane were generally higher for InPc derivatives. Even though InPc derivatives showed better photocatalytic results than GaPc derivatives, the former were less stable relative to the latter. Both type I and type II mechanism were implicated in the photocatalysis mechanism.

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LIST OF SYMBOLS

α	- fraction of light absorbed - non-peripheral position
β	- peripheral position - nonlinear absorption term
ϵ	- molar extinction coefficient - dielectric constant
ϵ_S	- singlet state molar extinction
ϵ_T	- triplet state molar extinction
η	- refractive index
n	- number of electrons transferred
E_{pa}	- anodic peak potential
E_{pc}	- cathodic peak potential
Φ_{Δ}	- singlet oxygen quantum yield
Φ_{DPBF}	- DPBF quantum yield
Φ_{IC}	- internal conversion quantum yield
Φ_{ISC}	- inter system crossing quantum yield
Φ_P	- triplet state quantum yield
Φ_F	- fluorescence quantum yield
Φ_{PD}	- photodegradation quantum yield
Φ_T	- photodegradation quantum yield
τ_F	- fluorescence lifetime
τ_N	- natural lifetime
τ_T	- triplet lifetime
γ	- second order susceptibility
σ_{ex}	- absorption cross section of the excited state
σ_g	- absorption cross section of the ground state
ΔA	- change in absorbance
A	- absorbance
C	- concentration
ΔE	- difference in peak potentials
E^0	- formal potential

List of Symbols

$E_{1/2}$	- half-wave potential
E_p	- peak potential
f	- f is Lorentz local field factor
I_{abs}	- amount of light absorbed by sensitizer
I	- light intensity - current
I_{abs}	- intensity of light absorbed
I_p	- peak current
I_{pa}	-anodic current
I_{pc}	- cathodic current
$I_m[\chi^{(3)}]$	- third order susceptibility
k	- ratio of the absorption cross section of the singlet and triplet states
k_F	- fluorescence rate constant
k_{ISC}	- intersystem crossing rate constant
k_{PD}	- photodegradation rate constant
N_A	- Avogadro's constant
$^1O_2(\Delta_g)$	- excited singlet oxygen
$^1O_2(^3\Sigma_g)$	- ground state molecular oxygen
S_0	- ground singlet state
S_1	- excited singlet state
T	- transmittance
T_1	- first excited triplet state
T_2	- second excited triplet state
ω^*	- frequency

LIST OF ABBREVIATIONS

A	- absorbance
Ac₂O	- acetic anhydride
ADMA	- tetrasodium anthracene-9.10-bis-ethylmalonate
A_s	- area of the sample under an emission band
A_{std}	- are of the standard under an emission band
C	- concentration
CH₂CN	- methyl cyanide
CHCl₃	- chloroform
CT	- charge transfer
CDCl₃	- deuterated chloroform
CV	- cyclic voltammetry - cyclic voltammogram
DABCO	- 1,4-diazobicyclo-octane
DBU	- 1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	- dichloromethane
DMF	- dimethylformamide
DMSO	- dimethylsulfoxide
DMS	- dimethly sulfide
DNA	- deoxyribonucleic acid
DPBF	- 1,3-diphenylisobenzene-furan
F	- fluorescence
(Cl)GaPc	- gallium phthalocyanine
(Cl)GaPcS_n	- differently sulfonated gallium (III) chloride
GCE	- glassy carbon electrode
H₂O₂	- hydrogen peroxide
H₂Pc	- metal-free phthalocyanine
¹H-NMR	- proton nuclear magnetic resonance
HOMO	- highest occupied molecular orbital
HPLC	- high performance liquid cchromatography
IC	- internal conversion
I_{lim}	- limiting threshold intensity

List of Abbreviations

(Cl)InPc	- indium phthalocyanine
IR	- infrared
ISC	- intersystem crossing
LMCT	- ligand to metal charge transfer
LUMO	- lowest unoccupied molecular orbital
MLCT	- metal to ligand charge transfer
MPc	- metallophthalocyanine
NH₂	- amino
NIR	- near infrared
NLO	- nonlinear optics - nonlinear optical
NPcs	- naphthaphthalocyanines
OL	- optical limiting
ODS	- optical data storage
OTTLE	- optically transparent thin-layer electrodes
P	- Phosphorescence
Pc	- phthalocyanine
Ps	- photosensitization
PDT	- photodynamic therapy
<i>p</i>-TMP	- <i>p</i> -trifluoromethylphenyl
TBAP	- tetrabutylammonium perchlorate
RSA	- reverse saturable absorption
SA	- saturable absorption
THF	- tetrahydrofuran
TLC	- thin layer chromatography
TX	- Triton X-100
UV/Vis	- ultraviolet/visible
VR	- vibrational relaxation

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1 INTRODUCTION

1.1 THE HISTORY AND STRUCTURE OF PHTHALOCYANINES

Phthalocyanines (Pcs) (**1**), Fig. 1.1 were discovered by chance in 1907 by Braun and Tcherniac. The brightly coloured compound, blueish in colour, was a by-product of synthesis of o-cyanobenzamide from phthalamide [1, 2]. Twenty years later, other phthalocyanine (Pc) derivatives were again observed from the synthesis of phthalonitriles from o-dibromobenzene and cuprous cyanide by Diesbach and von der Weid [3]. The structure of the metal free, unsubstituted Pc was determined only about a quarter of a century later by the comprehensive researchers of Linstead and co-workers [4 - 7]. Linstead was the first to use the term phthalocyanine [4] which was derived from the Greek words *naphtha* (rock oil) and *cyanine* (blue) and the X-Ray diffraction analysis of Pcs was done by Robertson and co-workers [8-10].

Porphyrins (**2**) and other related tetrapyrrolic pigments (Fig. 1.1) are commonly found in nature. Phthalocyanines (**1**), however, are not found in nature. The replacement of all four *meso* carbon bridges in porphyrins by nitrogens gives a porphyrazine (**3**). The fusion of four iminoisoindoline units linked by four nitrogen atoms gives a phthalocyanine (**1**) [1]. A Pc (**1**) molecule is a planar macrocycle with an 18 π -electron system. The structure of Pcs grants them their renowned stability, both chemically and thermally. The pyrrole nitrogen atoms form a cavity into which metal ions can be incorporated [11]. More than seventy metals/metalloids can be (and have been) incorporated in the phthalocyanine core.

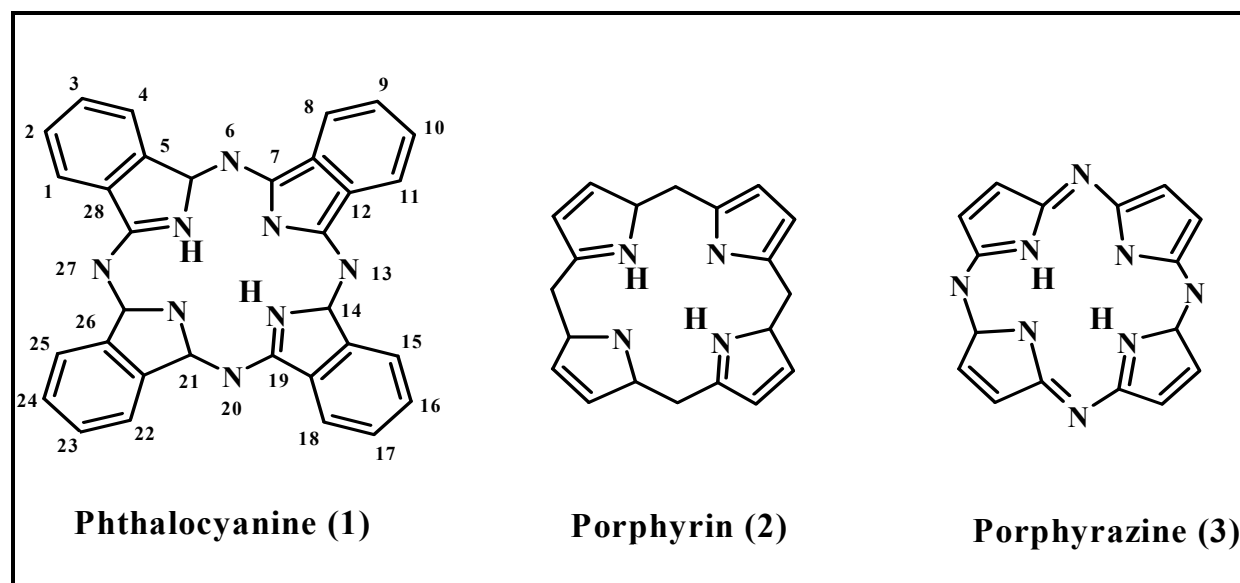


Figure 1.1: Molecular structures of tetrapyrrolic pigments

The structure of a Pc ring is versatile and thus allows the incorporation of different substituents on the peripheral {(2, 3), (9, 10), (16, 17) or (23, 14)} or non-peripheral {(1, 4), (8, 11), (15, 18) or (22, 25)} positions of the ring. The above alterations change the properties of phthalocyanines such as solubility.

Due their flexibility and their chemical and thermal stabilities, Pcs have been extensively explored for their potential use in a number of applications. Conventionally, Pcs have been widely used as dyes and pigments because of their intense blue-green colour [11]. For many years, Pcs have been a target of intensive investigation, particularly considering their properties as dyes [11, 12]. Currently, the focus of research on Pcs has been directed to applications in material science [13-17]. These include Pcs as liquid crystals [18-20], as langmuir-Blodgett films [21-25], in electrophotographic applications [26-29], optical data storage [30-32], in fuel cells [33], electrochemical sensors [34-36], and in nonlinear optics (NLO) [37-40].

Pcs have also attracted a lot of attention in medical applications, in particular photodynamic therapy (PDT), a cancer treatment that uses photosensitizers (Pcs or porphyrins) [1, 41-43], laser light and oxygen.

Aims of thesis

The aim of the project is to explore the photophysical and photochemical behaviour of Ga and In phthalocyanines which have potential for applications in PDT and NLO.

1.2 ABSORPTION SPECTRA OF PHTHALOCYANINES

The geometry of metal free phthalocyanines, H_2Pc , is square planar with a D_{2h} symmetry and C_2 axes in the x, y and z directions. If the planarity is maintained when a metal is incorporated into the phthalocyanine cavity, the symmetry increases from D_{2h} to D_{4h} . This means that a metallated phthalocyanine has a D_{4h} symmetry. The increase in symmetry results in the reduction of allowed transitions.

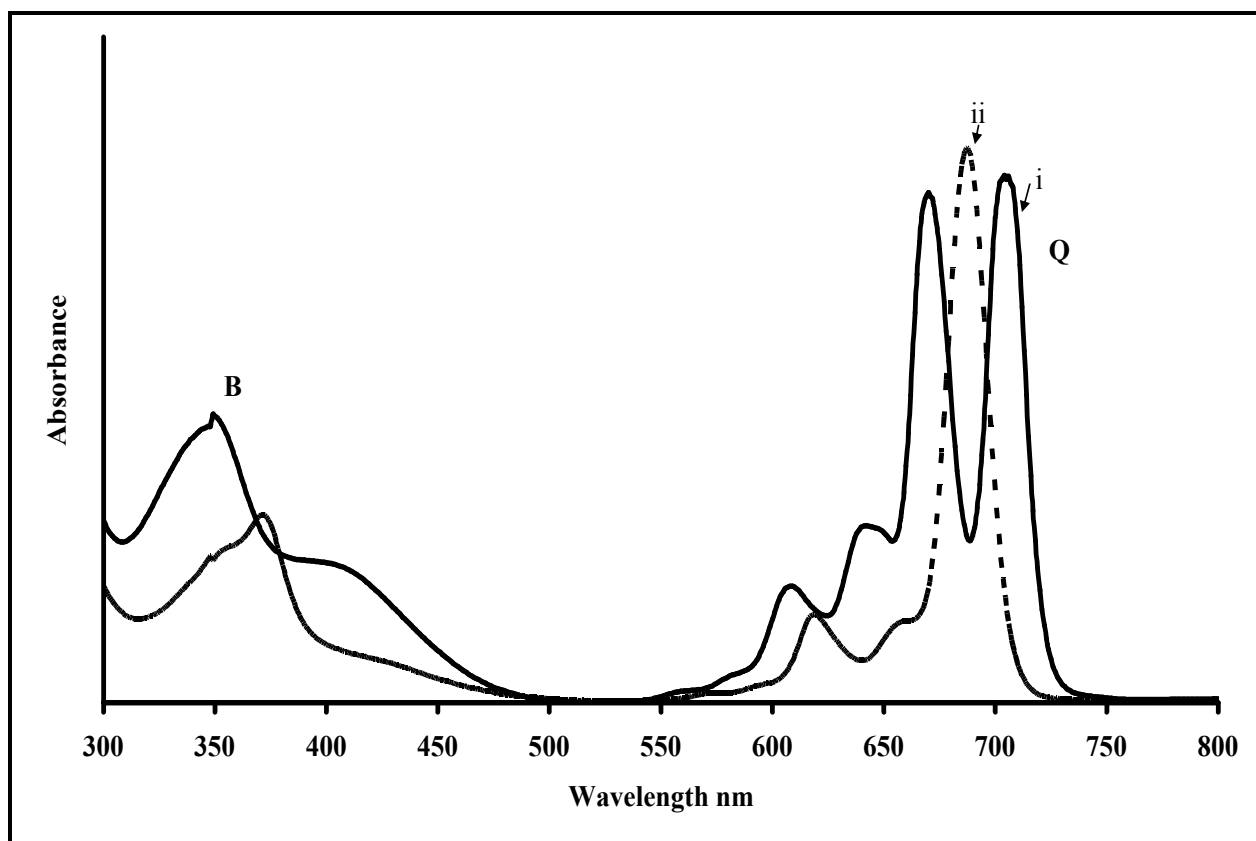


Figure 1.2: Ground state electronic absorption of an unmetallated phthalocyanine (i) and metallated phthalocyanine (ii)

Metallophthalocyanines (MPcs) are characterized by a distinct strong absorption in the visible region of the spectrum ($\sim 670\text{nm}$), namely the Q band and a weaker absorption called the B band [44], Fig. 1.2. The assignment of the Q and B bands are based on the four-orbital model (Fig. 1.3), proposed by Gouterman's group [44-46]. The Q band arises from $\pi - \pi^*$ transitions and can be best explained in terms of linear combination of transitions from a_{1u} and a_{2u} , the highest occupied molecular orbitals (HOMO) of the MPc ring to the lowest unoccupied molecular orbitals (LUMO), e_g^* . The symmetry of an unmetallated Pc, H_2Pc , is less (because of the two protons in the cavity), and this results in the splitting of the Q band (Fig. 1.2). As a result of the protons in the cavity of the H_2Pc , the e_g orbital loses its degeneracy resulting in two allowed transitions of different energies which gives a split Q band.

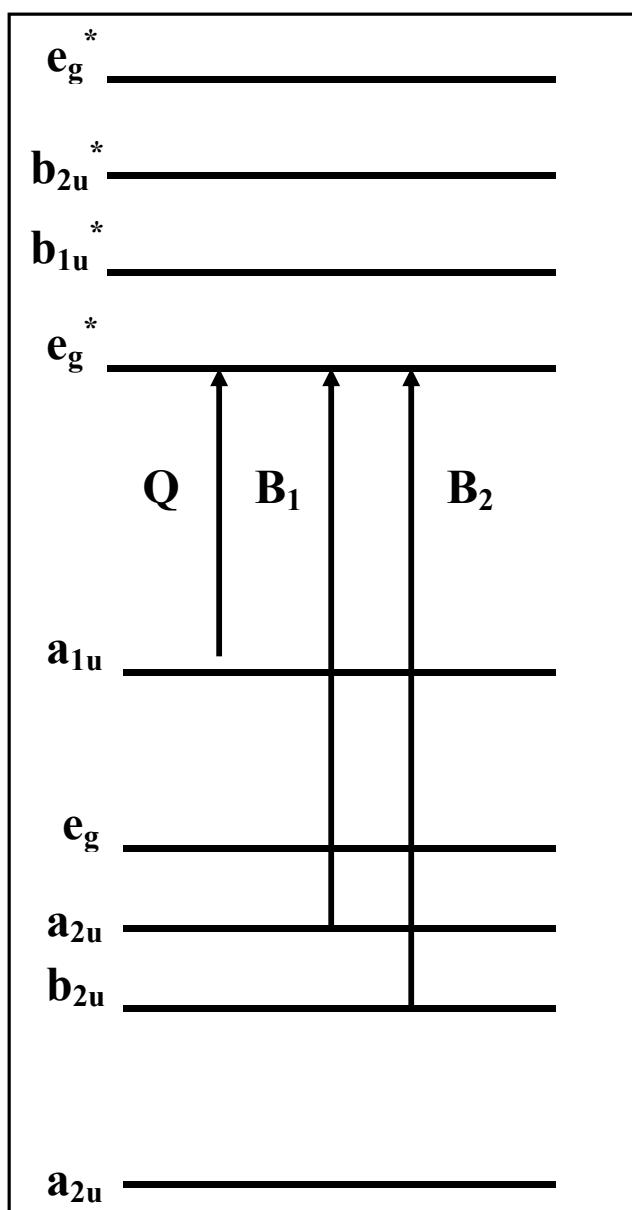


Figure 1.3: Electronic transitions in phthalocyanines

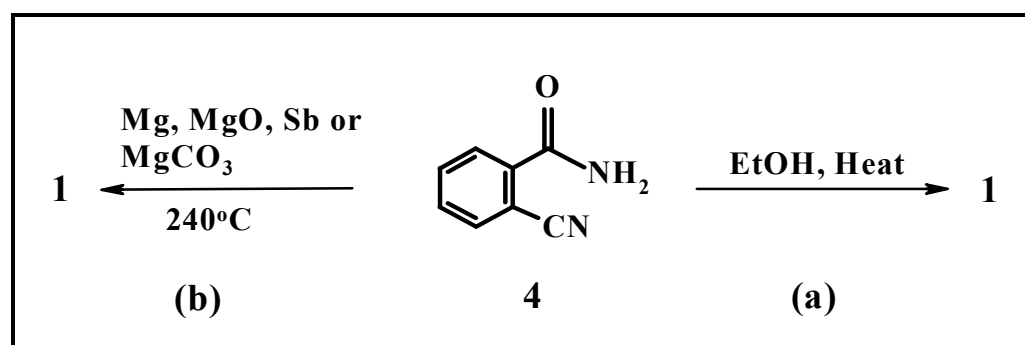
There are other bands which are characteristic of MPcs, namely the N, L and C bands.

These are found at higher energies (below 300 nm) in the ground state electronic absorption spectra. They are primarily due to $\pi - \pi^*$ transitions [47].

1.3 SYNTHESIS OF PHTHALOCYANINES

1.3.1 Metal free phthalocyanines

Originally, the synthesis of metal free phthalocyanines (**1**), H₂Pc, was achieved by refluxing o-cyanobenzamide (**4**) in ethanol (**Scheme 1.1a**) to give a blue product in small quantities [2]. It was only later that Linstead and his co-workers [4] showed that better yields were achieved when catalysts such as magnesium or its salts and antimony metal were included in the reaction mixture and heating up the reaction to over 230°C (**Scheme 1.1b**).

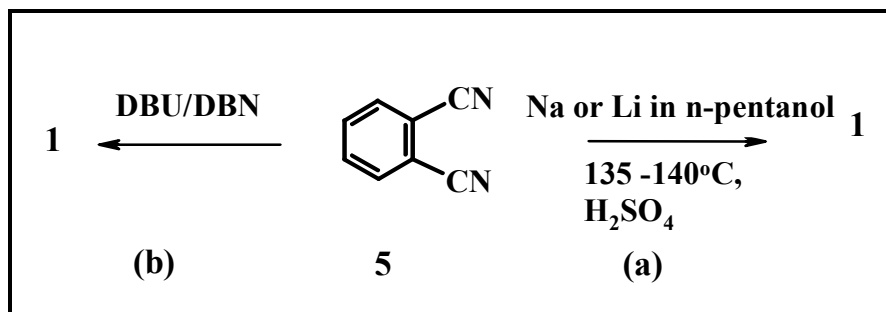


Scheme 1.1: Synthesis of unmetallated phthalocyanine (**1**) using o-cyanobenzamide

A very easy synthesis that guarantees good yields at shorter times, about 30 minutes, can be achieved when a phthalonitrile (**5**) is used as starting material, and treating it with sodium or lithium in n-pentanol (**Scheme 1.2a**) or other alcohols at 135-140°C. This affords disodium or dilithium phthalocyanines that can easily be demetallated by treatment with concentrated H₂SO₄ or glacial acetic acid [5, 48, 49].

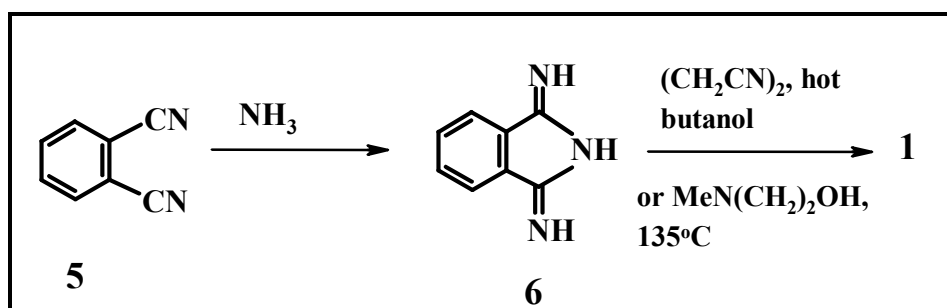
An improved method that was reported by Tomoda *et al.* [50, 51] in the 1980s, makes use of a phthalonitrile as the starting material in alcohol with 1,5-diazabicyclo[4.3.0]non-5-en (DBN) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base (**Scheme 1.2b**). Yields as high as 70 - 80 % were achieved from this

method. This method is favoured because it gives better yields and also avoids unwanted side products that are obtained with other strong bases.



Scheme 1.2: Synthesis of unmetallated phthalocyanine (1) from a phthalonitrile (5)

Alternatively, phthalonitriles (5) can be easily converted into 1,3-diiminoisoindoline (6) in the presence of ammonia gas. This can be achieved at room temperature in methanol solution (**Scheme 1.3**) [52]. The advantage in using 1,3-diiminoisoindoline (6) is that cyclization is achieved without difficulty. When 1,3-diiminoisoindoline (6) is refluxed in the presence of a hydrogen donor such as succinonitrile or boiling tetralin, a metal free phthalocyanine is produced.



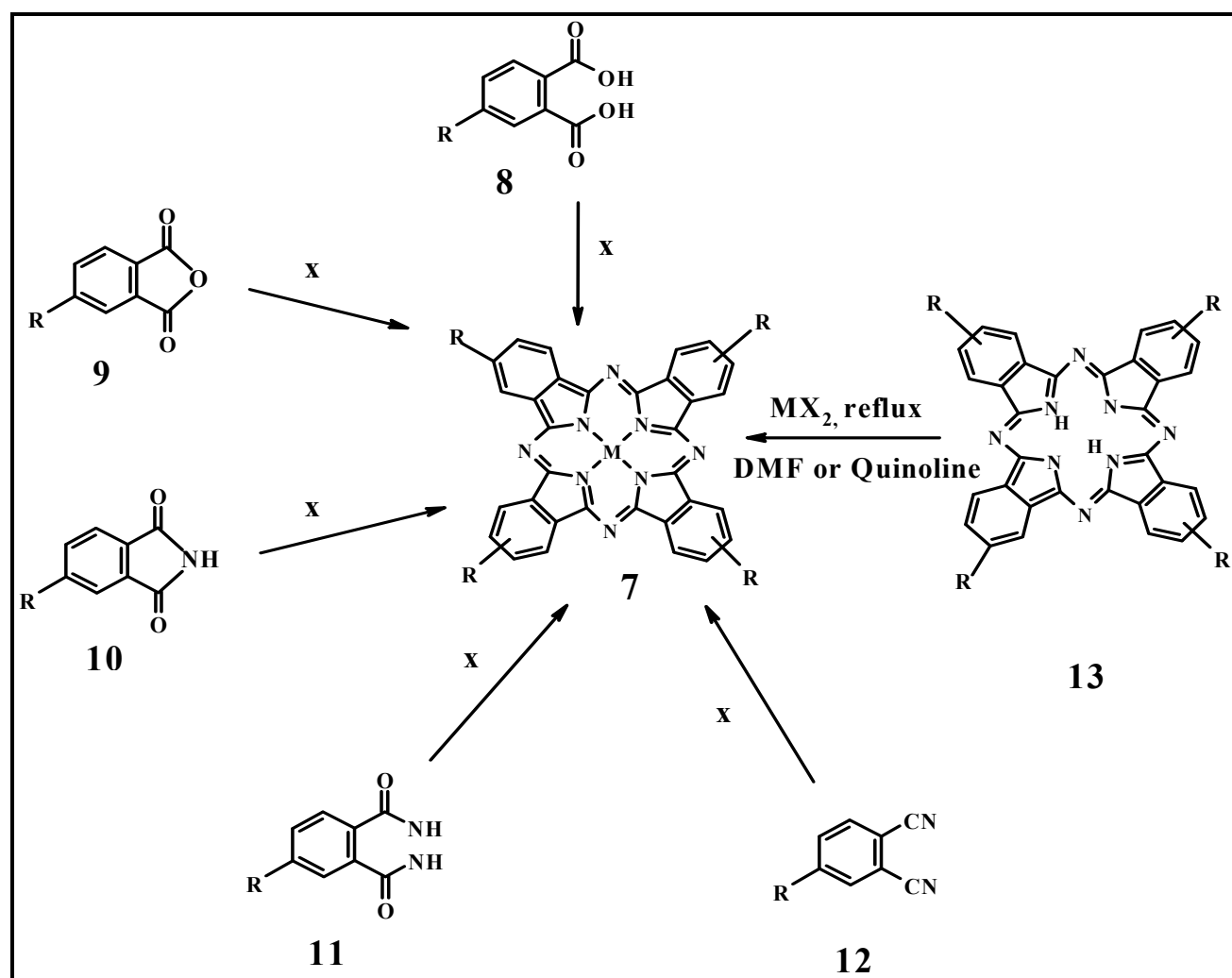
Scheme 1.3: Synthesis of unmetallated phthalocyanine (1) from 1,3-diiminoisoindoline (6)

1.3.2 Metallated unsubstituted phthalocyanines (MPc)

Metallated unsubstituted phthalocyanines (7) can be achieved by reacting unsubstituted (R = H, **Scheme 1.4**) phthalic acid (8), phthalic anhydride (9),

phthalimide (**10**) or phthalamide (**11**) with urea and a catalyst such as ammonium molybdate or zirconium [53 - 55], **Scheme 1.4**.

A phthalonitrile (**5**), 1,3-diiminoisoindoline (**6**) or o-cyanobenzamide (**4**) and an appropriate metal hydride or metal chloride may also be used to achieve specific metallated phthalocyanines. Metal-free phthalocyanines (**1**) can also be used as precursors by refluxing them with the suitable metal hydride or metal chloride in high boiling solvents such quinoline or dimethylformamide [56], **Scheme 1.4**.



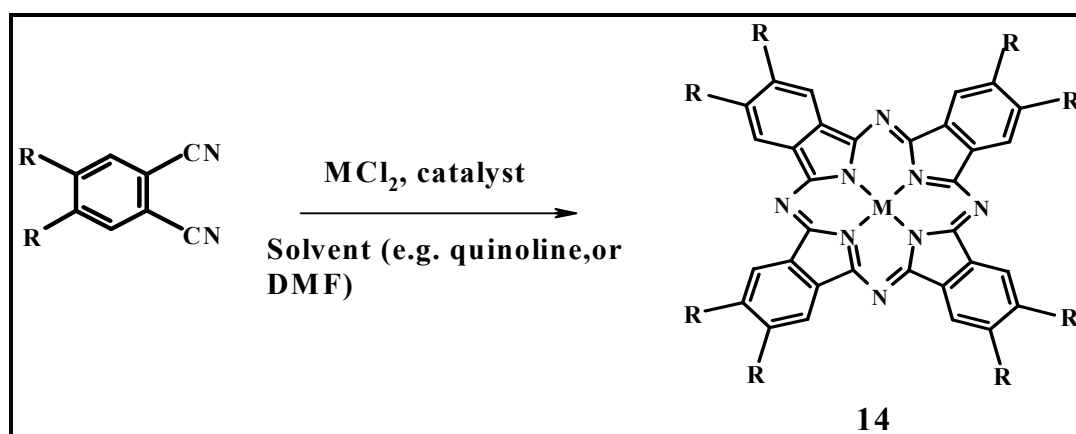
Scheme 1.4: Synthesis of metallated phthalocyanine from phthalic acid (**8**), phthalic anhydride (**9**), phthalimide (**10**), or phthalamide (**11**) or phthalonitrile (**12**) as starting material, where **x** = urea, MCl_2 , catalyst and solvent.

1.3.3 Ring substituted metallated phthalocyanines

Unsubstituted phthalocyanines are notorious for their poor solubility in common organic solvents due to intramolecular interactions between their π -system favouring a strong crystal lattice [38, 57]. The introduction of substituents onto the phthalocyanine ring either on the peripheral (2,3) or non-peripheral (1,4) positions, (see Fig. 1.1 for numbering) facilitates phthalocyanine solvation because they increase the distance between the stacked molecules [57, 58]. Substituting at the 1, 2, 3 or 4 positions of a phthalonitrile gives tetrasubstituted phthalocyanines and substituting at the 2, 3 or 1, 4 positions gives octasubstituted phthalocyanines. In general, the solubility of tetrasubstituted phthalocyanines is higher than that of octasubstituted phthalocyanines. This is due to the fact that tetrasubstituted phthalocyanines are prepared as a mixture of isomers consequently leading to a lower degree of order in the solid state, when compared to symmetrically octasubstituted phthalocyanines. Moreover, the less symmetrical isomers have a higher dipole moment derived from the more unsymmetrical arrangement of the substituents on the periphery of the phthalocyanine ring [13, 59 - 61].

More often than not, tetrasubstituted phthalocyanines are synthesized by the cyclotetramerization of substituted phthalonitriles, phthalic acid (**8**), phthalic anhydride (**9**), phthalimide (**10**), and phthalamide (**11**). (**Scheme 1.4**) [62, 63], or from substituting an already formed tetrasubstituted phthalocyanine ring (**13**) (**Scheme 1.4**). Tetrasubstituted phthalocyanines are formed as isomers and the separation of these isomers can be problematic. Nevertheless possible separation of these isomers has been shown by chromatographic techniques, for example high performance liquid chromatography (HPLC) [59, 60].

Octasubstituted phthalocyanines (**14**) can be achieved from the cyclotetramerization of 4,5-disubstituted phthalonitriles, **Scheme 1.5**. One major advantage of preparing octasubstituted phthalocyanines is that isomerically pure products are achieved and these are easier to purify than tetrasubstituted phthalocyanines.



Scheme 1.5: Synthesis of octasubstituted phthalocyanine (14) from a 4,5-disubstituted phthalonitrile (15)

Hence in this work only octasubstituted derivatives will be synthesized. Comparative work with already reported tetrasubstituted phthalocyanines will be explored briefly also. Since the aim of the thesis is to investigate photophysical and photochemical behaviour of MPcs, these parameters will now be discussed.

1.4 PHOTOPHYSICS AND PHOTOCHEMISTRY

Photochemistry can be defined as a discipline that is concerned with the chemical changes that are induced when light interacts with molecules or matter. The net physical processes that occur as a result of light's interaction with matter can be defined as photophysics.

1.4.1 The fate of an excited species

The fate of an excited species is best described by the Jablonski diagram (Fig. 1.4). Following excitation, molecules are promoted to the unoccupied orbitals of higher energy, S_1 and higher singlet states. If in solution or condensed phase, excited molecules are not long lived in the excited states due to collisions in a process called vibrational relaxation (VR) or vibrational cascade.

From the S_1 state the deactivation processes comprise of fluorescence (F), phosphorescence (P), internal conversion (IC) and intersystem crossing (ISC). In radiative processes, energy is lost in the form of light. The radiative processes include fluorescence (F) and phosphorescence (P), Fig. 1.4. Fluorescence is the radiative emission from an excited singlet state to the ground state. This process is short lived, the typical time scale lies in the picosecond (10^{-12}) to microseconds (10^{-6}) range, and its energy is less than that of absorbance, thus fluorescence appears at longer wavelengths [64]. If the spin multiplicity of the emitting state differs from that of the lower state, the emission is called phosphorescence (P), for example T_1 to S_0 . Phosphorescence is less intense than fluorescence and occurs less rapidly than fluorescence. The typical time scale is in the microsecond to second range [64].

Nonradiative transitions involve the conversion of one quantum state to another without emission of radiation. The nonradiative processes are internal conversion (IC), intersystem crossing (ISC) and vibrational relaxation (VR). Internal conversion is a process that involves the transfer of population between electronic states of the same spin multiplicity and intersystem crossing involves the transfer of population between states of different multiplicity [64].

In the midst of all these processes, an electronic excitation process may occur, where an energy rich molecule (in S_1 or T_1 state) transfers its energy to another molecule. This process is known as photosensitization, Fig. 1.4.

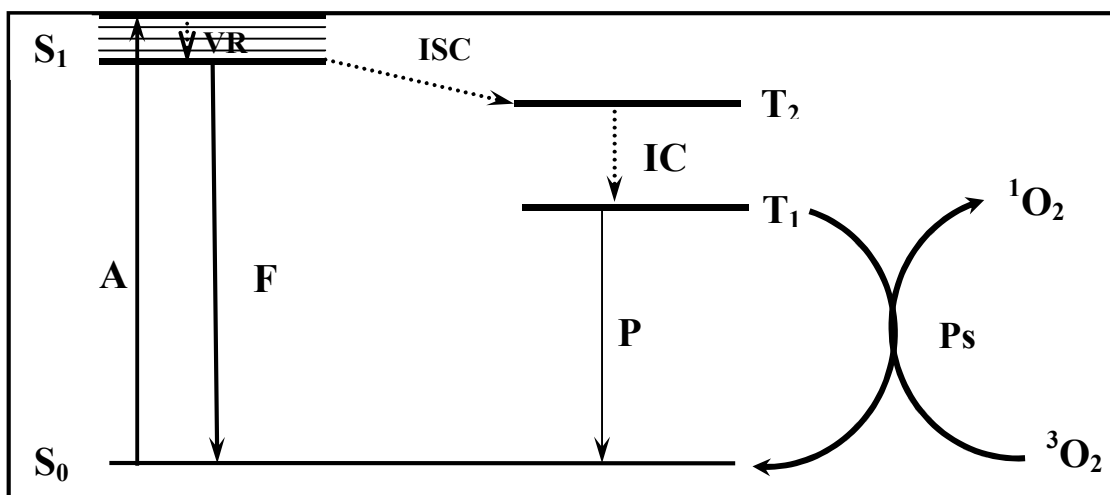


Figure 1.4: Jablonski diagram showing transitions between the excited and ground states, where A = Absorption; VR = Vibrational relaxation, IC = Internal conversion, ISC = Intersystem crossing; F = Fluorescence; P = Phosphorescence; Ps = photosensitization

1.4.2 Photophysical processes

1.4.2.1 Fluorescence quantum yield and lifetime

To determine and quantify the efficiency of emission from the singlet state, fluorescence quantum yield (Φ_F) is employed. Quantum yield is defined as the number of molecules taking part in an event for every photon absorbed. Thus fluorescence quantum yield (Φ_F) may be defined as the ratio of molecules fluorescing to the number of photons absorbed. Φ_F may be determined comparatively [65, 66] using compounds that have known fluorescence quantum yields, for example ZnPc in DMSO (Φ_F) = 0.20 [67], using equation 1.1

$$\Phi_F = \Phi_{F(\text{Std})} \frac{F \cdot A_{\text{Std}} \cdot \eta^2}{F_{\text{Std}} \cdot A \cdot \eta_{\text{Std}}^2} \quad (1.1)$$

where F and F_{Std} are the areas under the fluorescence curves of the sample and standard respectively. A and A_{Std} are the respective absorbances of the sample and standard at the excitation wavelengths, and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Low concentrations are necessary for these studies to avoid or minimise self quenching. Factors such as temperature, molecular structure and solvent parameters (polarity, viscosity, refractive index and the presence of heavy atoms in the solvent molecule) are widely known to influence the values of Φ_F .

The lifetime, τ , of an excited species is the time needed for a concentration of the species to decrease to $1/e$, of its original value [68]. The fluorescence lifetime, τ_F , is related to the radiative lifetime, τ_0 , defined by equation 1.2

$$\Phi_F = \frac{\tau_F}{\tau_0} \quad (1.2)$$

By definition, τ_0 is the lifetime of an excited molecule in the absence of radiationless transitions.

Fluorescence lifetimes may also be determined the programme PhotochemCAD [69]. The determination of fluorescence lifetimes is based on the method proposed by Strickler and Berg [70], which uses parameters derived from spectral (absorption and emission) data of the fluorescing material. Equation 1.3 gives the modified Strickler-Berg equation:

$$\frac{1}{\tau_N} = 2.88 \times 10^{-9} \cdot \eta^2 \frac{\int \frac{F(\lambda)}{\lambda^2} \cdot d(\lambda)}{\int F(\lambda) \lambda \cdot d(\lambda)} \int \frac{\varepsilon(\lambda)}{\lambda} \cdot d(\lambda) \quad (1.3)$$

where $F(\lambda)$ is the fluorescence intensity and $\varepsilon(\lambda)$ is the molar absorption coefficient at a given intensity.

1.4.2.2 Triplet quantum yield and lifetimes

A technique called flash photolysis is used to determine the triplet lifetime and the change in absorbance in the triplet state, which is directly related to the triplet quantum yield [64].

The triplet state parameters include the triplet quantum yield (Φ_T), and the triplet lifetime (τ_T). The lifetimes of the triplet state, τ_T , are determined by fitting data obtained from the ND-Yag laser oscilloscope into OriginPro 7.5 software. The triplet quantum yield (Φ_T) is used to quantify and determine the efficiency of the triplet state. Laser flash photolysis is based on absorption of light by the triplet state. For phthalocyanines the triplet absorption is ~ 500 nm, far from the ground singlet state absorption making it possible to conduct these measurements. The change in absorbance (ΔA) in the triplet state is directly related to the quantum yield of the triplet state, Φ_T .

The triplet quantum yields (Φ_T) may be determined by the triplet absorption or singlet depletion methods. The triplet absorption method was employed in this work hence it is discussed. A comparative method [71] using zinc phthalocyanine as a standard may be employed for the calculations, Equation 1.4.

$$\Phi_T = \Phi_T^{\text{Std}} \cdot \frac{\Delta A_T \cdot \epsilon_T^{\text{Std}}}{\Delta A_T^{\text{Std}} \cdot \epsilon_T} \quad (1.4)$$

where ΔA_T and ΔA_T^{Std} are the changes in the triplet state absorbances of the sample and the standard, respectively. ϵ_T and ϵ_T^{Std} are the triplet state molar extinction coefficients for the sample and the standard, respectively. Φ_T^{Std} is the triplet quantum yield for the standard, ZnPc (e.g. $\Phi_T = 0.65$ in DMSO [72]). ϵ_T and ϵ_T^{Std} were

determined from the molar extinction coefficients of their respective ground singlet state (ϵ_S and ϵ_S^{Std}), the changes in absorbances of the ground singlet states (ΔA_S and ΔA_S^{Std}) and changes in the triplet state absorptions, (ΔA_T and ΔA_T^{Std}) according to Equations 1.5a and 1.5b:

$$\epsilon_T = \epsilon_S \frac{\Delta A_T}{\Delta A_S} \quad (1.5a)$$

$$\epsilon_T^{Std} = \epsilon_S^{Std} \frac{\Delta A_T^{Std}}{\Delta A_S^{Std}} \quad (1.5b)$$

1.4.3 Photochemical processes

Photochemical parameters of interest in this work are singlet oxygen (Φ_Δ) and photodegradation (Φ_{pd}) quantum yields.

1.4.3.1 Singlet oxygen

The ground state of molecular oxygen is in a triplet state. Ground state oxygen has two unpaired electrons in the antibonding orbitals (Fig. 1.5).

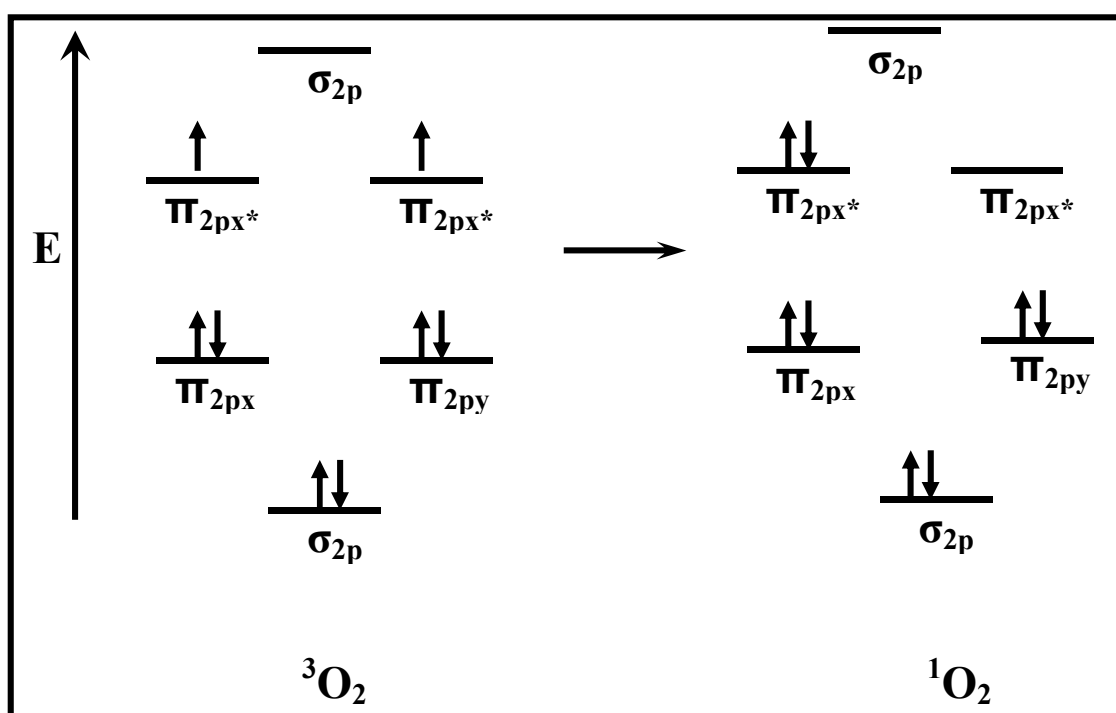
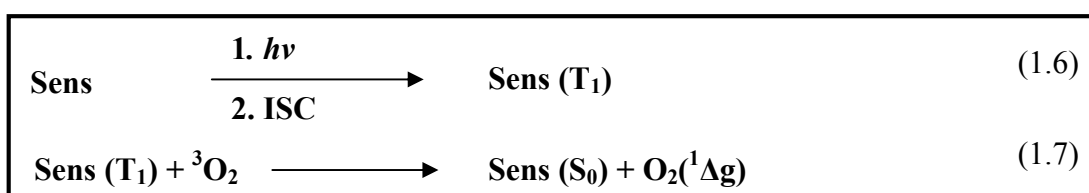


Figure 1.5: Molecular orbital diagram showing electron distribution in the triplet and singlet oxygen

If an external magnetic field is applied, three separate electronic configurations from the two unpaired electrons may subsequently be distinguished, i.e. both spins down, both spins up or one spin up and one down hence the reference to ground state oxygen as triplet state oxygen [64]. If the two electrons are paired up into the $2p\pi^*$ antibonding orbital due to interaction with sensitizer, singlet oxygen which is the excited state, is produced and is the highly reactive and potent species because of its instability relative to the triplet state oxygen. Singlet oxygen is responsible for oxidative damage in a number of systems [73-76]. Some of its many applications include the photodegradation of pollutants [77, 78], oxidation of alkenes and alkanes [79, 80], and in PDT [1, 41 – 43].

Singlet oxygen is generated when oxygen in its triplet state ($^3\text{O}_2$) interacts with a sensitizer in a method called photosensitization, (**Scheme 1.6**, see also Fig. 1.4). It is certainly the most common method for generating singlet oxygen $\text{O}_2(^1\Delta\text{g})$ in the laboratory.

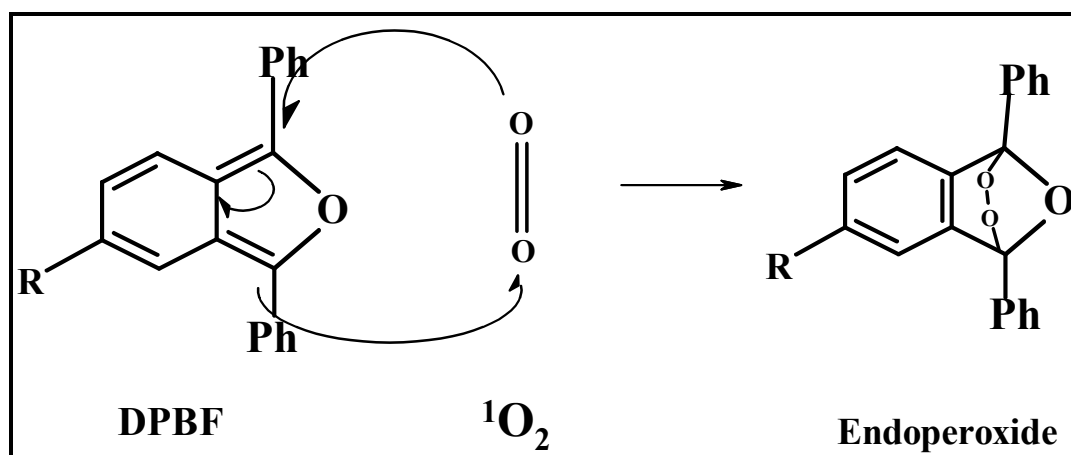


Scheme 1.6: Generation of singlet oxygen by photosensitizer (Sens)

1.4.3.2 Detection of singlet oxygen and determination of its quantum yields

Singlet oxygen may be determined by two main methods, using chemical quenchers or using luminescence at 1270 nm [81]. The method applied in this work makes use of singlet oxygen scavengers or quenchers. 1,3-diphenylisobenzofuran (DPBF) is known to be an exclusive and mostly used quencher in organic solvents. Other examples of

quenchers include tetrasodium anthracene-9,10-bis-methylmalonate (ADMA), thiols, carotene, ascorbate and histidine [81, 82]. The reaction of singlet oxygen with DPBF yields endoperoxide as shown in (Scheme 1.7)



Scheme 1.7:[4+2] cycloaddition of MPcs by singlet oxygen

As soon as singlet oxygen is generated, it can be trapped using singlet oxygen quencher (Scheme 1.7). The disappearance of the quencher can easily be followed spectroscopically.

Therefore quantum yields (Φ_{Δ}) of singlet oxygen photogeneration may be determined in air (no oxygen bubbled) using the relative method [82 - 86], with ZnPc as reference and DPBF as chemical quencher, using Equation 1.8:

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \cdot \frac{R_{DPBF}^{Std} I_{abs}^{Std}}{R_{DPBF}^{Std} I_{abs}} \quad (1.8)$$

where Φ_{Δ}^{Std} is the singlet oxygen quantum yield for the standard, e.g. ZnPc. R_{DPBF}

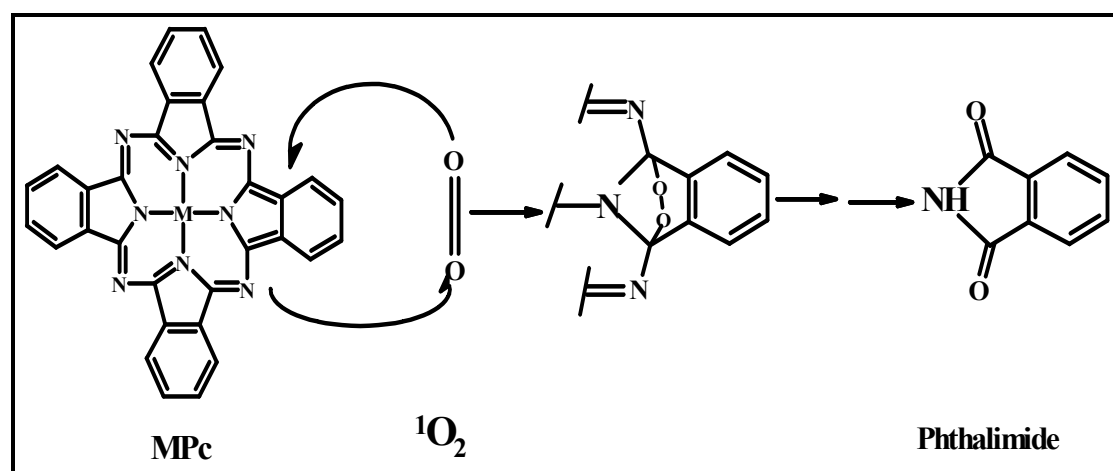
and R_{DPBF}^{Std} are the DPBF photodegradation rates in the presence of a sensitizer under

investigation and the standard respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the sensitizer and standard, respectively.

1.4.3.3 Photodegradation quantum yields (Φ_{pd})

Photodegradation is a photochemical process whereby the conjugated chromophore of the phthalocyanine ring gets degraded into smaller molecular fragments. This process is driven by singlet oxygen in the presence of light to afford the photo-oxidation products, phthalamide, as suggested by Scurpfeil *et al.* [87], **Scheme 1.8**.

The mechanism suggests that singlet oxygen reacts with tetra-azaporphyrin derivatives in a Diel-Alder [4+2]-cycloaddition, with the phthalocyanine acting as a diene and the singlet oxygen as the dienophile.



Scheme 1.8: [4+2] cycloaddition reaction of MPc with singlet oxygen

There are several factors that can influence the process of photodegradation. It has been reported [88, 89] before that electron releasing substituents on the phthalocyanine ring bring rapid degradation due to ease of oxidation brought by the presence of these substituents. Electron-withdrawing substituents, on the other hand have a tendency of stabilizing the phthalocyanine ring. This means that

phthalocyanines containing electron-withdrawing substituents are resistant to oxidative attack.

Solvents are highly influential on the photodegradation process. Photodegradation has been observed to occur faster in solvents such as chloroform (CHCl_3) and dichloromethane (DCM). This is due to radicals that are formed from C-Cl bond cleavage that assist in the photodegradation process. Enhanced photodegradation is also observed in deuterated solvents where singlet oxygen lifetimes are longer thus resulting in enhanced photodegradation [86, 88]. Furthermore, it was found that in the presence of 1,4-diazobicyclo-octane (DABCO), a singlet oxygen scavenger, photodegradation was reduced [88, 89]. This observation proves and supports the fact that singlet oxygen is indeed involved in the process of photodegradation. In aqueous media, photodegradation rates are low, presumably due to aggregation, given that the generation of singlet oxygen in aggregates is very low [90, 91].

Photodegradation quantum yield, Φ_{PD} , which is indicative of how many molecules are degraded per quantum of light absorbed, is a means of determining the stability of a phthalocyanine in the presence of light. It is identified by the decrease in absorbance of the Q band of the phthalocyanine under investigation, without the formation of new peaks in the visible region.

Photodegradation quantum yield may be calculated using equation 1.9 [82 - 86]:

$$\Phi_{pd} = \frac{\Delta A}{\Delta t} \cdot \frac{V}{\epsilon} \cdot \frac{1}{I_{abs}} \quad (1.9)$$

Where ΔA , Δt , V and ϵ are change in absorbance, change in time of irradiation, reaction volume and extinction coefficient of the solution under investigation, respectively.

$$I_{abs} = \frac{\alpha SI}{N_A} \quad (1.10)$$

Where α is the fraction of light absorbed, I the light intensity, S and N_A are the irradiated cell area (cm^2) and Avogadro's constant (mole^{-1}), respectively.

1.4.4 Review of the photochemical and photophysical properties of Ga and In phthalocyanines in organic media

Gallium and indium phthalocyanines have been extensively studied for nonlinear optics [37, 92–107] and relatively very little of their photochemical and photophysical properties have been reported [108 - 114],

Table 1 lists the reported photophysical and photochemical parameters of Ga and In complexes in different solvents. Figs. 1.6 and 1.7 give the structures of the reviewed Ga and In phthalocyanines.

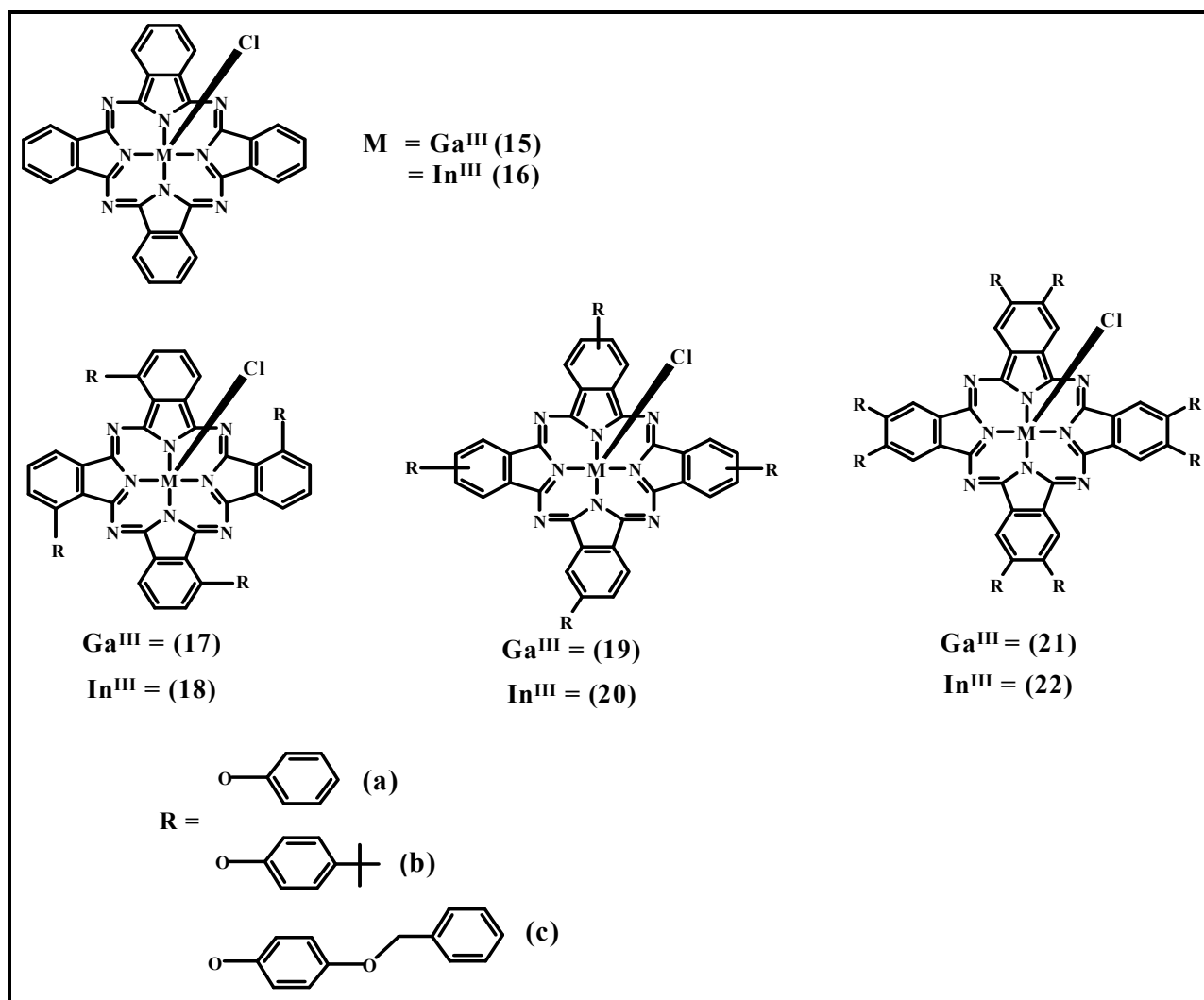
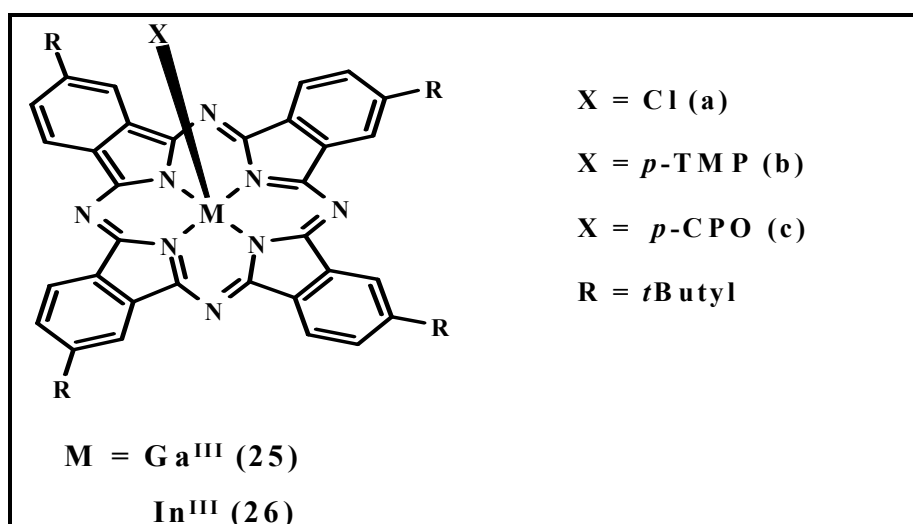
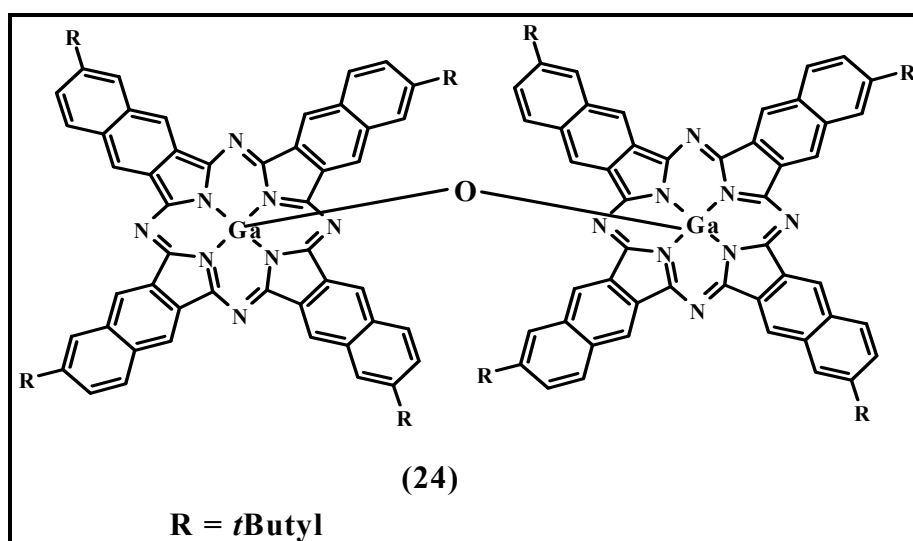
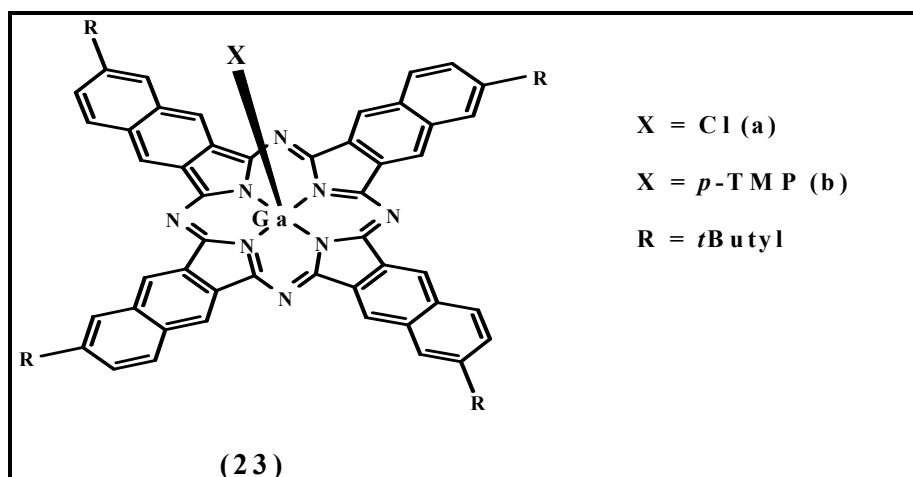
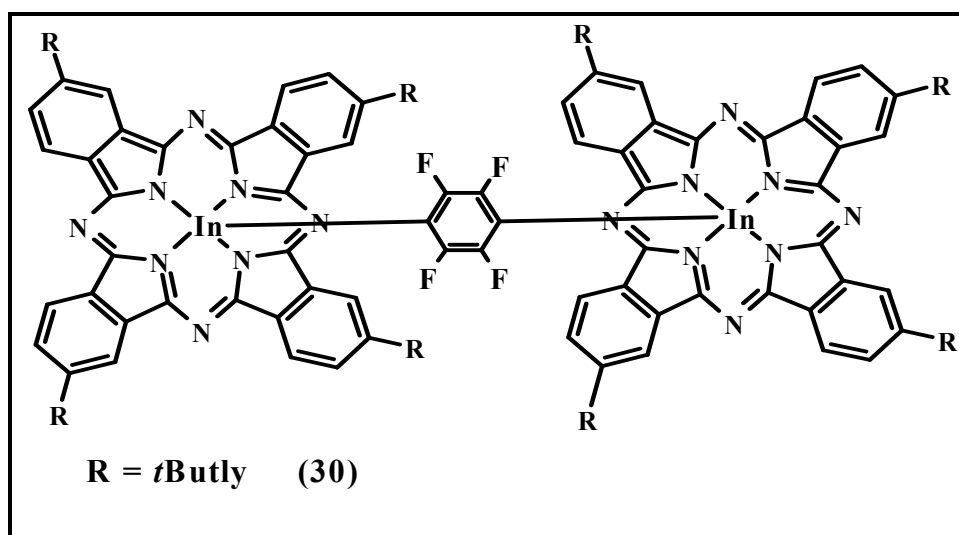
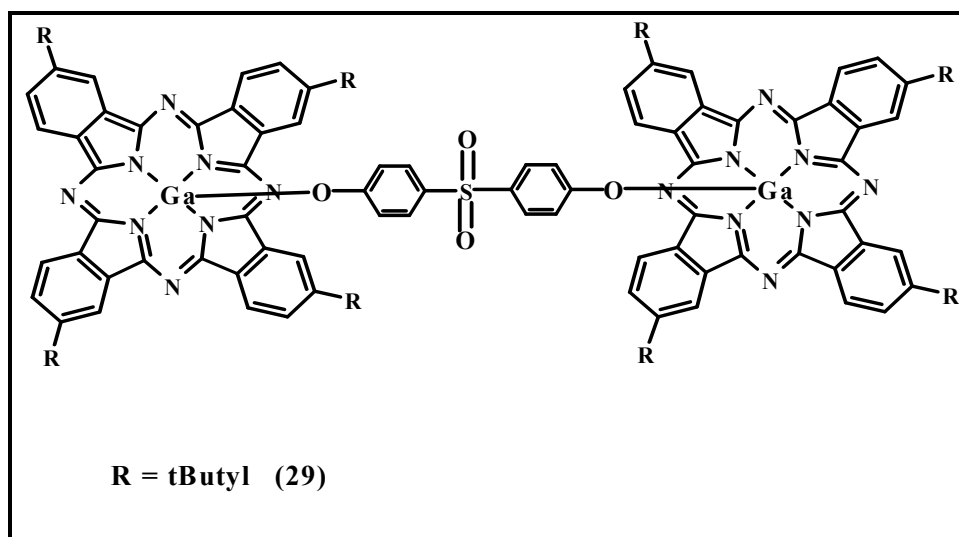
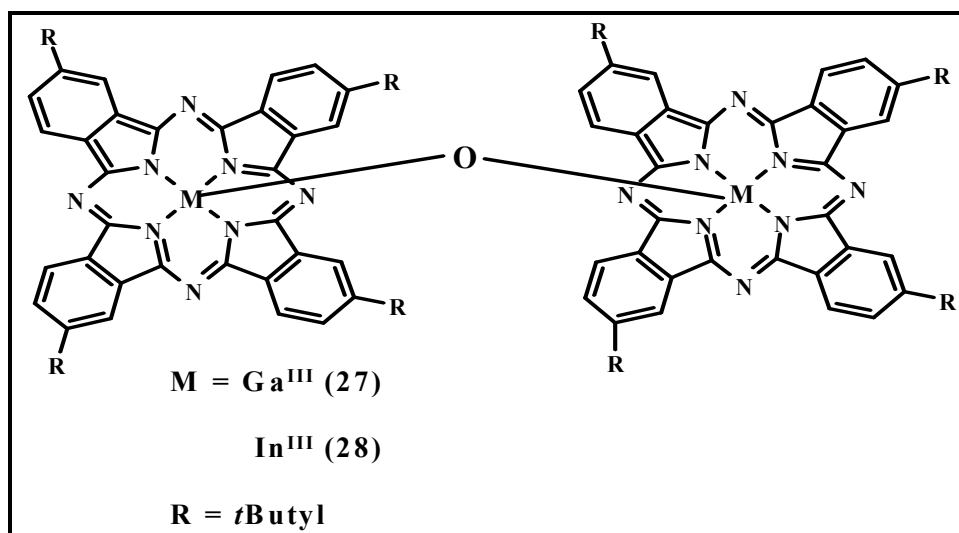


Figure 1.6: Structures of the Ga and In phthalocyanines reviewed





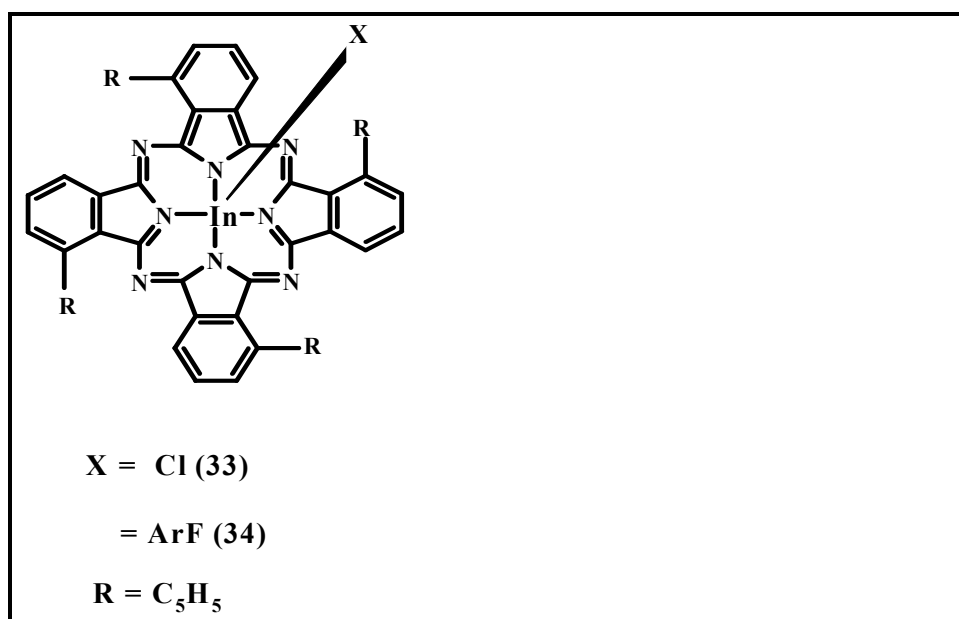
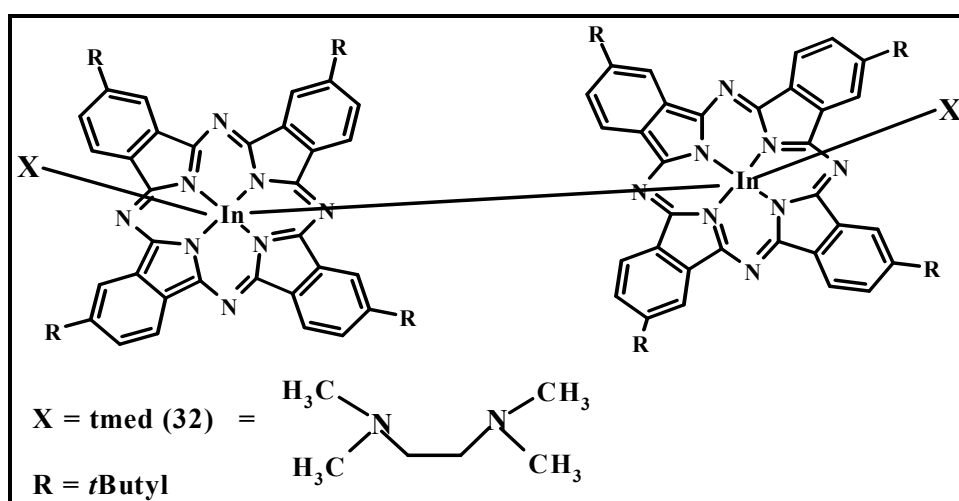
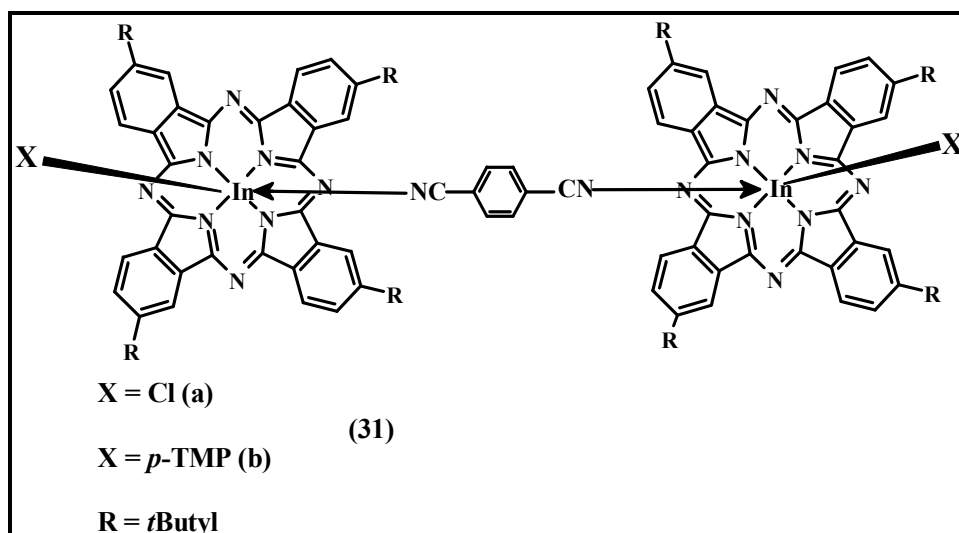


Figure 1.7: Structures of complexes in the review, $R = t\text{Butyl}$; $X = p\text{-TMP} = p\text{-trifluoromethylphenyl}$, $p\text{-CPO} = p\text{-chlorophenoxy}$

Table 1.1: Photophysical and photochemical parameters of Ga and In complexes in different solvents.

Complex	Solvent	Φ_F	Φ_T	Φ_A	Φ_{pd}	τ_F (ns)	τ_T (μ s)	Refs.
15	DMSO	0.30	0.69	0.41	2.75×10^{-4}	3.71	200	[108,109]
16	DMSO	0.018	0.91	0.61	9.90×10^{-4}	0.90	50	[108,109]
	1-Chloronaphthalene	0.031	0.90	-	-	-	-	[110]
17a	DMSO	0.14	0.62	0.64	1.19×10^{-4}	0.92	230	[109]
17b	DMSO	0.15	0.54	0.62	2.03×10^{-4}	1.01	350	[109]
17c	DMSO	0.15	0.77	0.64	0.27×10^{-5}	1.39	280	[108]
18a	DMSO	0.048	0.78	0.88	0.92×10^{-4}	0.51	40	[109]
18b	DMSO	0.015	0.59	0.92	1.39×10^{-4}	0.14	40	[109]
18c	DMSO	0.013	0.97	0.94	0.30×10^{-5}	0.12	40	[108]
19a	DMSO	0.19	0.61	0.64	2.82×10^{-4}	1.29	270	[109]
19b	DMSO	0.20	0.45	0.58	2.32×10^{-4}	1.19	340	[109]
19c	DMSO	0.23	0.75	0.62	1.92×10^{-5}	1.90	210	[108]
20a	DMSO	0.032	0.69	0.87	2.44×10^{-4}	0.12	50	[109]
20b	DMSO	0.019	0.60	0.88	2.14×10^{-4}	1.90	50	[109]
20c	DMSO	0.017	0.91	0.87	0.97×10^{-5}	0.16	50	[108]
21c	DMSO	0.13	0.74	0.51	0.50×10^{-5}	0.70	200	[108]
22c	DMSO	0.017	0.89	0.78	0.27×10^{-5}	0.09	70	[108]
23a	CHCl ₃	-	-	-	-	1.89	21	[100, 107]
23b	CHCl ₃	-	-	-	-	1.79	18	[100, 107]
24	CHCl ₃	-	-	-	-	2.33	14	[100, 107]
25a	Toluene	-	-	-	-	2.57	257	[100,107,114]
25b	Toluene	-	-	-	-	2.48	200	[100,107,114]
25c	Toluene	-	-	-	-	-	-	[100,107,114]
26a	Toluene	-	-	-	-	0.47	46	[100,107,114]
26b	Toluene	-	-	-	-	0.28	22	[97]
27	Toluene	-	-	-	-	3.57	357	[97]
28	Toluene	-	-	-	-	0.64	42	[97]
29	Toluene	-	-	-	-	3.46	667	[97]

30	Toluene	-	-	-	-	0.35	35	[97]
31	Toluene	-	-	-	-	0.40	33	[113]
32	Toluene	-	-	-	-	0.38	40	[113]

DMSO = dimethylsulfoxide

1.4.4.1 Photophysical parameters

Table 1.1 lists the fluorescence quantum yield (Φ_F) values and as expected the Φ_F values for all the InPc derivatives were much smaller than Φ_F values for GaPc derivatives. For example, Φ_F values for GaPc complexes (**17**, **19**, and **21**) ranged from 0.13 – 0.23 compared to their corresponding InPc complexes (**18**, **20** and **22**) that had Φ_F values that ranged from 0.013 – 0.048. This is due to the fact that In is a heavy diamagnetic metal, it therefore encourages intersystem crossing through spin orbit coupling. The Φ_F values all the GaPc derivatives were typical of metallophthalocyanines (MPc), however Φ_F values were found to be lower for substituted GaPc derivatives (**17**, **20**, **21**) when compared to the unsubstituted (Cl)GaPc (**15**), Fig. 1.6. This suggests that the substituents may have quenched the singlet excited state.

On the effects of the position of the substituents on the phthalocyanine ring, Φ_F values for the peripherally substituted complexes (**19**, **20**) were higher than the corresponding non-peripherally substituted derivatives (**17**, **18**). This implies that there is less quenching of the excited states by the peripherally substituted phthalocyanines. The Φ_F values for the substituted GaPc derivatives (**17**, **19**, **21**) are almost equal, within experimental error limits, suggesting that having different substituents on the phthalocyanine ring has no significant effects. A different behaviour was observed for InPc substituted derivatives. Φ_F values for phenoxy

substituted InPc derivatives (**18a**, **20a**) were much larger than Φ_F values for 4-*tert*butylphenoxy (**18b**, **20b**) and benzyloxyphenoxy (**18c**, **20c**) In derivatives.

The fluorescence lifetimes of InPc and GaPc derivatives, τ_F , are well within the range reported for MPcs [112]. However, τ_F values, were lower for all the substituted GaPc derivatives (**17**, **19**, **21**) compared to unsubstituted GaPc derivatives. Again this suggests and confirms that the substituents may have quenched the excited state. The Ga naphthalocyanines (Ncs) (**23**, **24**) had lower τ_F values compared to their corresponding GaPc derivatives (**25**) and the other GaPc derivatives (**17**, **19**, **21**). This is attributed to the extended conjugated structure of Ncs which may have influenced fluorescence quenching. The fact that these were carried out in different solvents cannot be ruled out since fluorescence quantum yields and lifetimes can be influenced by a number of factors that include solvent parameters (polarity, viscosity, presence of heavy atoms in the solvent molecule and refractive index) [82]. The τ_F values for the GaPc dimers (**27**, **29**) were higher than all the substituted GaPc monomers (**17**, **19**, **21**, **25**). Similar behaviour was observed for GaNc oxo-dimer (**24**); its τ_F was higher than τ_F values for GaNc monomer (**23**). The fluorescence lifetimes for InPc dimers (**28**, **30**, **31**, **32**) were slightly higher than InPc derivatives (**18**, **20**, **22**, **26**, **28**), suggesting that there is less quenching of the singlet excited states by the InPc dimers. The InPc dimer with direct In-In bond (**32**) has the lowest τ_F value, amongst the InPc dimers.

The triplet quantum yields (Φ_T), listed in Table 1.1, for the InPc complexes (**16**, **18**, **20**, **22**) were higher than Φ_T values for their corresponding GaPc complexes. This is yet again attributed to the fact that In is a heavy diamagnetic metal, it thus enhances intersystem crossing this way resulting in high Φ_T values. Based on the substituent factor, higher Φ_T values were obtained for the unsubstituted ClGaPc (**15**) and

(Cl)InPcs (**16**) relative to the phenoxy (**17a**, **19a**) and *tert*butylphenoxy (**17b**, **19b**) substituted GaPc and InPc complexes. The Φ_T values for octasubstituted (**21c**, **22c**) were not significantly different from Φ_T values for tetrasubstituted (**17** – **20**). The triplet lifetimes for all InPc derivatives were smaller than triplet lifetimes for GaPc derivatives. This could be due to the fact that larger Φ_T values were obtained for InPc derivatives. Lower triplet lifetimes were obtained for GaNPcs (**23**) relative to their corresponding GaPc derivatives (**25**). Again differences in solvents could also be a contributing factor to the differences. InPc complexes possessing a strong electron-withdrawing ligand, (**26a**) have longer triplet lifetimes than InPc dimers (**30**) possessing bridges similar to the ligands for the InPc monomers. GaPc dimers with an 4,4'-sulfonyldiphenoxy (SDPO) bridge (**29**) exhibited the longest triplet lifetime followed by the μ -oxo-GaPc dimer (**27**).

1.4.4.2 Photochemical parameters

Table 1.1 also lists photochemical parameters that include singlet oxygen (Φ_Δ) and photodegradation quantum yields (Φ_{pd}) for the reported GaPc and InPc complexes. Benzyloxyphenoxy substituted complexes (**17c** – **22c**) are more stable than the phenoxy (**17a** – **20a**) and *tert*butylphenoxy (**17b** – **20a**) tetrasubstituted GaPc and InPc complexes, with Φ_{pd} in the order 10^{-4} for the latter. The Φ_{pd} values for benzyloxyphenoxy octa- and tetrasubstituted (**24** – **26**) were in the 10^{-5} range and this is typical of phthalocyanines.

Good singlet oxygen quantum yields were obtained for all the substituted GaPc and InPc complexes. However, lower Φ_Δ values were obtained for unsubstituted complexes (**15**, **16**).

1.4.5 Water soluble gallium and indium phthalocyanines

Table 1.2, lists the reported [111, 112, 117-119] photochemical and photophysical parameters of water soluble GaPc and InPc derivatives. Fig. 1.8 gives the structures of the water soluble MPcs in this review.

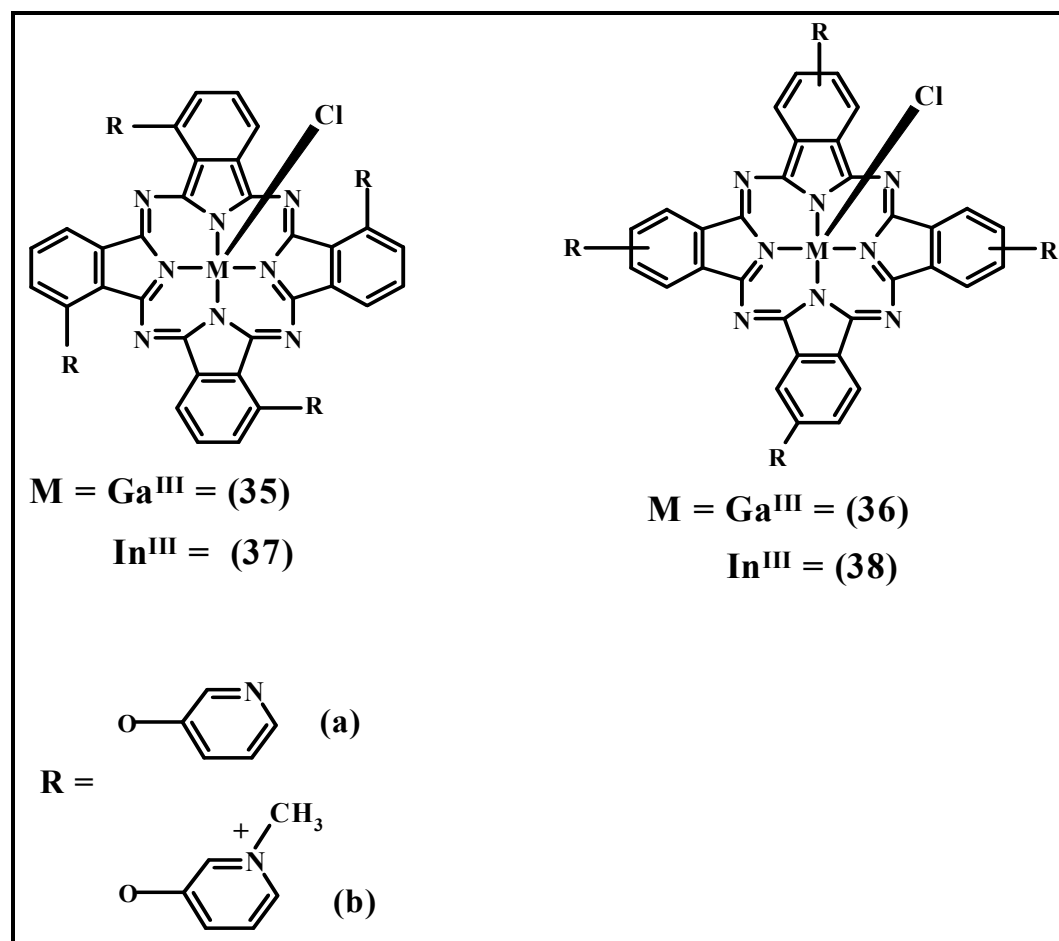


Figure 1.8: Structures of the water soluble GaPc and InPc complexes

Table 1.2: Photochemical and photophysical parameters of water soluble GaPc and InPc derivatives in different solvents.

Complex	Solvent	Φ_F	Φ_T	Φ_A	Φ_{Pd}	τ_F (ns)	τ_T (μ s)	Refs.
35a	DMSO	0.12	-	0.48	-	1.28	-	[112]
	H ₂ O	-	-	-	-	-	-	[112]
35b	DMSO	0.19	-	0.53	-	1.50	-	[112]
	H ₂ O	0.07	-	0.41	-	0.72	-	[112]
36a	DMSO	0.19	-	0.59	-	2.05	-	[112]
	H ₂ O	-	-	-	-	-	-	[112]
36b	DMSO	0.24	-	0.51	-	1.93	-	[112]
	H ₂ O	0.12	-	0.44	-	1.06	-	[112]
37a	DMSO	0.018	0.93	0.86	0.30×10^{-4}	0.22	40	[111]
37b	DMSO	0.020	0.94	0.68	0.49×10^{-4}	0.35	50	[111]
	H ₂ O	0.002	0.73	0.57	6.80×10^{-4}	0.08	7.2	[111]
	H ₂ O + TX	0.008	0.82	0.70	10.3×10^{-4}	0.19	20	[111]
38a	DMSO	0.017	0.73	0.65	0.24×10^{-4}	0.17	50	[111]
38b	DMSO	0.082	0.81	0.44	0.50×10^{-4}	1.61	70	[111]
	H ₂ O	0.017	0.66	0.56	7.12×10^{-4}	0.59	8.2	[111]
	H ₂ O + TX	0.048	0.67	0.56	8.79×10^{-4}	1.43	20	[111]
GaPcS ₂	Methanol	-	0.36	0.38	-	-	390	[117,118]
GaPcS ₃	Methanol	-	0.36	0.38	-	-	425	[119]
GaPcS ₄	Methanol	-	0.36	0.38	-	-	420	[117]
GaPcS ₁ (C(CH ₃) ₃) ₃	Methanol	-	0.36	0.38			440	[117]
GaPcS ₂ (C(CH ₃) ₃) ₃	Methanol	-	0.36	0.38			360	[117]
GaPcS ₃ (C(CH ₃) ₃) ₃	Methanol	-	0.36	0.38			300	[117]

TX = Triton-X 100

Water soluble phthalocyanines are potentially useful as sensitizers for tumor treatment by photodynamic therapy (PDT), since they can be injected directly into the blood stream. One major drawback of water soluble phthalocyanines is their tendency to aggregate in solution, especially in polar media [118]. Hydrophilic moieties which have been incorporated on phthalocyanine rings include sulfonates [82], carboxylates

[120], phosphonates [121] and quaternized amino groups [122]. The reviewed GaPc and InPc derivatives in this section were quaternized by treatment with dimethylsulfate (DMS) in dimethylformamide (DMF) as a solvent, to make them water soluble.

1.4.5.1 Photophysical parameters

For the GaPc complexes (**35**, **36**), the Φ_F values are typical of phthalocyanines, Table 1.2. On the effects of substituents, the quaternized GaPc complexes (**35b**, **36b**) yielded higher Φ_F values than the corresponding non-ionic complexes (**35a**, **36a**). Furthermore, somewhat higher Φ_F values were obtained for peripherally substituted GaPc phthalocyanines (**36**) relative to the corresponding non-peripherally substituted phthalocyanines (**35**). This suggests that there is quenching by non-peripheral substituents. On solvent effects, GaPc derivatives, (**35b**, **36b**) showed higher (Φ_F) values in DMSO than in water. This is attributed to the fact that DMSO is more viscous than water. The Φ_F values for InPc complexes (**37**, **38**) were lower than GaPc complexes (**35**, **36**); this is attributed to the fact that In is a heavy diamagnetic metal, it thus enhances intersystem crossing. On the effects of substituents, the same trend that was observed for GaPc complexes was observed for InPc complexes. The quaternized InPc derivatives (**37b**, **38b**) had higher Φ_F values in DMSO than their corresponding non-ionic complexes (**37a**, **38a**). For the quaternized InPc complexes (**37b**, **38b**), Φ_F values were lower in water than in DMSO, due to aggregation and also due to the high viscous nature of DMSO. However on adding Triton X-100, Φ_F values increased, validating that indeed aggregation had an influence on the low Φ_F values in water.

The triplet lifetimes, τ_T , for complexes **37** and **38** range from 7.2 to 70 μs in DMSO, H_2O or $\text{H}_2\text{O} + \text{TX}$ (Table 1.2). These short τ_T values correspond to the large triplet state quantum yields of the InPc complexes. τ_T were lower in water than in DMSO due to aggregation. τ_F values for the quaternized InPc complexes (**37b**, **38b**) were slightly higher than their corresponding unquaternized substituted phthalocyanines (**37a**, **36a**) in DMSO. Once again, the addition of Triton X-100 improved the lifetimes in water. The triplet lifetimes for the sulfonated Ga phthalocyanines were very high, ranging from 300 - 440 μs in methanol. These correspond to their relatively low triplet quantum yields (Φ_T), which were all the same for all the sulfonated GaPc complexes in methanol, showing that the substituents had no influence on the Φ_T values.

1.4.5.2 Photochemical parameters

The singlet oxygen quantum yield, Φ_Δ , values for the sulfonated GaPc complexes were the same in methanol, $\Phi_\Delta = 0.38$, meaning that the substituents had no effect on the results. Singlet oxygen quantum yield values were higher for quaternized GaPc complex (**35b**) in DMSO than its corresponding non-ionic complex (**35a**). The opposite was observed for InPc complexes, quaternized InPc complexes (**37b**, **38b**) had lower Φ_Δ values in DMSO than the nonionic complexes (**37a**, **38a**). Φ_Δ values were lower in water, for InPc complexes, however on adding Triton X 100, the Φ_Δ values improved significantly.

Photodegradation quantum yields were determined for InPc complexes (**37**, **38**). They were of the range of 10^{-4} , hence were not stable

Aims of the thesis

Figs. 1.6 -1.8 as well as Tables 1.1 and 1.2 show that mainly tetrasubstituted GaPc and InPc complexes have been studied in terms of photochemical and photophysical behaviour. The aim of the thesis is to synthesize Ga^{III} and In^{III} octasubstituted phthalocyanines. Ga^{III} and In^{III} metals have been chosen as central atoms in this study due to their heavy and diamagnetic nature which is crucial in photophysical and photochemical studies done in this work. Octasubstituted and not tetra substituted phthalocyanines were synthesized due to the fact that isomerically pure products are formed. The aim is to carry out a comprehensive study of the synthesized Ga^{III} and In^{III} octasubstituted phthalocyanines, i.e. carry out calculations that will aid in determining their stability, singlet oxygen efficiency, lifetimes in the triplet state as well as the population in the triplet state. The studies are to be carried out in different solvents to determine the effects of solvents on photochemical and photophysical parameters.

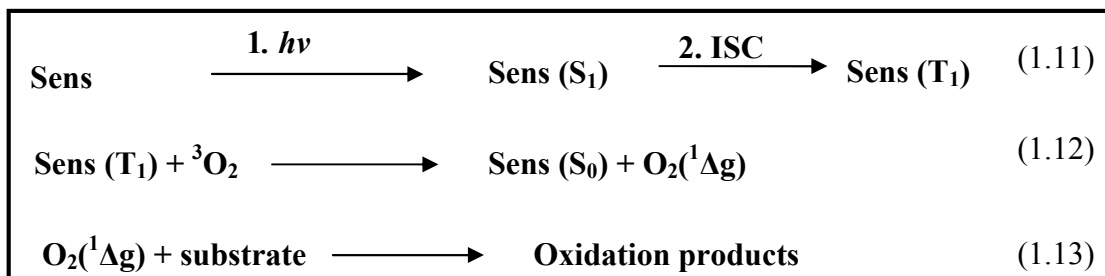
1.5 PHOTOCATALYTIC OXIDATION OF 1-HEXENE

In this work, the synthesized complexes were also tested for their photocatalytic behaviour towards transformation of industrial compounds, such as alkenes, hence this section discusses photocatalytic behaviour of InPc and GaPc complexes.

Alkanes and alkenes are produced in thousands of tonnes by petroleum industrial companies as byproducts [123]. Because of the increasing need to conserve natural resources, it is imperative that such products be used as starting materials in other industrial processes. Alkanes and alkenes can be partially oxidized to fine chemicals such as alcohols, ketones and aldehydes to mention but a few [124].

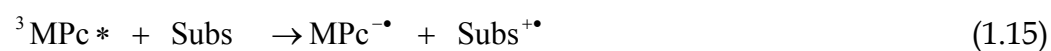
The oxidation of alkenes has become very important and it is of great interest in industries as useful intermediates such as epoxides are produced; which are used in industries as intermediates, for example in the manufacturing of ethylene glycol, automobile antifreeze, fine chemicals and polymers such as oxygen containing natural products [124].

Phthalocyanines are able to generate single oxygen species through the process of photosensitization where energy is transferred from the energy rich phthalocyanine to molecular oxygen in its triplet state (**Scheme 1.6**), a mechanism otherwise known as Type II mechanism (**Scheme 1.9**). Singlet oxygen, $^1\text{O}_2$, is then involved in the process of phototransformation as shown in **Scheme 1.9**.



Scheme 1.9: Phototransformation of alkenes, where substrate can be alkenes. Type II mechanism

Type I mechanism (**Scheme 1.10**) may also be involved in these type of reactions, however it is not common. It involves the production of radical ions when an MPC in the triplet state interacts with molecular oxygen in its ground state which then forms superoxides and hydroperoxyl radicals which can oxidize the substrate.



Scheme 1.10: Type I mechanism

The oxidation reactions of alkenes using porphyrins are more popular than those catalysed by phthalocyanines [125]. The major downside of using porphyrins is that they are less stable than phthalocyanines, thus decompose readily, especially in oxidative media [126]. Their stability has been in many cases increased by the substitution of halogens or with electron-withdrawing substituents which are less prone to oxidative attack. Also, porphyrins are not accessible on an industrial scale and are thus expensive as catalysts [126]. Phthalocyanines have been extensively used as enzyme-like catalysts for the degradation of pollutants such as chlorinated phenols [127 - 129] and toxic sulfonated compounds [130 - 132]. However their use as photocatalysts has received less attention hence their exploration in this work.

No work has been reported on the photocatalytic oxidation of 1-hexene using Ga or In phthalocyanines. However, photocatalytic oxidation using oxotitanium phthalocyanines has been [133]; which gave low % conversion values that ranged

from 12.36 to 18.02%. The transformation of 1-hexene by oxotitanium phthalocyanines was found to yield 1,2-epoxyhexene as a major product.

The aim of this thesis is to use the synthesized Ga and In phthalocyanines for the photocatalytic oxidation of 1-hexene with the aim of improving % conversion and selectivity for products. These complexes gave excellent photophysical and photochemical parameters hence were employed for photocatalysis.

1.6 NONLINEAR OPTICS (NLO)

Ga and In phthalocyanines are known for their good NLO behaviour, hence in this thesis, the newly synthesized octasubstituted complexes were studied for NLO behaviour.

Nonlinear optics is a branch of optics that is associated with the changes in the optical properties of material when it interacts with light. Several optical devices or technologies such as optical rectifiers, optical switches, dynamic holography, and optical data-recording and optical limiters are based on nonlinear effects [37].

This thesis focuses on optical limiting. When interference light interacts with light-sensitive material or elements, damage may occur if a protective device is not available. This is where optical limiting becomes crucial; in the protection of light sensitive elements such as optical sensors, human eyes and other light sensitive material. Since the discovery and invention of intense light sources based on laser mechanisms in the 1960s [92, 134], the need for development of protective devices for light sensitive material against hostile intense sources of light has motivated

substantial research in this field of study. Also, because today warfare is based on laser weapons, where in many cases laser weapons are used as threats, especially for civil pilots on landing approach or in the army, the need to do research and come up with highly efficient protective devices is important. For example, within the South African army reliance is on laser illumination warning and on training air crew. Also, the sensors currently in use do not cover the complete range of laser threats and thus not reliable in protecting eyes, hence the interest in developing efficient and stable optical limiting material in South Africa [135].

The structural requirement for NLO material is the presence of a network of conjugated electrons delocalised in π -type orbitals. The conjugated structure affords high polarizability and thus fast charge redistribution on interaction with intense laser radiations [136 – 138]. Among the emerging classes of conjugated compounds are molecular materials such as conjugated organic materials, or polymers. Phthalocyanines and related compounds such as naphthalocyanines (Ncs) are also a class of emerging attractive compounds in this field due to the properties they hold. Phthalocyanines are of great interest in this work for they have several advantages over inorganic material currently in use for optical limiting. The advantages include:

1. fast response times (subpicosecond), the faster the response the better. A device that responds slowly would be useless for protecting light sensitive optical elements because the reduction of transmission would occur after the device has been damaged [100, 102],
2. small dielectric constants (ϵ) [37], i.e. its ability to conduct electricity and the smaller ϵ is the better; and,
3. they are relatively easy to fabricate or process.

The primary role played by Pcs as active material for NLO in optical limiting (OL) applications has been widely recognised since the early discoveries of OL effects at the end of the 1960s [139]. Up to now, the viability of Pcs as NLO material in OL devices has been devoted on the measurements of NLO properties of many different phthalocyanines together with basic understanding of the origin of nonlinearities in diverse compounds [38, 140, 141]. On the other hand, relatively scarce attention has been paid on the optimization of the relevant NLO properties for OL through the design of molecular structure. This is believed to be due to the different experimental conditions adopted by different research groups [102].

1.6.1 Optical limiting: a nonlinear effect

An optical limiter is a device that strongly reduces intense light while transparent to normal light. The effects of optical limiting consist of a transmission of a constant flux of photons (I_{out}) through an optical limiter (for example, a phthalocyanine) once the incident flux of photons (I_{in}) exceeds a system-characteristic threshold values, I_{lim} , Fig. 1.9. What this means is that no matter how many photons are pumped into the optical limiting device, the flux of photons passing through the optical limiter remain constant once the threshold limiting value has been reached, i.e. $I_{in} > I_{lim}$. Fig. 1.9, represents the ideal behaviour of an optical limiter, where I_{in} increases linearly with I_{out} until a limiting point I_{lim} is reached [37, 92, 99, 102, 103].

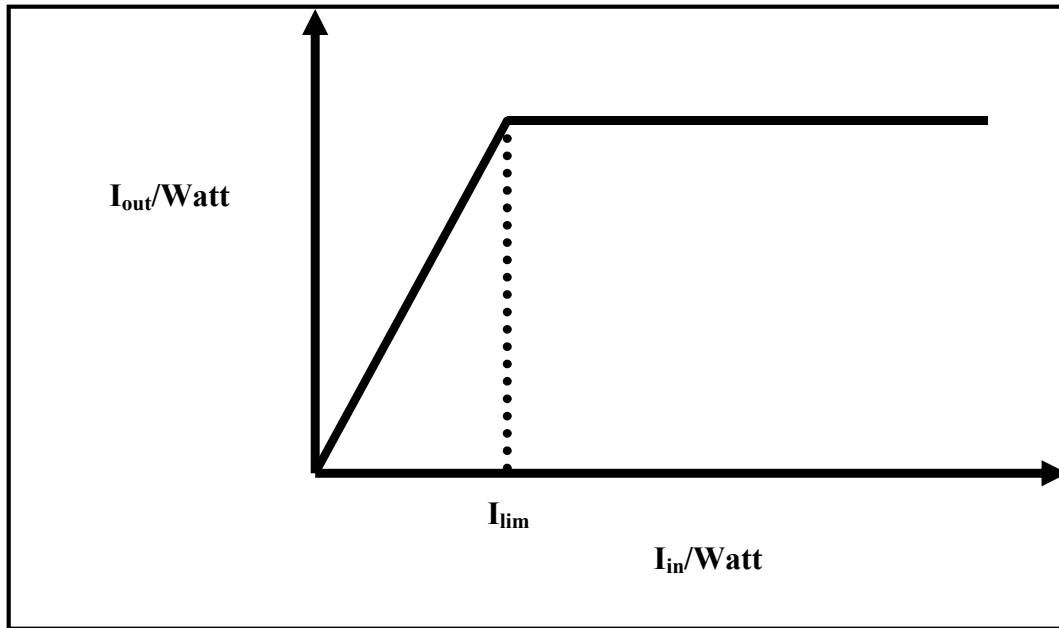


Figure 1.9: The response of an optical limiter

The nonlinearity arises from the fact that the response I_{out} of the optical limiter is not directly proportional to the input values I_{in} .

There are several mechanisms that give rise optical limiting effects. These include a perturbation of the electronic distribution in the material as a response to the electric field of the incident (low intensity) light resulting in normal linear polarization, molecular reorientation and optical pumping [100]. Of these mechanisms, optical pumping is the most effective in producing good optical limiting effects. The optical pumping mechanism involves real transitions, where light interacts with the absorbing material (optical limiting material) which then results in transitions to the excited states. Optical pumping gives rise saturable (SA) and reverse saturable absorption (RSA). Most materials show SA, they absorb a large fraction of the incident light when the input fluence is low, where absorption decreases with increasing intensity of light. Physically this takes place because the absorption cross section of the ground state, σ_g , is larger than that of the state excited state, σ_{ex} , Fig. 1.10.

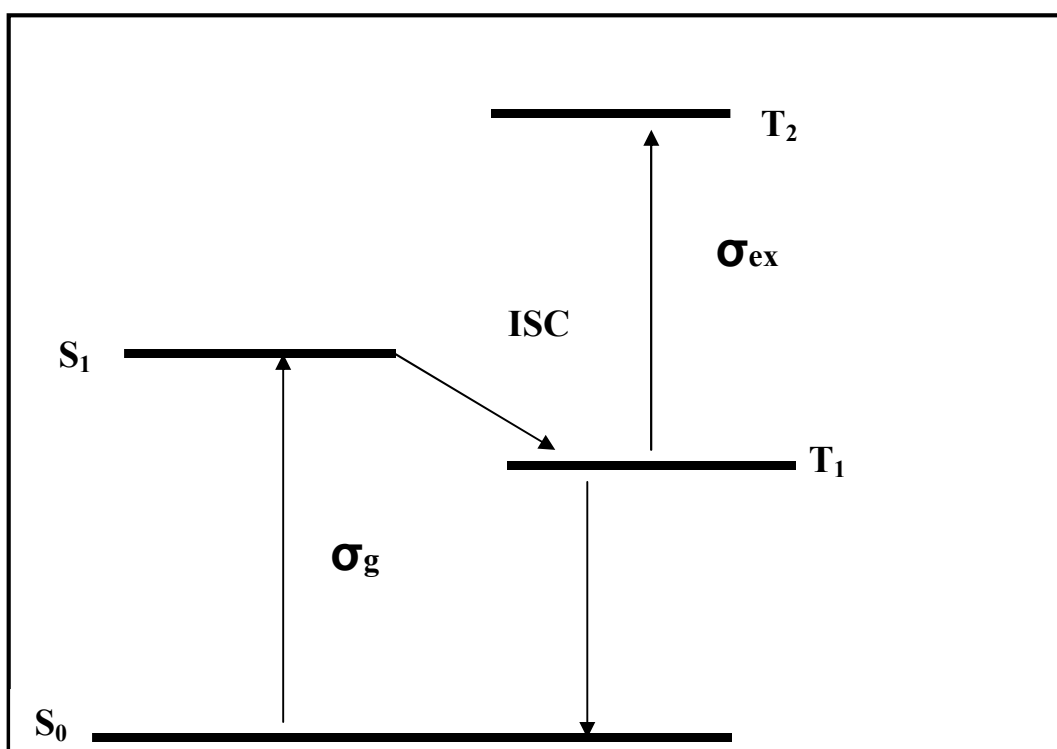


Figure 1.10: Jablonski diagram for phthalocyanines showing the absorption and decay pathways. Where σ_g and σ_{ex} are absorption cross sections for the ground and excited states, respectively.

With RSA, the absorption cross section of the excited state, σ_{ex} , exceeds that of the ground state, σ_g . Absorbance increases with increasing intensity until a limit is reached, I_{lim} . Increase in absorption reflects an increase in the excited states relative to the ground state [37, 100, 102]. RSA is responsible for optical limiting effects and its best described by the Jablonski diagram in Figure 1.10

An efficient optical limiter should, therefore, have [37, 100 - 104]: (i) a larger triplet states cross section absorption compared to that of the ground state ($\sigma_{ex} \gg \sigma_g$); (ii) a long lifetime and high population in the triplet state; (iii) a rapid intersystem crossing; (iv) optical stability, to minimize degradation of the optical limiting material under irradiation; (v) and good processibility.

1.6.2 Nonlinear optical parameters

The important parameters in this section are k which is the ratio of the absorption cross section of the singlet and triplet state; I_{lim} , the safety threshold limit intensity, otherwise known as limiting intensity; $I_m[\chi^{(3)}]$ and γ , the third and second order susceptibilities, respectively.

k ratio can be calculated using equation 1.20. A good optical limiter should have k ratio of more than one.

$$k = \frac{\sigma_{ex}}{\sigma_g} \quad (1.20)$$

1.6.2.1 Limiting threshold intensity (I_{lim})

The limiting intensity values are calculated using equation 1.21 [37, 104]:

$$I_{lim} = \frac{h\omega^*}{2\pi\sigma_s\tau_T} \quad (1.21)$$

where ω^* , σ_s and τ_T are the frequency at which the system absorbs, singlet absorption cross section and triplet lifetimes, respectively.

It therefore makes sense in this regard to mention that an ideal optical limiter should have a low threshold limit value (I_{lim}) for if it is too high, it becomes less reliable in terms of eye or light sensitive protection.

1.6.2.2 Third order susceptibility $\chi^{(3)}$ and second hyperpolarizability, γ

The third order susceptibility, $\chi^{(3)}$, is given by equation 1.22

$$I_m[\chi^{(3)}] = \frac{2c^2\eta^2\beta}{\pi\omega^*} \times 10^{-22} \quad (1.22)$$

where η and ω^* are respectively the linear refractive index and the frequency at the wavelength of interest. The term β represents a nonlinear absorption term which averages the molar extinction coefficient ϵ_S and ϵ_T according to equation 1.23

$$\beta = 5.3\epsilon_S\epsilon_T[C]\Phi_{ISC} \quad (1.23)$$

where ϵ_S and ϵ_T are extinction coefficients for the ground and triplet state, respectively, $[C]$ is the concentration of active species in the triplet state and Φ_{ISC} is the intersystem crossing quantum yield.

At a molecular level, $\chi^{(3)}$ is directly related to the second hyperpolarizability, γ , through equation 1.24 [37, 98, 102]

$$\gamma = \frac{\text{Im}[\chi^{(3)}]}{f^4[C]N_a} \quad (1.24)$$

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

These nonlinear parameters, $I_m[\chi^{(3)}]$ and γ , are used to quantify the nonlinear absorption.

1.6.3 Review of nonlinear parameters for GaPc and In complexes

This review presents the selected nonlinear optical parameters that are of interest. These include the absorption cross section ratio k , and limiting intensities, I_{lim} , which is also referred to as the saturation energy density, F_{sat} , second, γ , and third order, $I_m[\chi^{(3)}]$, hyperpolarizabilities. Table 1.3 lists all the above parameters. To be noted is that only substituted Ga phthalocyanines and (Cl)InPc (**16**) were reviewed in this section.

Table 1.3: Summary of nonlinear optical parameters of GaPc and In phthalocyanines
(See Fig. 1.6 and 1.7 for the number of complexes)

Complex	k ($\sigma_{\text{ex}}/\sigma_{\text{g}}$)	$F_{\text{sat}}/\text{J. cm}^{-2}$	$I_m[\chi^{(3)}]/10^{-11}$ esu	$\gamma/10^{-32}$ esu	Refs.
16			0.15		[37]
24	11.3	13.5	1.30	1.76	[98]
25a	13.5	27.0	1.20	0.84	[98]
25b	13.6	8.4	1.10	0.86	[98]
25c	9.5	16.3	0.88	0.69	[98]
29	4.8	7.5	0.73	1.13	[98]
33	16.1	10.1	1.2	7.3	[106]
34	16.2	9.5	1.3	8.1	[106]

As stated before, a good optical limiter should have a k ratio of more than one. All the compounds in Table 1.3 satisfied the above requirement, with complex **33** and **34** (Fig. 1.7) displaying the largest excited to ground state ratios, k . The saturation energies, F_{sat} , for complexes **24**, **25** and **29** ranged from 7.4 – 27 J. cm⁻². The second and third order hyperpolarisabilities are also presented in Table 1.3. These are used to quantify nonlinear absorption. A good optical limiter should fall within the 10⁻¹⁵ to 10⁻

⁹ range for $I_m[\chi^{(3)}]$ and 10^{-34} and 10^{-29} range for γ [37]. The GaPc complexes fell well within the expected ranges for phthalocyanines for both second and third order hyperpolarisabilities in Table 1.3. The substituted In complexes (**33**, **34**) showed good results, with k ratios of 16.1 and 16.2, respectively. The difference in the parameters of the two substituted InPc complexes (**33** and **34**) was not significant. This suggests that the different axial substituents do not have much of an effect in the results.

Aims of thesis

A lot of work has been done already on the nonlinear optical parameters of GaPc and InPc complexes. However, no work has been done on octasubstituted complexes. The aim is to further explore this using the synthesized octasubstituted GaPc and InPc complexes which are isomerically pure and may improve the NLO parameters. The aim is to determine the nonlinear optical parameters stated above. This is driven by the need to develop optical limiters for the protection of eyes for soldiers in warfare. Today's warfare is based on laser weapons, it therefore goes without saying that laser light can be hazardous to human eyes, so it is important that measures are taken to research and develop optical limiters so as to minimise eye damage.

1.7 ELECTROCHEMISTRY

Several techniques were employed to characterize the synthesized GaPc and InPc derivatives; these include electrochemistry, UV/Vis, IR and NMR spectroscopies. In this section a brief overview of cyclic voltammetry and spectroelectrochemistry is provided since these are less common techniques.

1.7.1 Electrochemistry of phthalocyanines

Phthalocyanines exist as a dianion, i.e. Pc^{2-} , which may be reduced or oxidized. The redox activity of phthalocyanines is directly related to the frontier orbitals, highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO, e_g) in the molecule. Oxidation is the removal of electron(s) from HOMO (a_{1u}) while reduction is the addition of electron(s) to the LUMO (Fig 1.3). Successive removal of up to two electrons from HOMO (a_{1u}) results in the formation of $\text{Pc}(-1)$ and $\text{Pc}(0)$. In the same way, successive addition of up to four electrons to the LUMO results in the formation of Pc^{-3} , Pc^{-4} , Pc^{-5} and Pc^{-6} [142]. The above redox activity is common in H_2Pcs and phthalocyanines with metals that are not redox active, such as Ga^{+3} and In^{+3} .

There are several factors that can influence the redox properties of phthalocyanines. They include the nature of substituents on the ring, solvent, nature and oxidation state of the central metal and the nature of the axial ligand [143]. Electron releasers increase the electron density making MPcs easier to oxidise. On the other hand, electron-withdrawing substituents decrease electron density, making oxidation more difficult.

A few electrochemical techniques that include cyclic voltammetry, square-wave voltammetry and spectroelectrochemistry were employed in this study and the section that follows gives their overviews briefly

1.7.2 Cyclic voltammetry (CV)

In cyclic voltammetry an applied potential, $E(V)$, is scanned from the initial potential, E_i , to a final potential, E_f , and back to the E_i completing one cycle where the resulting

current (i) in Amps (A) is measured and hence the name cyclic voltammetry. During this cycle, the potential of the working electrode is measured against a reference electrode, such as a silver|silver chloride, Ag|AgCl. Fig. 1.11 presents a typical cyclic voltammogram.

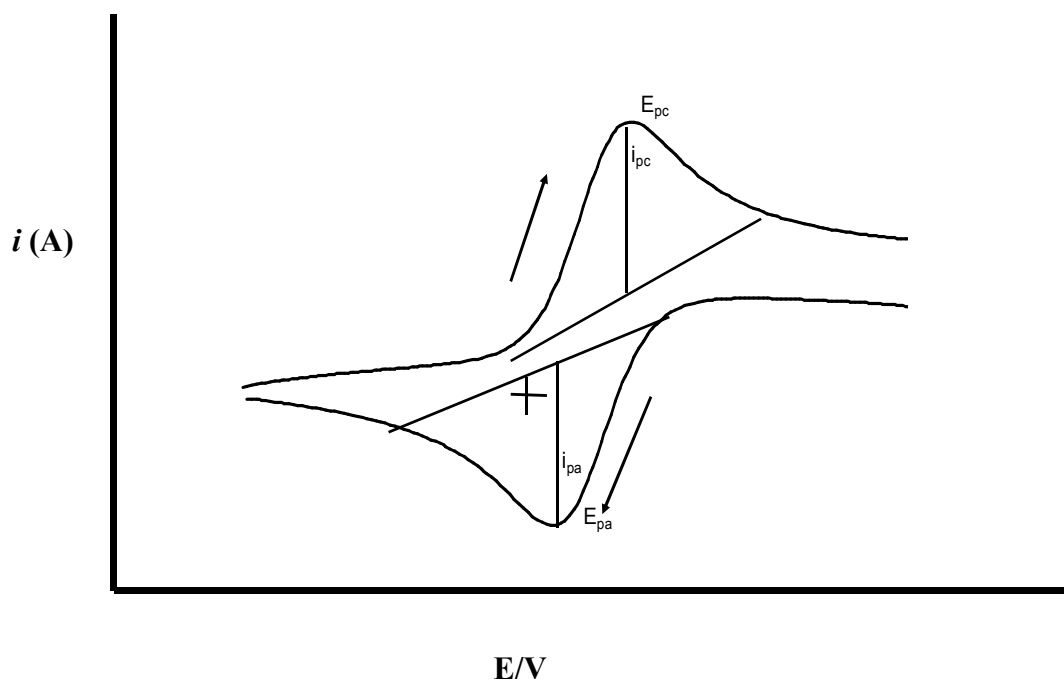


Figure 1.11:A typical cyclic voltammogram

A starting potential is applied and scanned in (either) a negative (or positive direction) resulting in the appearance of a cathodic peak as soon as reduction begins. A maximum current (i_{pc}) is reached followed by a sudden drop of current. The sudden drop is due to the much slower diffusion of molecules towards the electrode surface when compared to the reduction of molecules. On reversing the potential an anodic peak is obtained.

Three processes occur in cyclic voltammetry. These are reversible, irreversible and quasi-reversible processes. A reversible system or couple is achieved if there is a

rapid exchange of electrons by both the species with the working electrode. It is identified by measuring the potential differences between the cathodic and anodic components of the couple.

For a reversible couple, equation 1.25 can be employed to determine the number of electrons transferred at 25°C

$$\Delta E = E_{pa} - E_{pc} = \frac{2.3RT}{nF} \approx \frac{0.059V}{n} \quad (1.25)$$

Where **n** is the number of electrons, **E_{pa}** is the anodic peak potential, **E_{pc}** is the cathodic peak potential, R is the gas constant, T is the temperature and F is the Faraday constant.

The formal reduction potential, which is more or less equal to the half wave potential of the couple, **E_{1/2}**, can be calculated using equation 1.26

$$E_{1/2} \approx E^0 = \frac{E_{pa} + E_{pc}}{2} \quad (1.26)$$

An irreversible couple is characterised by the separation of peak potentials that are much greater than 0.059V/n, or by the absence of return peaks and by the peak potentials which are dependent on the scan rate [144]. Irreversible couples are caused by slow exchange of electrons with working electrode

A quasi-reversible process is the simultaneous occurrence of charge and mass transport. The voltammograms show more drawn out behaviour with large peak potential separations, ΔE_p . The peaks are broader when compared to reversible processes.

Square wave voltammetry (SWV) is a type of voltammetry that offers the advantage of high sensitivity in determining $E_{1/2}$ [144]. With SWV, potential is increased in small amounts from an initial E_i to E_f , where current signals are collected at two points. The differences in the two current points are plotted as a function of applied potential to give peaks.

1.7.3 Spectroelectrochemistry

Spectroelectrochemistry is a study that combines electrochemical and spectroscopic techniques to observe eletrogenerated products in homogeneous reactions without interference by the starting material [145]. Optically transparent thin layer electrodes (OTTLE) are used in this study as they allow transmittance of the optical beam through the metal minigrids in the OTTLE cell. These minigrids are easily incorporated into a thin layer cell [145].

The number of electrons transferred during the redox processes can be established using equation 1.27

$$Q = nFVC \quad (1.27)$$

where V is the volume of the cell, F is the Faraday constant, C is the concentration of the analyte and n is the number of electrons.

The aim of spectroelectrochemistry is to distinguish redox processes for metallophthalocyanines that cannot be distinguished by CV alone. These processes may take place at the central metal or the ring. Processes that are ring based often result in colour change, whilst for metal based processes there's less colour changes [146]. A shift in the Q band is due to the oxidation or reduction of the metal [47] and

a decrease in the Q band intensity together with an increase in intensity in the 500 – 600 nm region is as a result of ring oxidation or reduction [115].

There is no reported work in the electrochemistry of Ga and In phthalocyanines. The electrochemistry of Ga(III) porphyrins has been reported [147].

The electrochemistry of porphyrins is said to be straight forward. Each complex shows two reversible oxidations and two reversible reductions, all are ring based.

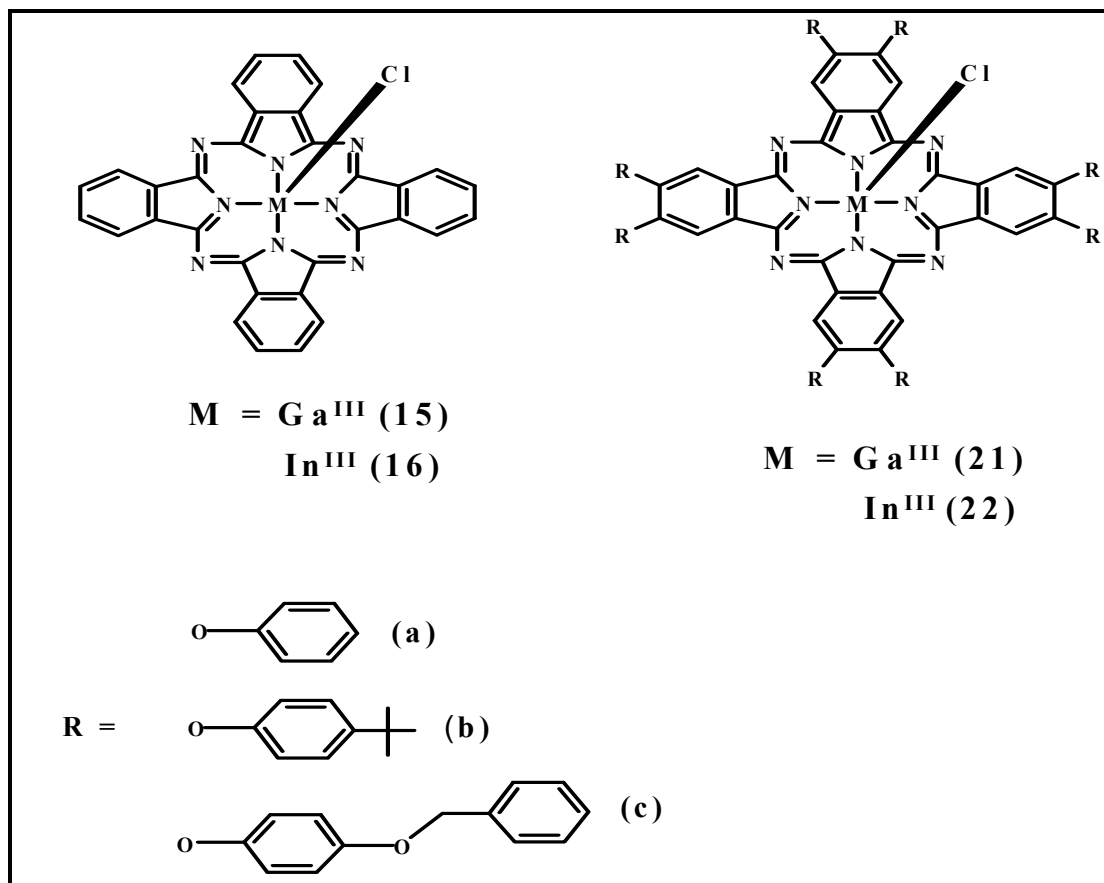
1.8 SUMMARY OF AIMS

1. To synthesize Ga and In metallophthalocyanine (MPc) complexes, shown in Fig. 1.12, where characterization of these complexes will be carried out using UV/Vis, IR, NMR spectroscopies and electrochemistry
2. Carry out comprehensive photophysical photochemical calculations and experiments to determine the following parameters:
 - Triplet quantum yield (Φ_T), fluorescence quantum yield (Φ_F), photodegradation quantum yield (Φ_{pd}), and singlet oxygen quantum yield (Φ_Δ); lifetimes – triplet lifetime (τ_T) fluorescence lifetime (τ_F).

The photochemical and photophysical parameters are to be carried out in various solvents to determine the effects of solvent parameters, such as viscosity, polarity, refractive index and the presence of heavy atoms in the solvent molecule, on these parameters.

3. Photocatalysis of 1-hexene with the synthesized GaPc and InPc derivatives. % selectivity and % conversion (discussed in section 3.2.3) will be determined.

4. Determine NLO parameters, these include k , which is the ratio of the absorption cross section of the singlet and triplet state; I_{lim} or F_{sat} , the safety threshold limit intensity, otherwise known as limiting intensity; $I_m[\chi^{(3)}]$ and γ , the third and second order susceptibilities, respectively.



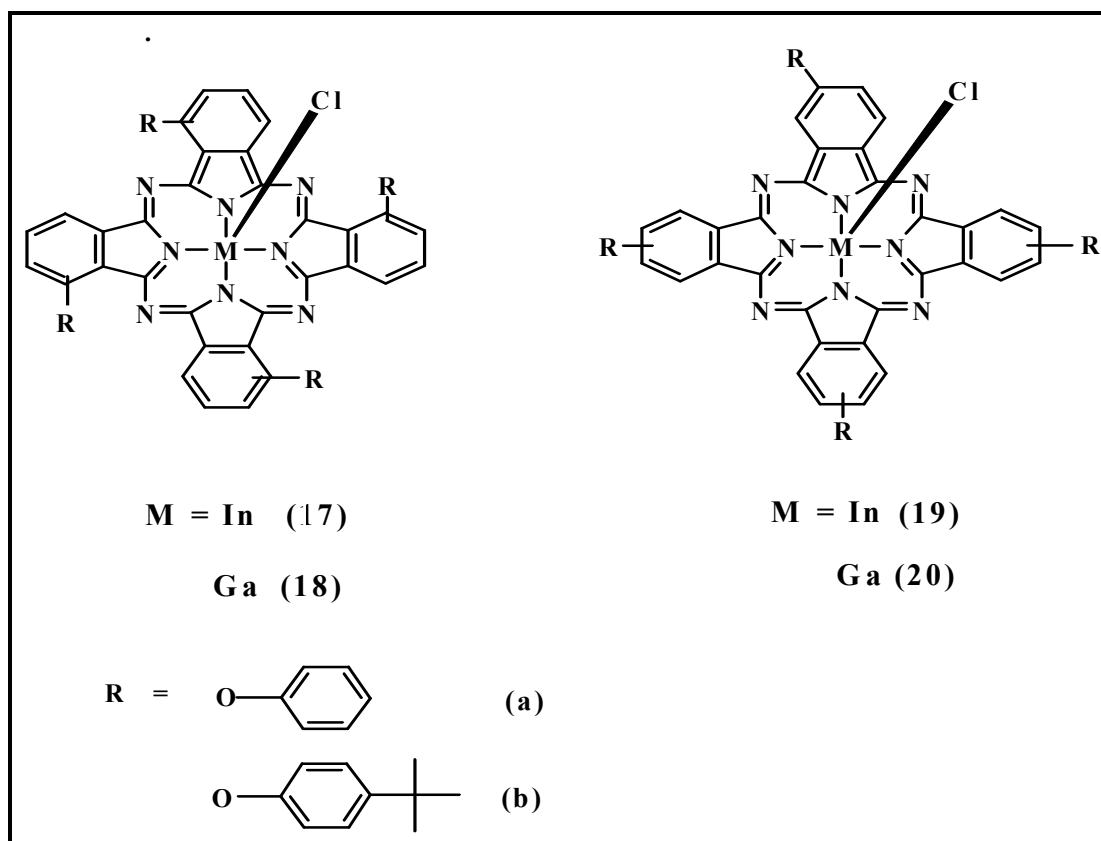


Figure 1.12: Structures of Ga and In phthalocyanines studied

2 EXPERIMENTAL

2.1 EQUIPMENT USED

Column chromatography was performed on silica gel 60 (0.04 – 0.063 mm) and preparative thin layer chromatography was performed on silica gel 60 PF₂₅₄.

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 Cary Eclipse Fluorescence spectrophotometer. Elemental analyses were performed at the University of Cape Town. Matrix-assisted laser desorption/ionization – time of flight (MALDI-TOF) spectra were recorded with Perspective Biosystems Voyager DE-PRO Biospectrometry Workstation and Processing Delayed Extraction Technology at the University of Cape Town.

Photo-irradiations were done using a General electric Quartz line lamp (300W). 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 and 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 MAX 5100 (Molelectron detector incorporated) power meter. A schematic representation of the set-up for photo-irradiation reactions is shown below (Fig. 2.1).

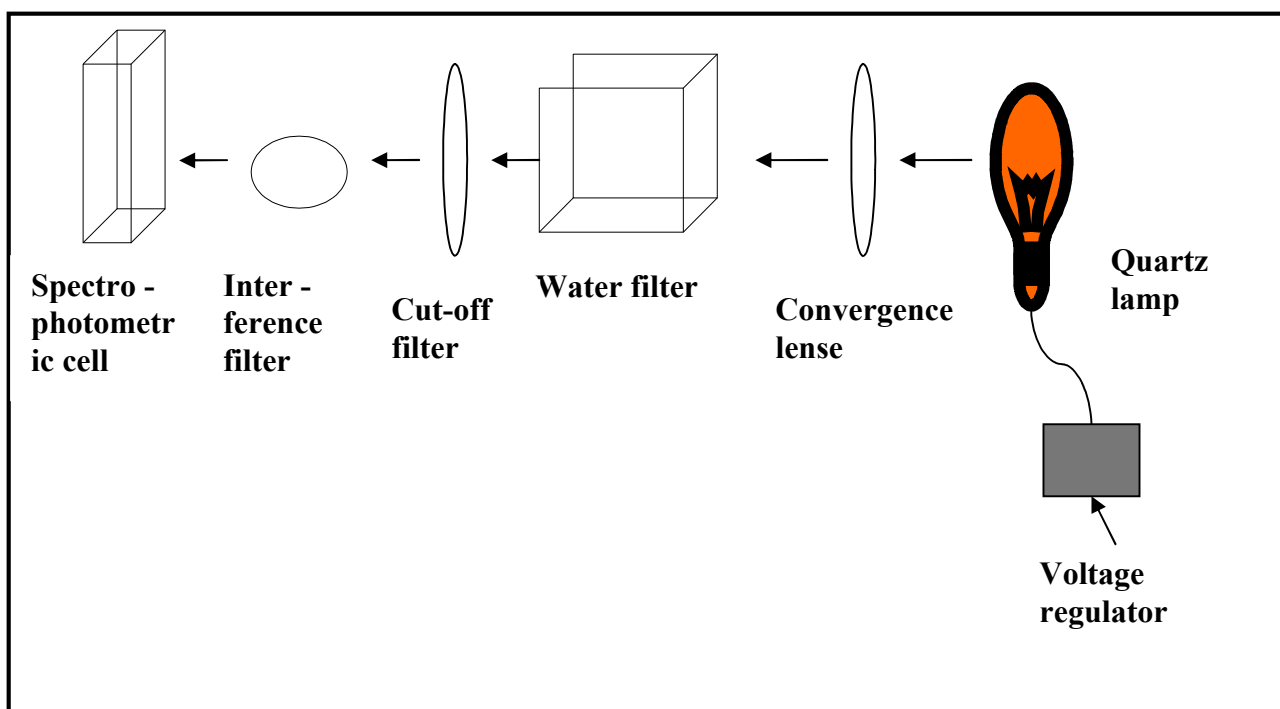


Figure 2.1: Set-up for photoirradiation reactions.

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, 1.5 J / 90 ns) pumped tunable dye laser (Lambda Physic FL 3002, Pyridine 1 dye in methanol). The analyzing beam source was derived 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. Products for the photocatalytic oxidation of 1-hexene were analyzed using a Hewlett-Packard HP 5890 gas chromatograph fitted with an Flame Ionization Detector (FID) detector, using a PONA (crossedlinked methyl siloxane) capillary column (50 m length, 0.2 mm internal diameter, 0.5 μm film thickness and 100 phase ratio). Mass spectra were recorded with Funnigan GC-MS using the same column described above.

Cyclic (CV) and Square wave (SWV) voltammetry experiments were performed using Autolab potentiostat PGSTAT 30 (Eco Chemie, Utrecht, The Netherlands) driven by the General Purpose Electrochemical System data processing software (GPES, software version 4.9, Eco Chemie), using a conventional three-electrode system. A glassy carbon electrode (GCE, 3.0 mm diameter) was used at the working electrode. Silver-silver chloride (Ag|AgCl) or silver silver chloride in solution of sodium chloride (Ag|AgCl, 3.0 mol. L⁻¹ NaCl) and platinum wire (3.00 mm diameter) were used as pseudo-reference and counter electrodes respectively. Ag|AgCl pseudo-reference electrode is related to Ag|AgCl (3.0 mol. L⁻¹ NaCl) by 0.0015 V. Spectroelectrochemical data was recorded using an optically transparent thin-layer electrochemical (OTTLE) cell which was connected to a Bioanalytical System (BAS) CV 27 voltammograph.

2.2 MATERIALS

Acetic anhydride (Ac₂O), acetone, ammonia solution (NH₄OH), methanol (MeOH), 1-chloronaphthalene, hexane and deuterated chloroform (CDCl₃) were obtained commercially and dried before use, except ammonia solution; formamide (HCONH₂), potassium carbonate (K₂CO₃), phthalonitrile, thionyl chloride (SOCl₂), phenol, 4-*tert*-butylphenol, zinc(II) phthalocyanine (ZnPc), chlorophyll a, 1-hexene, 1-hexen-3-ol, 1,2-epoxyhexane, 1,3-diphenylisobenzofuran (DPBF) and 1,4-diazobicyclo-octane (DABCO) were obtained from Aldrich. Chloroform (CHCl₃) dimethylsulfoxide (DMSO), *N,N'*-dimethylformamide (DMF, freshly distilled), tetrahydrofuran (THF) and toluene were purchased from SAARCHEM, and dried in alumina before use. High performance liquid chromatography (HPLC) grade dichloromethane (DCM) was

used for the photocatalytic transformation experiments. Tetrabutylammonium tetrafluoroborate (TBABF₄) was purchased from Aldrich and was used at the electrolyte for electrochemical experiments.

2.3 SYNTHESIS

Tetra substituted complexes **17 – 20** have been reported before [109]

2.3.1 Unsubstituted metallophthalocyanines (Scheme 3.1) [148]

(Chloro)gallium (III) phthalocyanine [148]: the preparation of (Cl)GaPc (**15**) was achieved by following a previously reported method [148]. Phthalonitrile (**5**) (2 g, 0.72 mmol) and GaCl₃ (0.32 g, 0.27 mmol) were placed in a preheated oil bath (215°C) followed by the addition of 1-chloronaphthalene (0.3 mL). The reaction mixture was refluxed under dry inert gas (N₂) at this temperature for 1.5 - 2 hours. After cooling, the product was added to methanol. The precipitate was filtered, washed intensely with methanol, followed by acetone. The precipitate was then allowed to dry in vacuum. Yield: 0.74g (23 %), UV/Vis (DMSO): λ_{max} (log ϵ); 680 nm(5.14), 6.45 (4.92), 611 (4.04), 355 (4.42). IR (KBr): ν_{max} /cm⁻¹; 1505 (C=C); ¹H NMR (DMSO-d₆) δ , ppm; 9.80 (8H, d, Pc), 8.60 (8H, d, Pc)

(Chloro)indium (III) phthalocyanine [148]: Synthesis and purification of (Cl)InPc (**16**) was as explained for compound **15**. However instead of using GaCl₃, InCl₃ was used. The amounts of reagents used were: Phthalonitrile (2g, 0.72 mmol), InCl₃ (0.60 g, 0.27 mmol), 31-chloronaphthalene (0.3 mL).

Yield: 0.83 g (21 %), Uv/Vis (DMSO): λ_{max} (log ϵ)686 nm(5.28), 6.50 (4.01), 616 (4.12), 355 (4.17). IR (KBr): ν_{max} /cm⁻¹; 1505 (C=C); ¹H NMR (DMSO-d₆) δ , ppm; 9.80 (8H, d, Pc), 8.60 (8H, d, Pc)

2.3.2 Phthalonitriles

2.3.2.1 4,5-Dichlorophthalonitrile (Scheme 3.2) [149]

4,5-Dichlorophthalic anhydride (40): A mixture of 4,5-dichlorophthalic acid (**39**) (60.0 g, 0.25 mol) and acetic anhydride (100 mL) was heated under reflux for 5 hours. After cooling, the light greyish to white product was filtered and intensively washed with petroleum ether (bp 40 – 60°C) and dried under vacuum. Yield: 50.3 g (93 %). IR [(KBr) ν_{max} /cm⁻¹]: 1824, 1775 (anhydride).

4,5-Dichlorophthalimide (41): 4,5-Dichlorophthalic anhydride (**40**) (50.0 g, 0.23 mol) was heated while stirring in formamide (68 mL) under reflux for 3 hours. After cooling, the greyish to white product was filtered, washed with water and dried in the fume hood overnight. Yield 47.8 g (97 %). IR [(KBr) ν_{max} /cm⁻¹]: 1770, 1710 (amide).

4,5-Dichlorophthalamide (42): A mixture of 4,5-Dichlorophthalimide (**41**) (47.0 g, 0.21 mol) and 25 % ammonia (640 mL) was stirred for 24 hours; followed by addition of 33% ammonia and continuous stirring for another 24 hours. The resultant product was filtered, washed with water and dried at 60°C. Yield: 41.2 g (76 %). IR [(KBr) ν_{max} /cm⁻¹]: 1651, 1620 (amide)

4,5-dichloro-1,2-dicyanobenzene (43): At 0°C thionyl chloride (140 mL) was added to dry DMF (200 mL) under stirring and nitrogen. After 2 hours, dry 4,5-dichlorophthalamide (**42**) (40 g, 0.176 mol) was added and the mixture was stirred for 5 hours at 0 – 5°C, followed by another 18 hours at room temperature. The mixture was added to ice water. The product was then filtered, washed with water and

recrystallised from methanol to achieve a white product. Yield: 22.6g (65 %).
[(KBr) $\nu_{\max}$ /cm⁻¹]: 2230 (nitrile). ¹H NMR (DMSO-d₆) δ , ppm 8.50 (2-H, s, Ar-H)

2.3.2.2 4,5-Disubstituted phthalonitriles (Scheme 3.3) [149]

4,5-Bis(phenoxy)-1,2-dicyanobenzene (**44a**)

4,5-Bis(phenoxy)-1,2-dicyanobenzene (**44a**) was synthesized from 4,5-dichloro-1,2-dicyanobenzene (**43**) and phenol in dried DMSO as previously reported [149]. A mixture of 4,5-dichloro-1,2-dicyanobenzene (**43**) (8.02 g, 40 mmol), phenol (7.52g, 80 mmol) and dried DMSO (80 mL) was stirred at 90°C, as anhydrous K₂CO₃ (27.6 g, 200 mmol) was added eight times at 5 minutes intervals. The reaction mixture was stirred at 90°C for an additional 40 minutes and allowed to cool. The reaction mixture was subsequently added to ice water (100 mL) and the aqueous phase was extracted with chloroform (3 x 45 mL). The combined extracts were first washed with sodium carbonate (5 %), then with water and dried over magnesium sulfate. The solvent was evaporated and the product was re-crystallised with methanol and was left in the fume hood to dry overnight.

Yield: 7.42g (59 %); IR (KBr): $\nu_{\max}$ /cm⁻¹; 3040 – 3051 (Ar-H), 2237 (C $\equiv$ N), 1209 (C-O-C); ¹H NMR (DMSO-d₆) δ , ppm; 7.7 (2H, s, Ar-H), 7.4 (4H, t, Ar-H), 7.2 (2H, t, Ar-H), 7.1 (4H, d, Ar-H).

2.3.2.3 4,5-bis(4-tert-butylphenoxy)-1,2-dicyanobenzene (**44b**) (Scheme 3.3)

Synthesis and purification of **44b** was similar to that of compound **44a**. The amounts of the reagents employed were: 4,5-dichloro-1,2-dicyanobenzene (**43**) (8.01 g, 40 mmol), 4-tert-butylphenol (12.00 g, 80 mmol), K₂CO₃ (27.6 g, 200 mmol) and dried

DMSO (80 mL). Yield: 9.83 g (58%); IR (KBr): $\nu_{\max}/\text{cm}^{-1}$; 3041 -3051 (Ar-H), 2213 (C $\equiv$ N), 1219 (C-O-C); ^1H NMR (DMSO- d_6) δ , ppm; 9.1 (2H, s, Ar-H), 7.1 (4H, d, Ar-H), 6.6 (4H, d, Ar-H), 1.2(s, 18H, CH₃).

2.3.2.4 4,5-bis[4-(Benzyloxy)phenoxy]phthalonitrile (**44c**) (Scheme 3.3)

The synthesis and purification of **44c** was similar to that of compound **44a**. The amounts of the reagents employed were: 4,5-dichloro-1,2-dicyanobenzene (**43**) (6.01 g, 40 mmol), 4-(benzyloxy)-phenol (18.32 g, 94 mmol), K₂CO₃ (67.4 g, 488 mmol) and dried DMSO (47 mL). Yield: 10.56 g (66 %); IR (KBr): $\nu_{\max}/\text{cm}^{-1}$; 3041 -3051 (Ar-H), 2236 (C $\equiv$ N), 1241 (C-O-C); ^1H NMR (DMSO- d_6) δ , ppm; 8.50 (2-H, s, Ar-H), 7.45 (8H, br d, Ar'-H), 7.10 (10H, d, Ar'-H), 5.21 (4H,s, CH₂).

2.3.3 Syntheses of Octasubstituted phthalocyanines (Scheme 3.3) [150]

2.3.3.1 Octaphenoxyphthalocyaninato gallium chloride (**21a**)

A mixture of 4,5-bis(phenoxy)-1,2-dicyanobenzene (**44a**) (3.12 g, 10 mmol), anhydrous GaCl₃ (0.88g, 5 mmol) and 1-chloronaphthalene (4 mL) was placed in a preheated oil bath (215°C). The reaction mixture was stirred at this temperature for 7 hours under a 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 thin layer chromatography (TLC) on 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: 1.59 g, (47%) UV/vis (DMSO): λ_{max} (log ϵ); 687 (5.10), 616 (4.56), 370 (4.90); IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$; 3034 - 3052 (Ar-H), 1588 (C=C), 1460, 1452, 1407, 1339, 1275 1201(C-O-C),, 1162, 1089, 1089, 1037, 1003, 860; ^1H NMR: (CDCl_3) δ ppm; 8.6 (d, 8H, Pc-H), 7.4 (t, 16H, phenyl-H), 7.3 (t, 16H, phenyl-H), 7.2 (m, 8H, phenyl-H). Calc. for $\text{C}_{80}\text{H}_{48}\text{N}_8\text{O}_8\text{GaCl}$: C, 69.10; H, 3.47; N, 8.06. Found: C, 68.14; H, 3.59; N, 7.34. MALDI-TOF-MS m/z : Cal. 1354.34; Found, 1352.00 $[\text{M}-2]^+$.

2.3.3.2 *Octakis(4-tert-butylphenoxy)phthalocyaninato gallium chloride (21b)*

Synthesis and purification of compound **21b** was similar to that of compound **21a**. However, instead of using **44a**, compound **44b** was used. The amounts of the reagents employed were: **44b** (3.16 g, 7.44 mmol), anhydrous GaCl_3 (0.65g, 3.72 mmol) and 1-chloronaphthalene (4mL); 1.11 g 35%; UV/vis (DMSO): λ_{max} (log ϵ); 690 (5.31), 620 (3.82), 347 (4.15); IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$; 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; ^1H NMR: (CDCl_3) δ ppm; 8.6 (broad s, 8H, Pc-H), 7.0-7.4(m, 32H, phenyl-H), 1.3 – 1.4 (m, 72H, CH_3); Calc. for $\text{C}_{112}\text{H}_{112}\text{N}_8\text{O}_8\text{GaCl}$: C, 74.60; H, 6.26; N, 6.21; Found: C, 73.03; H, 5.71; N, 6.03. MALDI-TOF-MS m/z : Calc. 1803.20; Found $[\text{M}-\text{Cl}]^+$ 1765.53.

2.3.3.3 *Octakis(4-benzyloxyphenoxy)phthalocyaninato gallium chloride (21c)*

The synthesis and purification of compound **21c** was achieved by mixing **44c** (3.50 g, 7.98 mmol), anhydrous GaCl_3 (0.50g, 2.85 mmol), urea (0.48, 7.98 mmol) and 1-octanol (28mL). The mixture was refluxed for 14 hours under dry nitrogen atmosphere at 150°C . After cooling, methanol (70 mL) was added and refluxed for 2

hours. After cooling, the mixture was filtered, washed with water and left in the fume hood to dry overnight. Purification of the crude product was carried in a silica gel column where THF was used as the eluting solvent. Following the removal of the solvent by evaporation, the product was washed with ethanol. The green solid product was dissolved in THF and was precipitated out by drop-wise addition of methanol to yield green crystals. Yield: 0.84 g (40%); UV/vis (DMSO): λ_{max} (log ϵ); 692 (5.40), 617 (4.47), 353 (5.13); IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$; 3035 (Ar-CH), 1599 (C=C), 1237 (C-O-C); ^1H NMR: (CDCl_3) δ ppm; 8.62-9.16 (8H, m, Pc-H), 8.09 - 8.41(8H, m, Phenyl-H), 7.36 – 7.61 (48H, m, Phenyl-H), 7.15 – 7.24 (16H, m, Phenyl-H), 5.12 (16H, d, CH_2); Calc. for $\text{C}_{136}\text{H}_{96}\text{N}_8\text{O}_{16}\text{GaCl}$: C, 74.13; H, 4.39; N, 5.09; Found: C, 74.01; H, 4.79; N, 5.24 %.

2.3.3.4 Octaphenoxyphthalocyaninato indium chloride derivatives (**22a**)

The synthesis and purification of complex **22a** was similar to that of compound **21a**, except InCl_3 was used instead of GaCl_3 . The amounts of reagents used were: **44a** (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). Yield: 1.38 g, (20%); UV/vis (DMSO): λ_{max} (log ϵ); 691 (5.23), 622 (3.59), 368 (4.08); IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$; 3034 - 3052 (Ar-H), 1588 (C=C), 1460, 1452, 1407, 1339, 1275 1201(C-O-C),, 1162, 1089, 1089, 1037, 1003; ^1H NMR: (CDCl_3 ,) δ ppm; 8.9 (s, 8H, Pc-H), 7.1 - 7.4 (m, 40H, phenyl-H). Calc. for $\text{C}_{80}\text{H}_{48}\text{N}_8\text{O}_8\text{InCl}$: C, 68.65; H, 3.45; N, 8.01. Found: C, 67.79; H, 3.37; N, 7.73.

2.3.3.5 *Octakis(4-tert-butylphenoxy)phthalocyaninato indium chloride (22b)*

Synthesis and purification of compound **22b** was similar to that of compound **21a**, except InCl_3 was used instead of GaCl_3 and also, instead of using **44a**, compound **44b** was used. The amounts of the reagents employed were: **44b** (3.18 g, 8.00 mmol), anhydrous InCl_3 (0.88g, 4.00 mmol) and 1-chloronaphthalene (4mL); Yield: 1.11 g, (35%); UV/vis (DMSO): λ_{max} (log ϵ); 692 (5.10), 622 (3.59), 367 (4.22); IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$; 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; ^1H NMR: (CDCl_3) δ 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 $\text{C}_{112}\text{H}_{112}\text{N}_8\text{O}_8\text{InCl}\cdot\text{CHCl}_3$: C, 68.97; H, 5.79; N, 5.69; Found: C, 69.42; H, 5.14; N, 5.29

2.3.3.6 *Synthesis of octakis(4-benzyloxyphenoxy)phthalocyaninato indium chloride (22c)*

The synthesis and purification was as explained for compound **21c**, except InCl_3 was used instead of GaCl_3 . The amounts of the reagents employed were: **44c** (3.5 g, 7.98 mmol), anhydrous InCl_3 (0.63g, 2.85 mmol), urea (0.48, 7.98 mmol) and 1-octanol (28mL). Yield: 0.97 g (16%); UV/vis (DMSO): λ_{max} (log ϵ); 696 (5.56), 641 (4.40), 3.55 (4.74); IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$; 3036 (Ar-CH), 1601 (C=C), 1190 (C-O-C); ^1H NMR: (CDCl_3) δ ppm; 8.62-9.16 (8H, m, Pc-H), 8.09 - 8.41(8H, m, Phenyl-H), 7.36 – 7.61 (48H, m, Phenyl-H), 7.15 – 7.24 (16H, m, Phenyl-H), 5.12 (16H, d, CH_2); Calc. for $\text{C}_{136}\text{H}_{96}\text{N}_8\text{O}_{16}\text{InCl}$: C, 70.64; H, 4.30; N, 4.98; Found: C, 72.58; H, 3.51 4.76; N, 5.05 %.

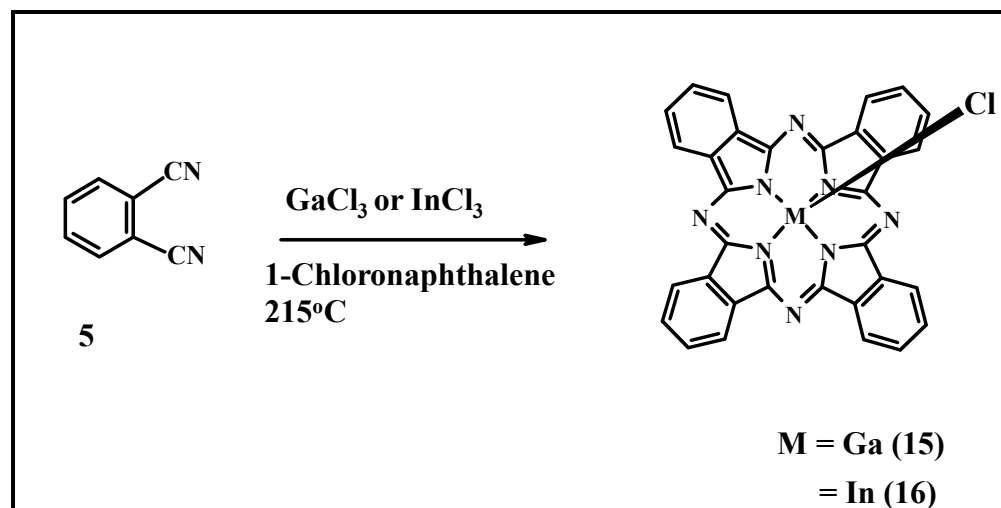
3 RESULTS AND DISCUSSION

The results presented in this thesis have been published in journals listed below:

1. “Novel Gallium(III) Phthalocyanine derivatives – Synthesis, Photophysics and Photochemistry”. **Vongani Chauke**, Abimbola Ogunsipe and Tebello Nyokong. *Polyhedron*, 26 (2007) 2663
2. “Photochemistry, photophysics and nonlinear optical parameters of phenoxy and *tert*-butylphenoxy substituted indium (III) phthalocyanines”. **Vongani Chauke**, Mahmut Durmuş and Tebello Nyokong, *J. Photochem. Photobiol. A: Chem.*, 192 (2007) 179
3. “Photocatalytic oxidation of 1-hexene of 1-hexene using GaPc and InPc octasubstituted derivatives”, **Vongani Chauke** and Tebello Nyokong (2007), submitted to *J. Mol. Cat. A: Chem*

3.1 SYNTHESIS AND CHARACTERIZATION

3.1.1 Unsubstituted gallium and indium phthalocyanines (Scheme 3.1)



Scheme 3.1:Synthetic route for (Cl)GaPc (**15**) and (Cl)InPc (**16**)

The syntheses, purification and characterisation of (chloro)gallium (**15**) and (chloro)indium (**16**) phthalocyanines have been reported before [148]. The GaPc (**15**) and InPc (**16**) complexes used in this work were synthesized as shown in Scheme 3.1. The complexes were obtained by refluxing a mixture of phthalonitrile (**5**), and the respective metal-salts (GaCl_3 and InCl_3) in 1-chloronaphthalene for two hours at 215°C [148]. The metal-salts employed in this work are moisture sensitive; synthesis was therefore performed under dry inert conditions. Purification of these complexes was achieved by washing the precipitate in warm to hot methanol several times, then finally in acetone.

The IR spectra revealed the disappearance of $\text{C}\equiv\text{N}$ stretches between 2212 and 2236 cm^{-1} , which are characteristic of dinitriles, indicating the formation of phthalocyanines.

The proton NMR for both complexes **15** and **16** were very similar, typical of unsubstituted phthalocyanines. The spectra showed two doublets at 8.55 ppm and 9.71 due to the respective equivalent peripheral and non-peripheral protons.

Fig. 3.1 shows the ground state electronic absorption spectra of complexes **15** and **16** in DMF. Un-substituted phthalocyanines are notorious for lack solubility in most common organic solvents; this is due to intramolecular interactions between their π -systems [38, 57]. They dissolve mostly in coordinating solvents such as pyridine. Complexes **15** and **16** behave likewise; they dissolve in polar and coordinating solvents such as DMSO, DMF and THF. The complexes were monomeric as judged by the sharp Q bands (Fig. 3.1), absorbing at 678 and 683 nm for **15** and **16**, respectively. The (Cl)InPc is slightly more red shifted than (Cl)GaPc, indicating that the size of the central metal has a partial influence on the absorption spectra, Table 3.1. The monomeric nature of the complexes is due to the presence of the chlorine axial ligands, which may prevent interaction between the rings and hence prevent aggregation.

Table 3.1: UV/Vis absorption and emission band positions of the gallium and indium phthalocyanines used in this study in different solvents.

MPc	Solvent	λ_Q/nm (log ϵ)	λ_{em}/nm	MPc	λ_Q/nm (log ϵ)	λ_{em}/nm
15	DMSO	680(5.14)	692	16	686(5.22)	700
	DMF	678(5.17)	687		683(5.25)	696
	THF	677(4.79)	691		687(5.28)	698
21a	DMSO	687(5.10)	699	22a	691(5.23)	700
	DMF	686(5.22)	702		686(5.08)	705
	THF	688(5.43)	700		696(5.25)	707
	Toluene	697(5.02)	709		698(5.32)	708
	CHCl₃	700(5.23)	708		700(5.16)	710
21b	DMSO	690(5.31)	701	22b	692(5.10)	702
	DMF	690(5.66)	702		686(5.15)	697
	THF	689(5.47)	700		697(5.64)	707
	Toluene	697(5.56)	706		698(5.56)	708
	CHCl₃	701(5.58)	709		701(5.23)	710
21c	DMSO	692(5.40)	698	22c	696(5.56)	706
	DMF	692(5.41)	700		693(5.56)	702

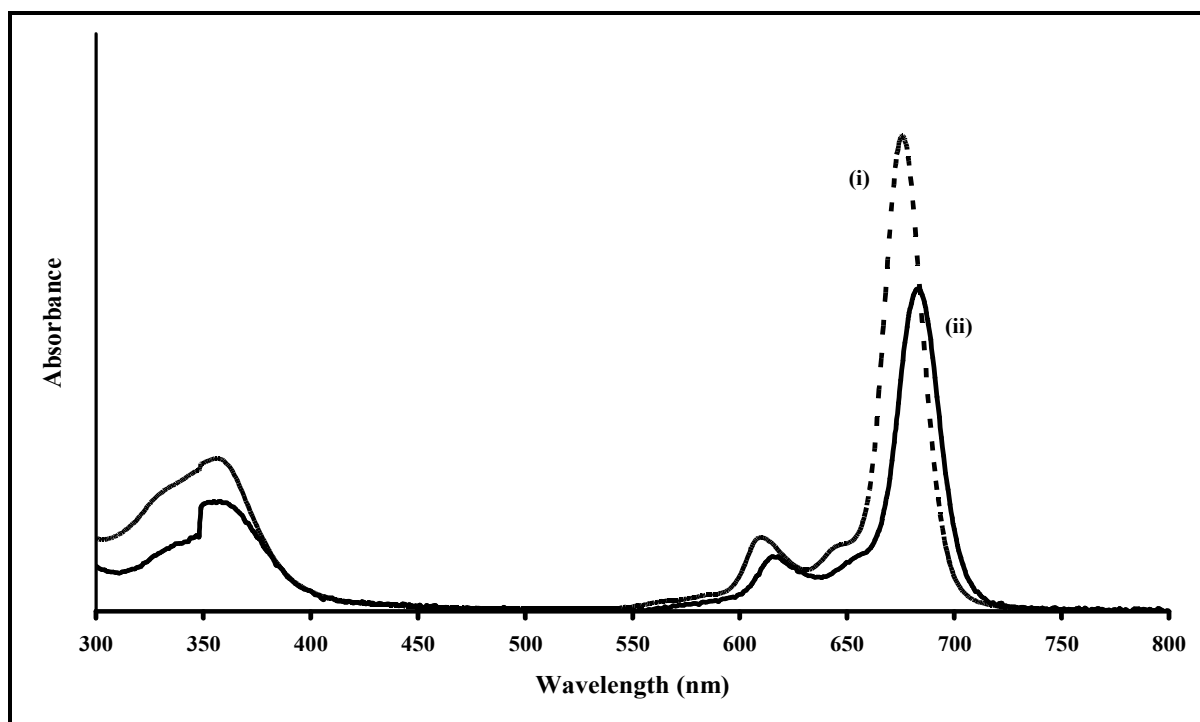
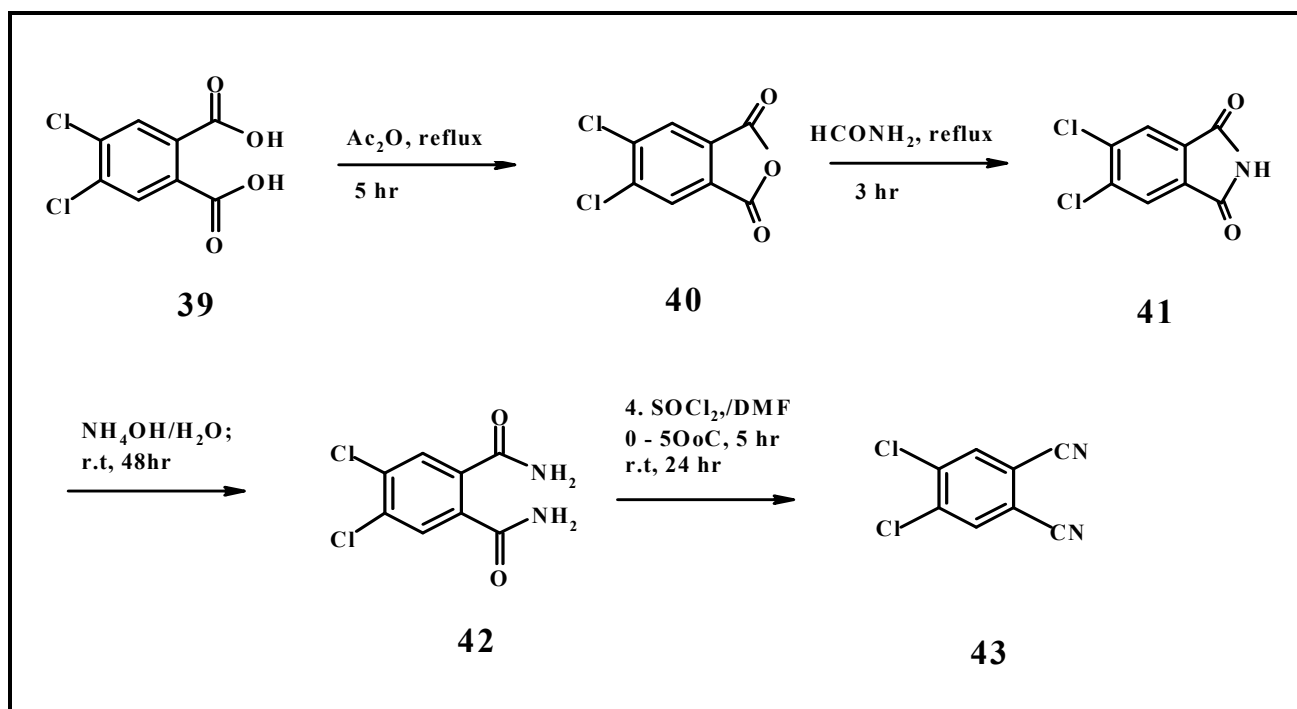


Figure 3.1: Ground state electronic absorption spectra of (i) - (Cl)GaPc (15) and (ii) - (Cl)InPc (16) in DMF. Concentration: $\sim 1.0 \times 10^{-6}$ mol dm⁻³

3.1.2 Octasubstituted gallium and indium phthalocyanines

3.1.2.1 4,5-Dichlorophthalonitriles



Scheme 3.2: Synthetic pathway to 4,5-dichloro-1,2-dicyanobenzene (51).

Scheme 3.2 shows the synthetic pathways followed to achieve the precursor [4,5-dichloro-1,2-dicyanobenzene (**43**)] used to prepare substituted phthalonitriles employed in obtaining substituted phthalocyanines in this work.

4,5-Dichloro-1,2-dicyanobenzene (**43**) was synthesized from the commercially available dichlorophthalic acid (**39**), through the dichlorophthalimide (**41**) and dichlorophthalamide (**42**) to yield the final product (**43**). Good yields that ranged from 65 to 93% were obtained for all the four synthetic procedures enroute to achieving the final product, 4,5-dichloro-1,2-dicyanobenzene (**43**). The purity of the 4,5-dichloro-1,2-dicyanobenzene (**43**) was shown by proton NMR. IR was used to confirm the presence of the characteristic C≡N stretches at 2230 cm⁻¹.

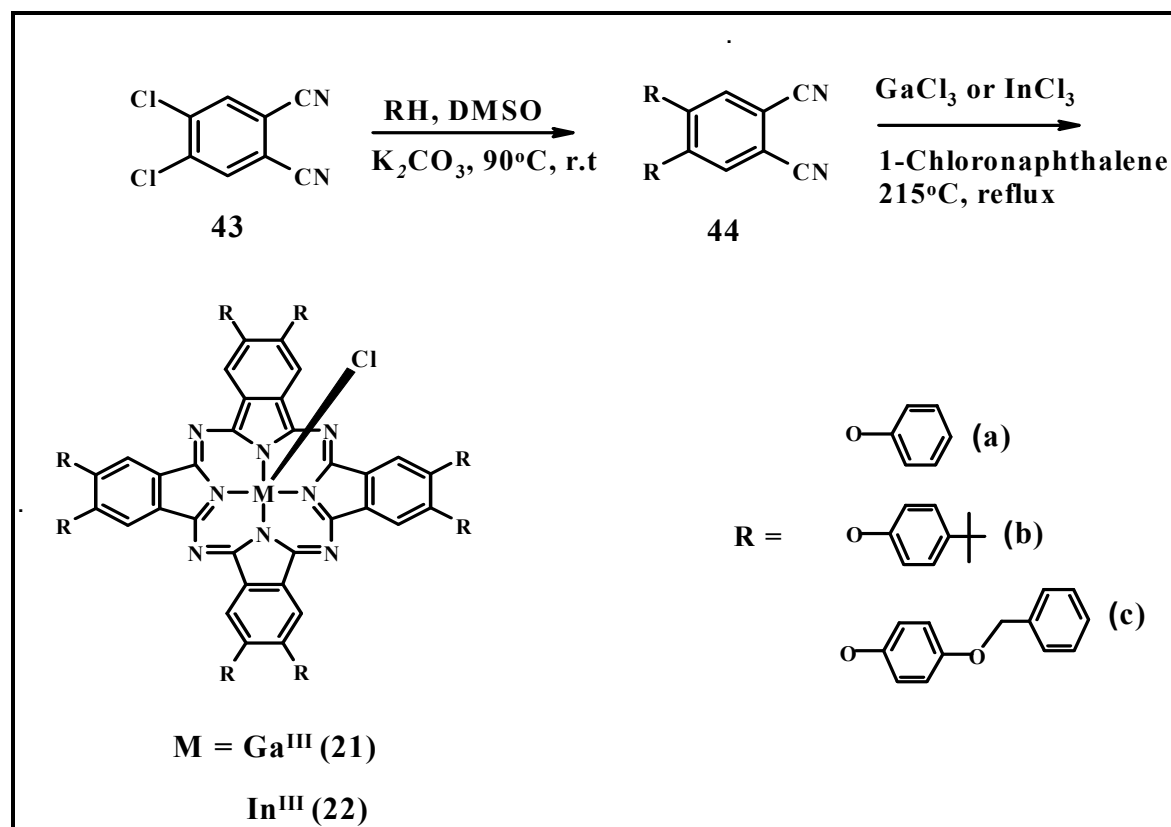
Through the base-catalysed nucleophilic aromatic displacement, disubstituted phthalonitriles (**44a – c**), **Scheme 3.3**, were prepared from the 4,5-dichloro-1,2-dicyanobenzene (**43**). The same route was applied to prepare phenoxy (**44a**), *tert*-butyl phenoxy (**44b**) and 4-(benzyloxy)-phenoxy (**44c**) substituted 1,2-dicyanobenzenes, **Scheme 3.3**. The characteristic C≡N, C-O-C and Ar-H stretches were observed in the ranges 2213 – 2237, 1209 – 1244 and 3040 -3051 cm⁻¹, respectively, for **44a**, **44b**, and **44c**. The appropriate resonances were observed in the proton NMR.

3.1.2.2 Octasubstituted Ga and In phthalocyanine

Octasubstituted phthalocyanines used in this study were synthesized from the appropriate 4,5-disubstituted phthalonitriles.

The syntheses of Ga (**21a – c**) and In (**22a – c**) octasubstituted phthalocyanines was achieved by following the typical cyclotetramerisation of substituted phthalonitriles, where the substituted phthalonitriles (**44a – c**) were reacted with the respective metal salts GaCl₃ and InCl₃ (**Scheme 3.3**) in 1-chloronaphthalene. Since 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 1-chloronaphthalene was used to achieve this purpose. Column and preparative TLC with silica gel were employed to obtain the pure products from the reaction mixtures.

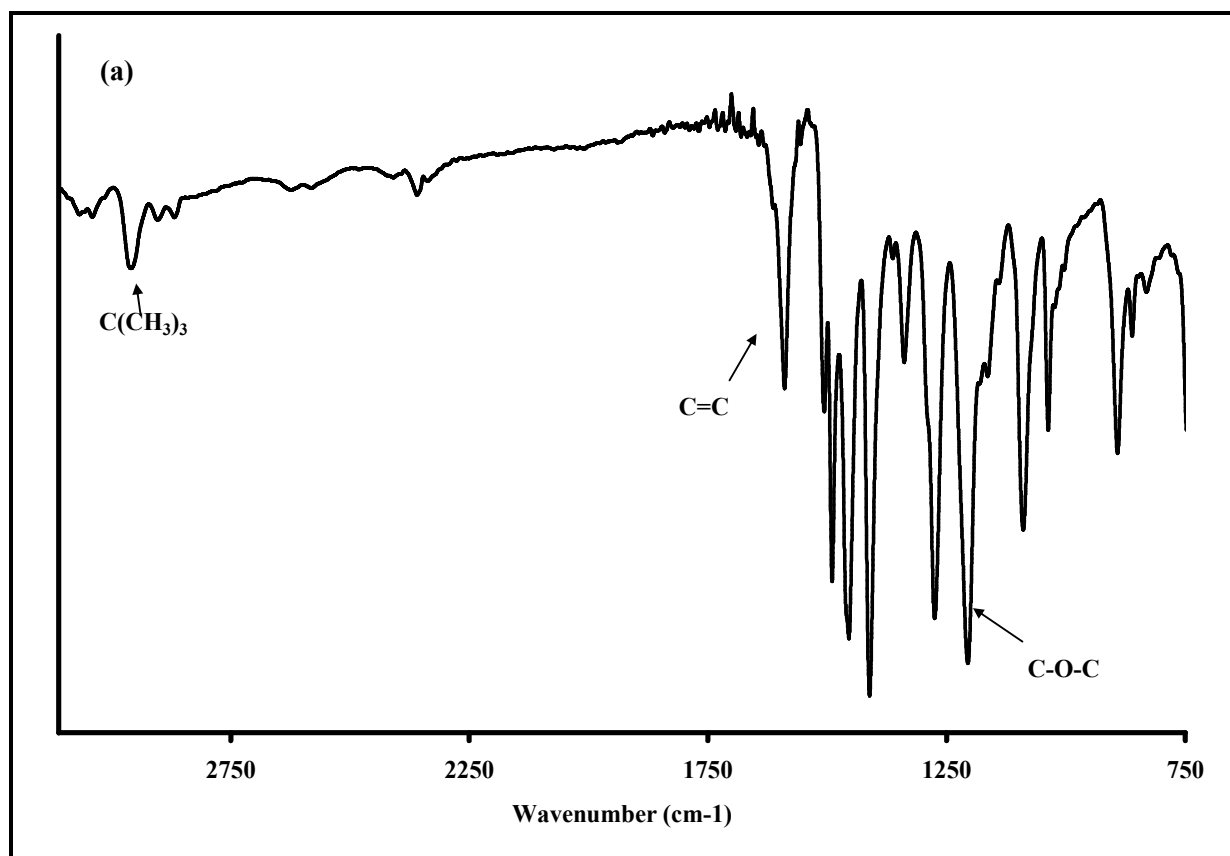
Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of phenoxy, 4-*tert*-butyl phenoxy and 4-(benzyloxy)phenoxy substituents on the ring increased their solubility. These substituted GaPc and InPc complexes {(**21a – c**) and (**22a – c**)} exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, toluene, acetone, DMSO.



Scheme 3.3: Synthetic pathway for Ga and In octasubstituted phthalocyanines.

GaPc and InPc derivatives were characterized by UV-vis, IR and NMR spectroscopies, and elemental analysis. These are consistent with the predicted structures as shown in the experimental section.

After conversion into gallium and indium phthalocyanines, the characteristic $\text{C}\equiv\text{N}$ stretch at 2237, 2213 and 2236 cm^{-1} of 1,2-dicyanobenzenes **44a - c** disappeared, indicating metallophthalocyanine formation. The characteristic vibrations corresponding to ether groups (C-O-C) were observed at 1201, 1205 and 1237 cm^{-1} for **21a - c** phthalocyanine complexes, respectively. Aromatic CH stretches were observed at 3034 to 3058 cm^{-1} . Fig. 3.2a shows the IR spectrum of complex **21b**. Fig. 3.2b shows the MALDI-TOF spectrum



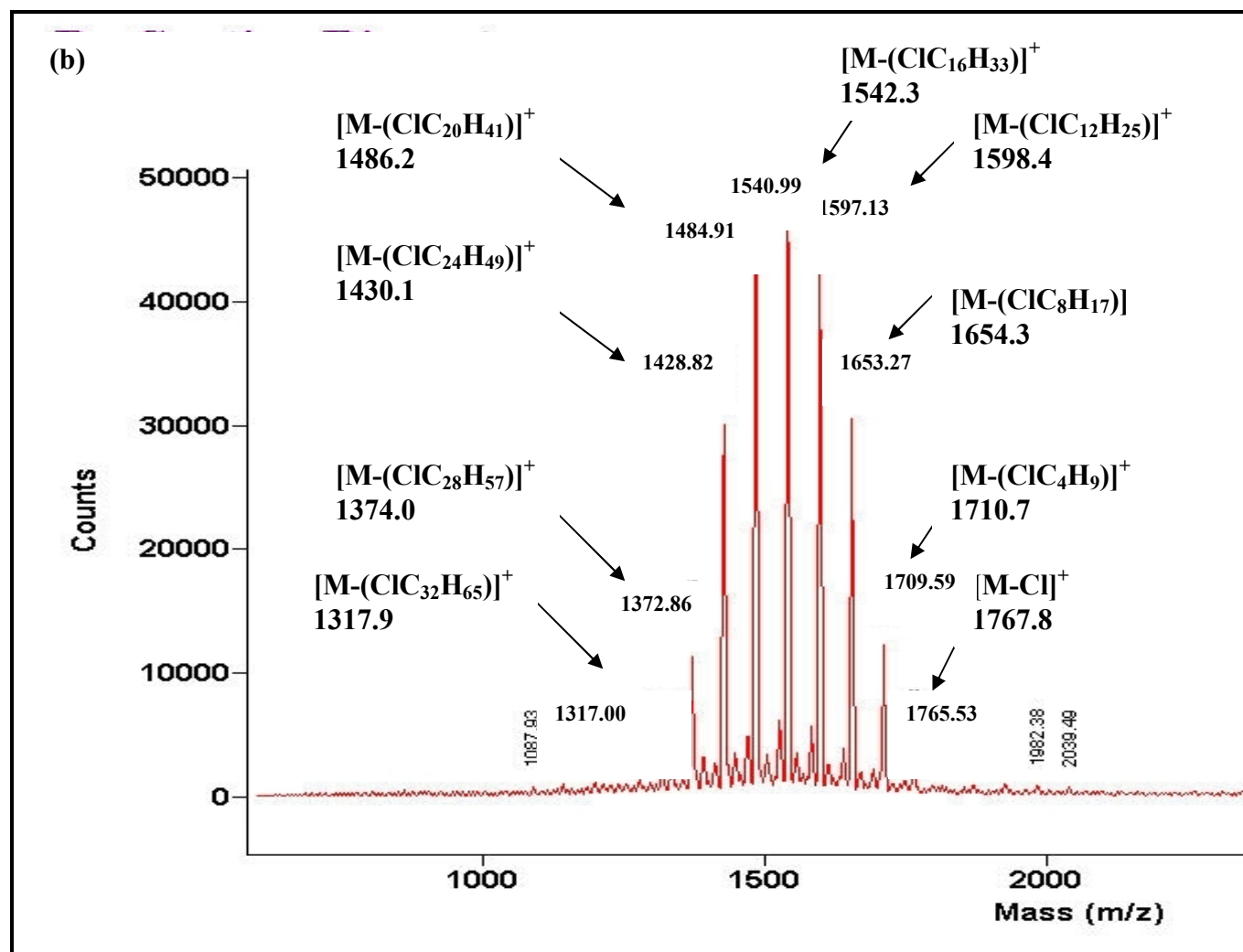


Figure 3.1: (a) is the IR spectrum of complex **21b** and (b) is the MALDI-TOF spectrum of complex **21b**.

The MALDI-TOF spectrum in Fig. 3.2b for complex **21b** shows a successive defragmentation of the *tert*butyl groups from the *tert*butylphenoxy substituents on periphery of the ring, thus confirming the structure of complex **21b**.

The substituted gallium(III) and indium (III) phthalocyanine complexes were found to be pure by 1H NMR (Fig. 3.3) with all the substituents and ring protons observed in their respective regions. The phenoxy substituted complex **21a** showed the resonances belonging to ring protons as a doublet at 8.6 ppm, a triplet at 7.4 ppm, a triplet at 7.3 ppm and a multiplet at 7.2 ppm, integrating for 8, 16, 16, 8 (all together integrated to give 40) protons each, making a total of 48 protons as expected (Fig. 3.3).

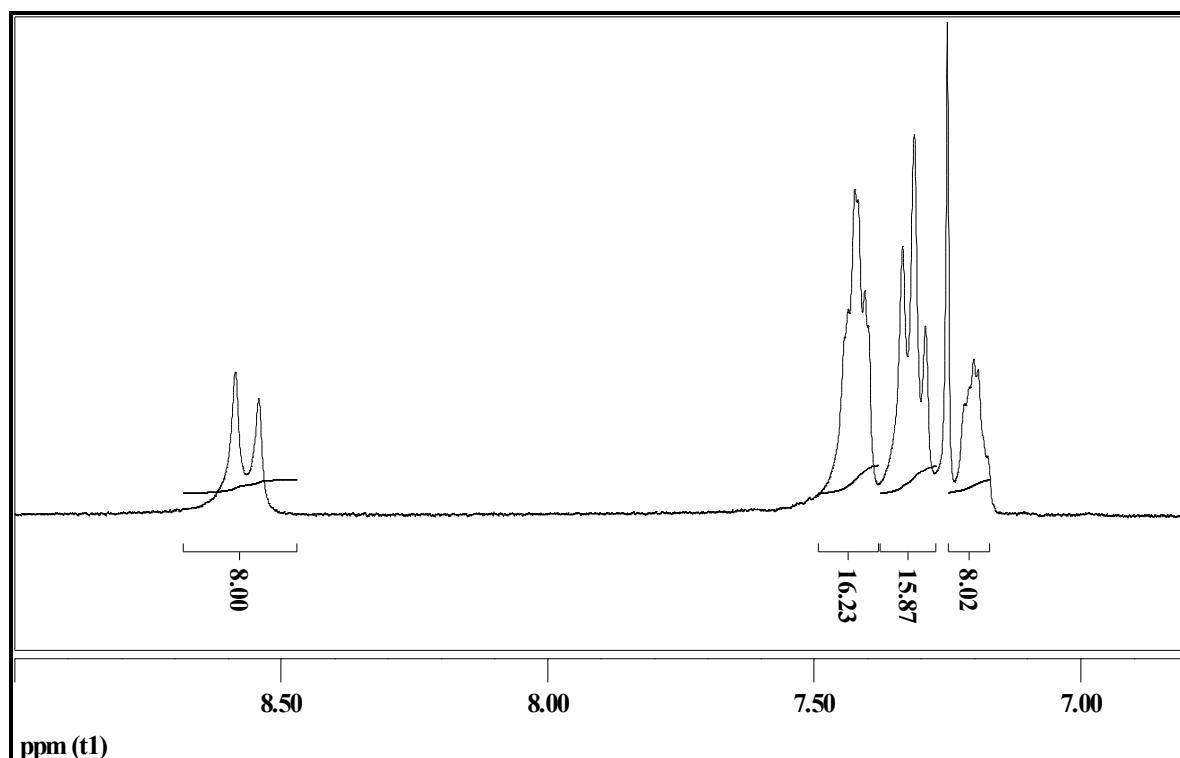


Figure 3.2: ^1H -NMR spectrum of complex **21a** in CDCl_3 .

The *tert*-butylphenoxy substituted complex (**21b**) showed the resonances belonging to ring protons as a singlet at 8.6 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 appeared as multiplets between 1.3 and 1.4 ppm integrating for 72 protons. The benzyloxyphenoxy substituted complex (**21c**) showed resonances belonging to ring protons between 8.62 – 9.16 ppm, giving 8 protons as expected upon integrating. The phenyl protons were observed between 8.09 – 8.41, 7.36 – 7.61, 7.15 – 7.24, amounting to 8, 48 and 16 protons on integrating, thus giving an overall total of 72 protons as expected.

The InPc complexes (**22a – c**) showed similar behaviour to their corresponding GaPc complexes. The phenoxy substituted complex **22a** 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 **22b** 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.

The benzyloxyphenoxy substituted complex (**22c**) showed resonances belonging to ring protons between 8.62 – 9.16 ppm, giving 8 protons as expected upon integrating. The phenyl protons were observed in the ranges 8.09 – 8.41, 7.36 – 7.61, 7.15 – 7.24, totalling to 8, 48 and 16 protons on integrating, thus giving an overall total of 72 protons as expected.

The ground state electronic absorption spectra of the synthesized GaPc and InPc (**21** and **22**) complexes show sharp single Q bands (Figs. 3.4a and b and Table 3.1), which depict the monomeric nature of these complexes in all solvents studied.

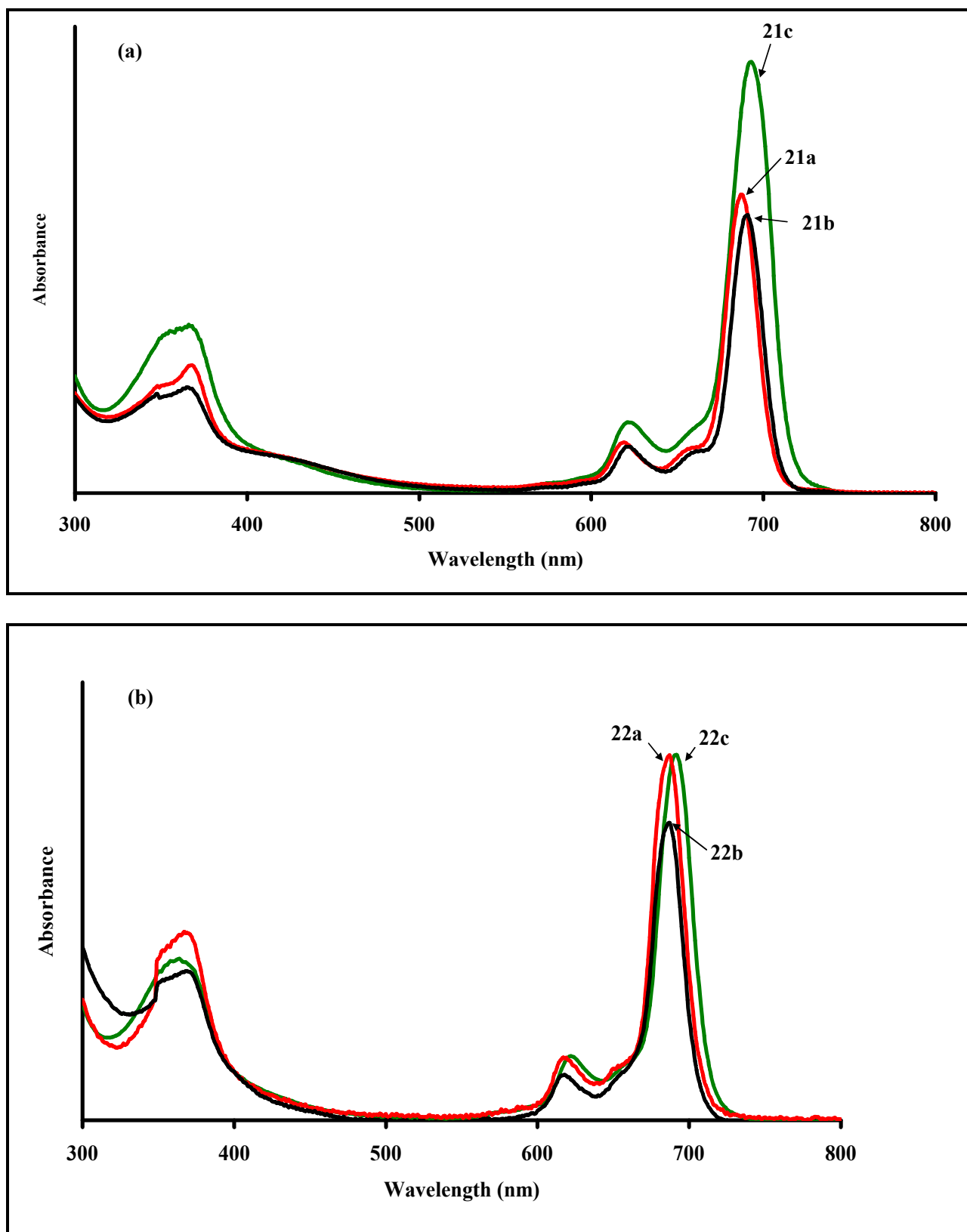


Figure 3.4: Ground state electronic absorption spectra of (a) GaPc and (b) InPc complexes in DMSO. Concentration: $\sim 1.5 \times 10^{-5}$ M.

As stated above, non-aggregated nature of these complexes is not unconnected with their possession of chlorine atoms at axial positions to the central metal atoms. Atoms or groups on MPc axial positions are known to prevent aggregation by restraining the overlap of two MPc units in solution [151]. The positions of the Q bands in complexes **21c** and **22c** are more red-shifted relative to **21a, b** and **22a, b**, respectively in DMSO and DMF. The presence of electron releasing benzyloxyphenoxy substituent on the phthalocyanine ring leads to red-shift of the Q band. For a particular MPc in different solvents, it can be observed that the longest Q absorption wavelengths are obtained in chloroform while the shortest are obtained in DMF (Fig. 3.5, Table 3.1).

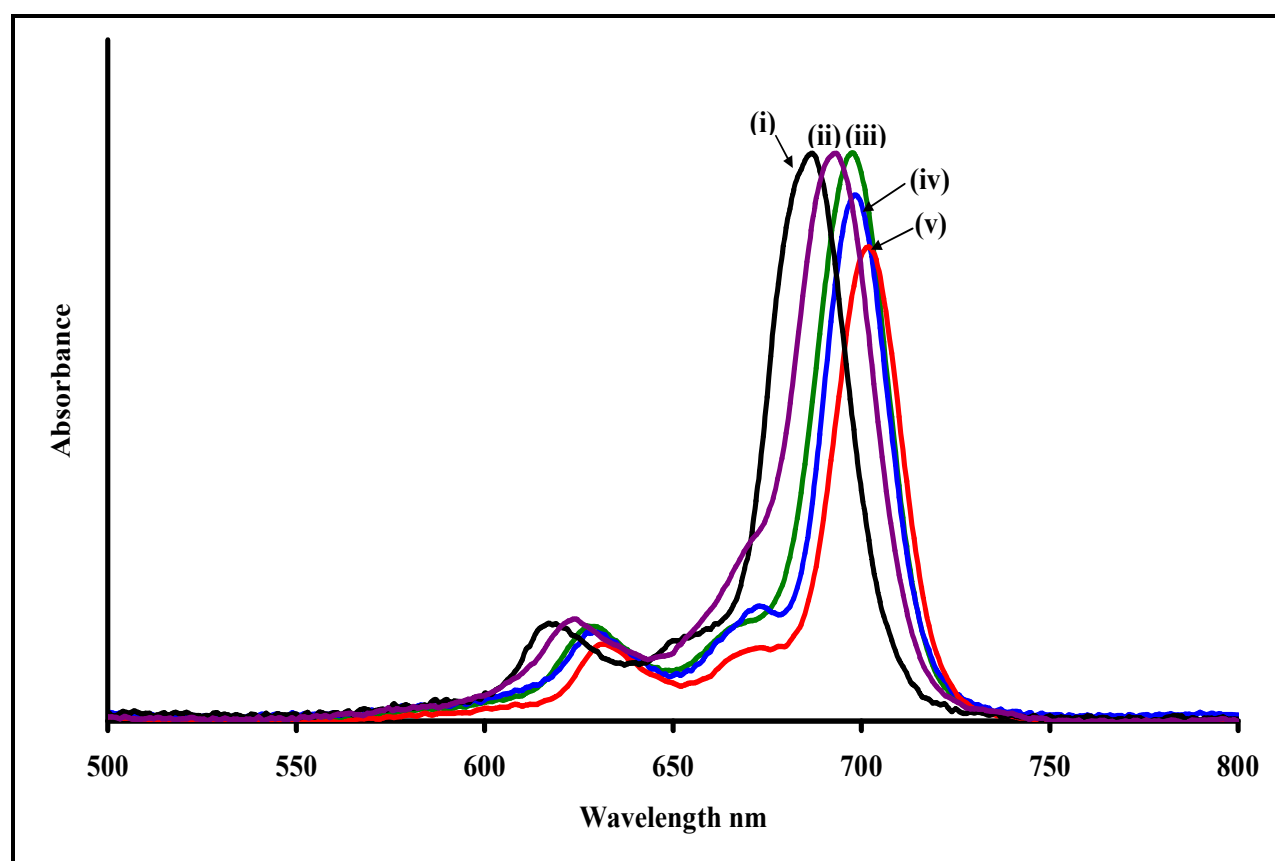


Figure 3.3: Ground state electronic spectra of **22a** in (i) DMF, (ii) DMSO, (iii) THF, (iv) Toluene and (v) CHCl_3 . Concentration: $\sim 1 \times 10^{-5} \text{ mol dm}^{-3}$.

This observation could partly 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 [82], i.e. solvents with smaller refractive indices tend to absorb in the blue region relative to those that have larger refractive indices such as chloroform. In all the solvents studied complexes **21a – c** and **22a – c** showed monomeric behaviour up to $\sim 1 \times 10^{-5} \text{ mol dm}^{-3}$.

For the substituted derivatives, new absorption bands are observed at $\sim 430 \text{ nm}$ in both coordinating (Fig. 3.4) and non-coordinating (Fig. 3.6) solvents. These bands seem to be very prominent in non-coordinating solvents. Since these are observed only for the substituted derivatives, they must be due to charge transfer transitions involving the substituents.

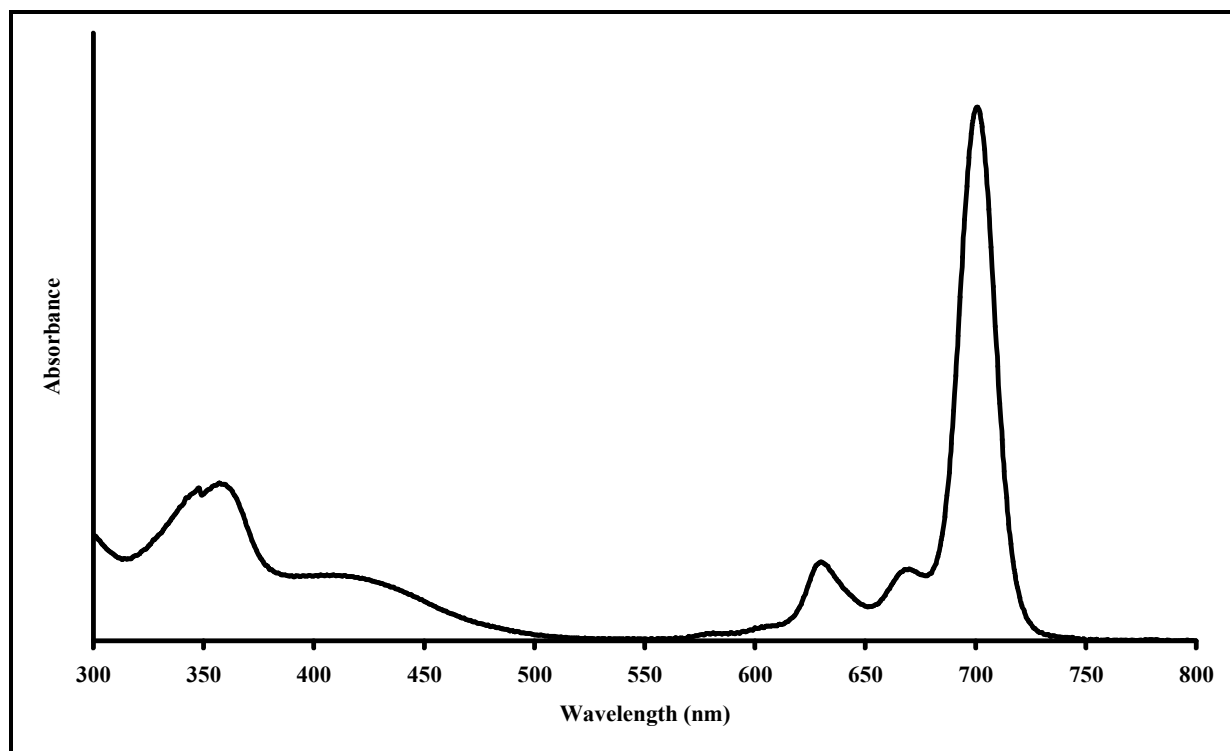


Figure 3.4:Ground state absorption spectrum of 21b in chloroform. Concentration: $1.6 \times 10^{-5} \text{ M}$.

The fluorescence spectral behaviours of the four GaPc derivatives are similar. Fig. 3.7 shows the fluorescence excitation and emission spectra for **21a** in DMSO. The excitation spectra are similar to absorption spectra and both are mirror images of the fluorescence spectra.

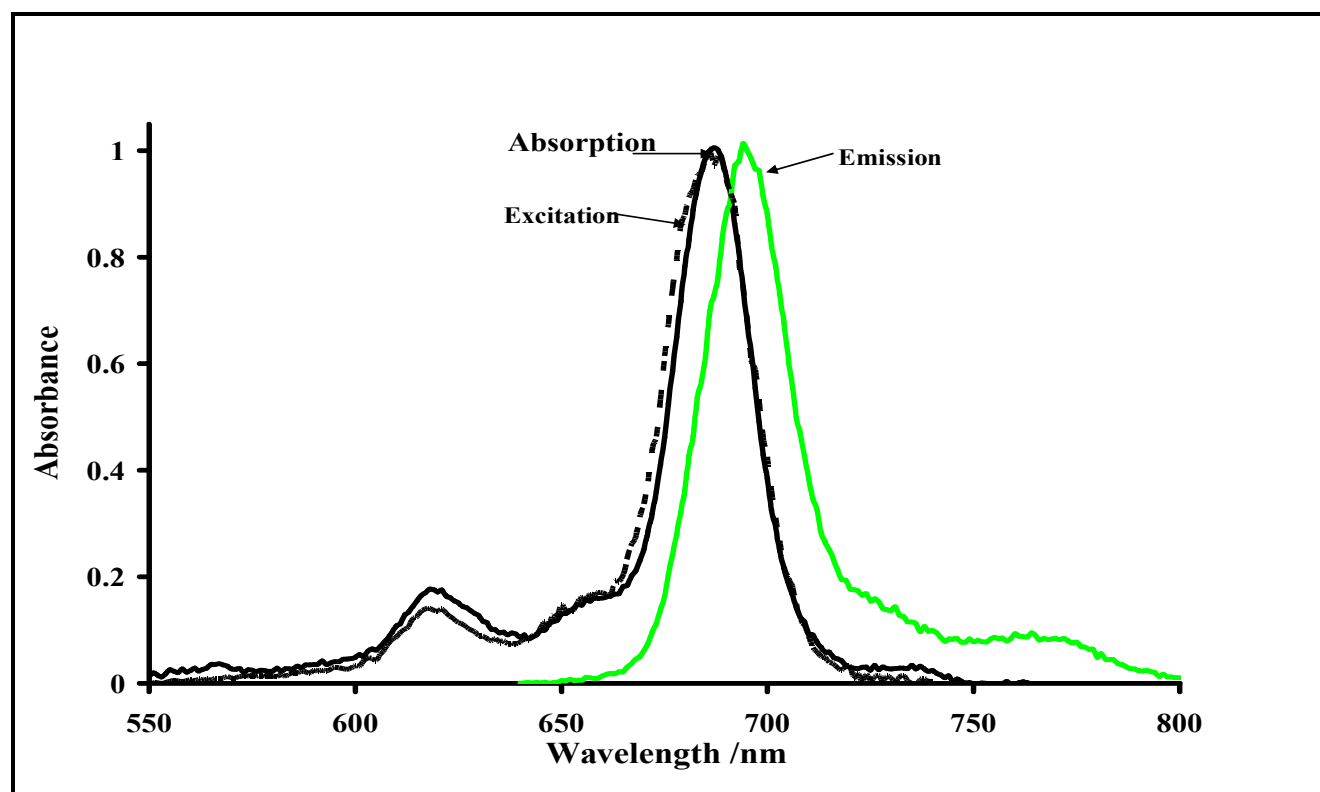


Figure 3.5: Absorption, fluorescence excitation and fluorescence emission spectra of **21a** in DMSO.

The octasubstituted InPc complexes studied in this work showed similar fluorescence behaviour in all the solvents. Fig 3.8. shows the absorbance and fluorescence spectra of **22a** in chloroform. The fluorescence spectra are mirror images of absorption spectra. The small Stokes shifts (Table 3.1) for both GaPc and InPc complexes suggest that there was no structural change between the ground and excited states. However the fluorescence spectra of InPc complexes, shown in Fig. 3.8, is slightly more broadened compared to the absorption spectra.

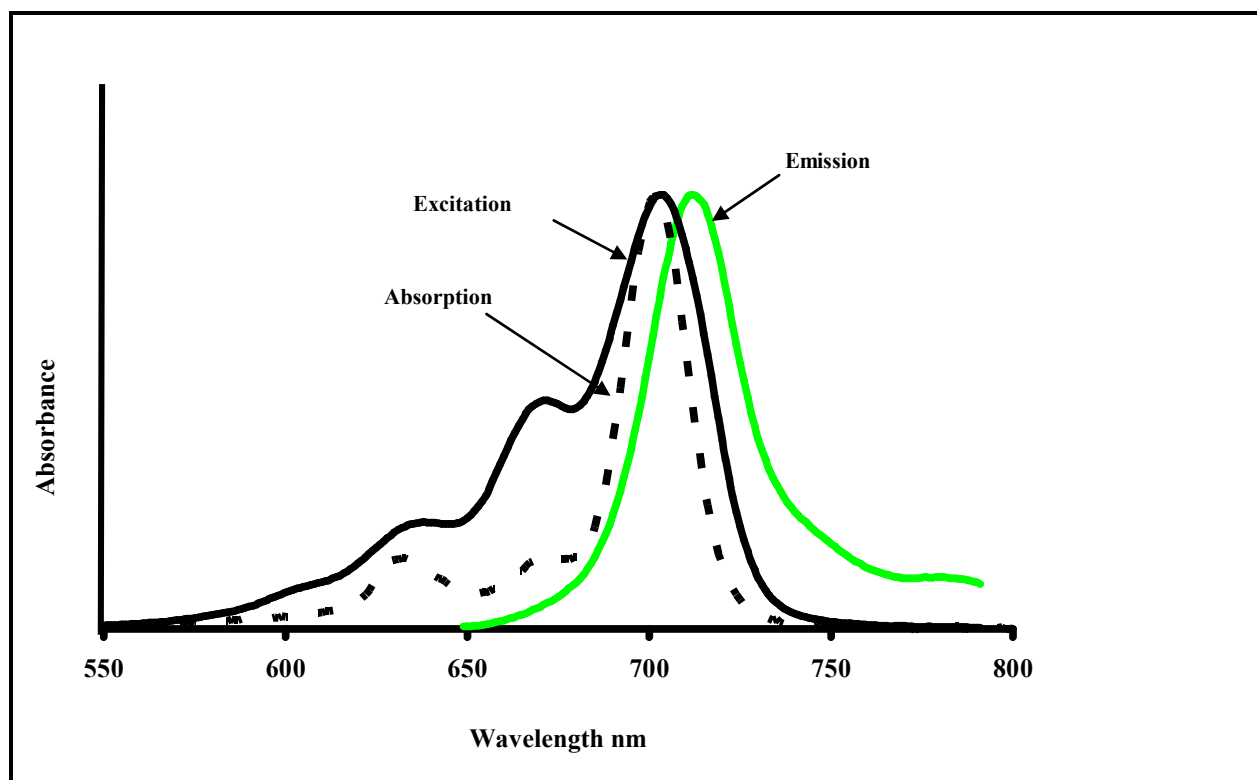


Figure 3.6: Fluorescence emission and absorbance spectra of 22a in CHCl₃.

The excitation spectra are different from absorbance spectra for InPc complexes, (Fig.3.8). The Q bands of all the excitation spectra for InPc complexes suggests that following excitation, there were some changes in the molecule, presumably due to loss of symmetry. This behaviour was not observed in the corresponding GaPc complexes (**21a - c**). 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. For InPc complexes, emission spectra showed a single band while the excitation spectra are split. This behaviour is characteristic of Pc complexes with low symmetry such as unmetallated Pcs [152], which fluoresce with only one main peak allocated as the 0-0 transition of the fluorescence [152]. This observation is therefore similar to that of unmetallated Pcs with a D_{2h} symmetry.

3.1.3 Electrochemistry

3.1.3.1 Voltammetric and spectroelectrochemical studies

Fig. 3.9 shows a typical cyclic voltammogram (CV) and square wave voltammograms (SWV) (inserts) for complex **21a**; recorded at the surface of a glassy carbon electrode in de-aerated DMF.

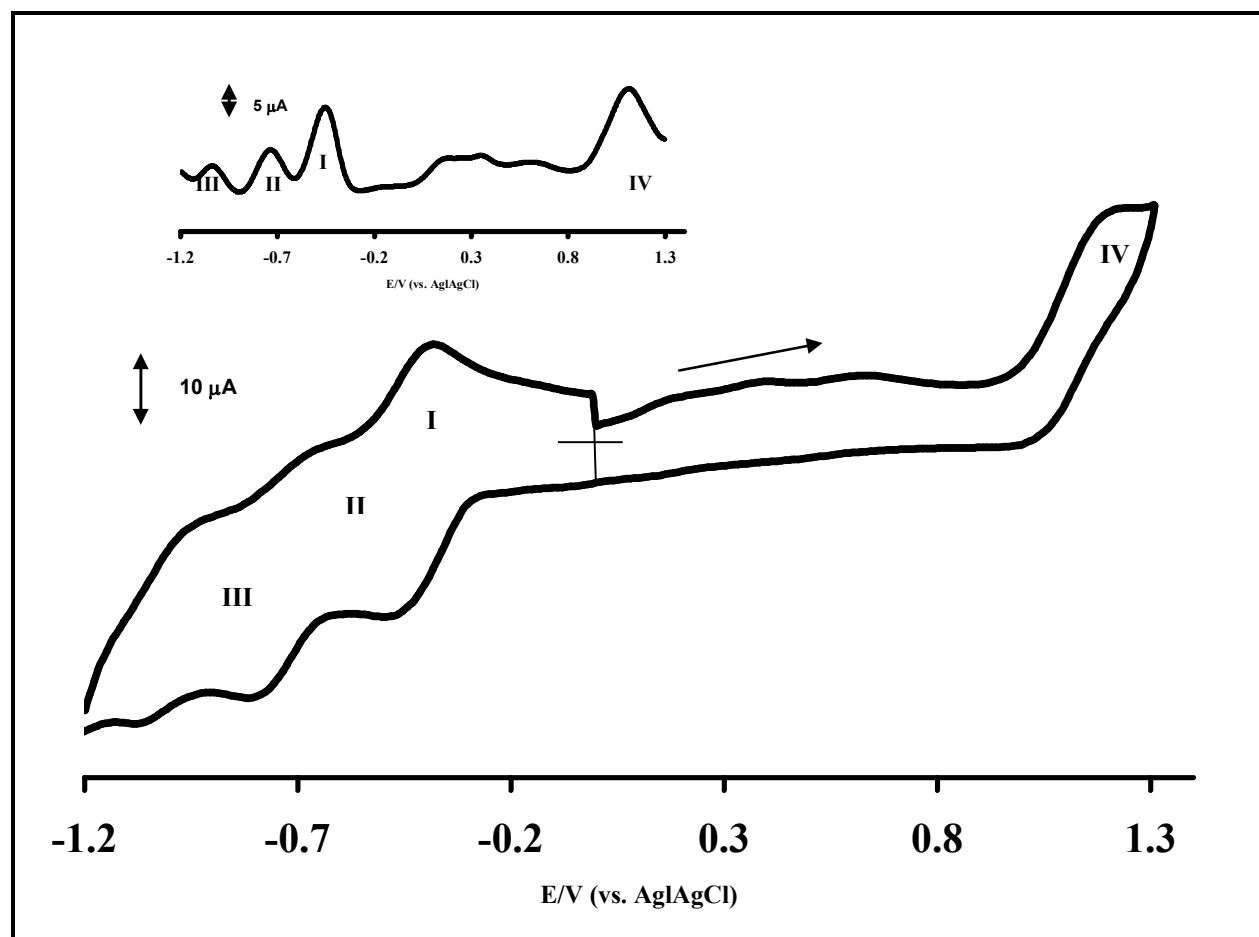


Figure 3.7: CV of **21a** at 100 mV s⁻¹ in DMF containing 0.1 M TBABF₄ electrolyte.

The CVs for all the complexes looked similar, hence only one has been shown in this report. The redox potentials are listed in Table 3.2.

Table 3.2: Redox potentials for Ga and In MPcs in DMF.

MPc	$E_{1/2}$ (V vs Ag AgCl)			
	I	II	III	IV
21a	-0.51	-0.81	-1.09	1.02
21b	-0.48	-0.87		1.10
22a	-0.35	-0.46		0.97
22b	-0.40	-0.67		1.05

All the complexes except for **21a** have two reduction processes and one oxidation peak. Both the oxidation and reduction occur at the ring because Ga^{3+} and In^{3+} metals are redox inactive, therefore the couples observed in this work are assumed to be due to ring based reductions and oxidation. The difference between the anodic and cathodic current for each couple, ΔE , ranged from 90 to 292 mV at the scan rate of 100 mVs^{-1} . These results suggest that the redox processes were quasi-reversible and irreversible, if compared to the ΔE of $\sim 90 \text{ mV}$ for the internal standard ferrocinium/ferrocene. Plots of peak current and square root of different scan rates (Fig. 3.10) gave straight lines for all four complexes (**21a**, **21b**, **22a** and **22b**) implying that the processes are diffusion controlled.

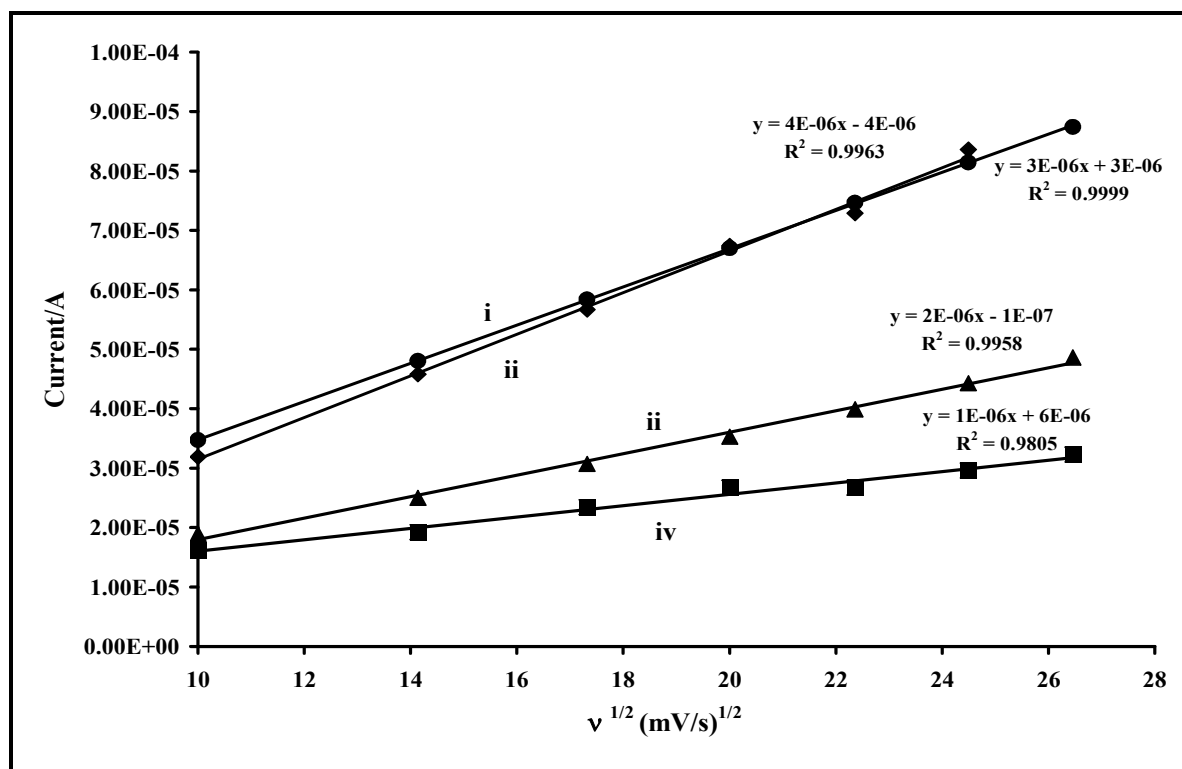


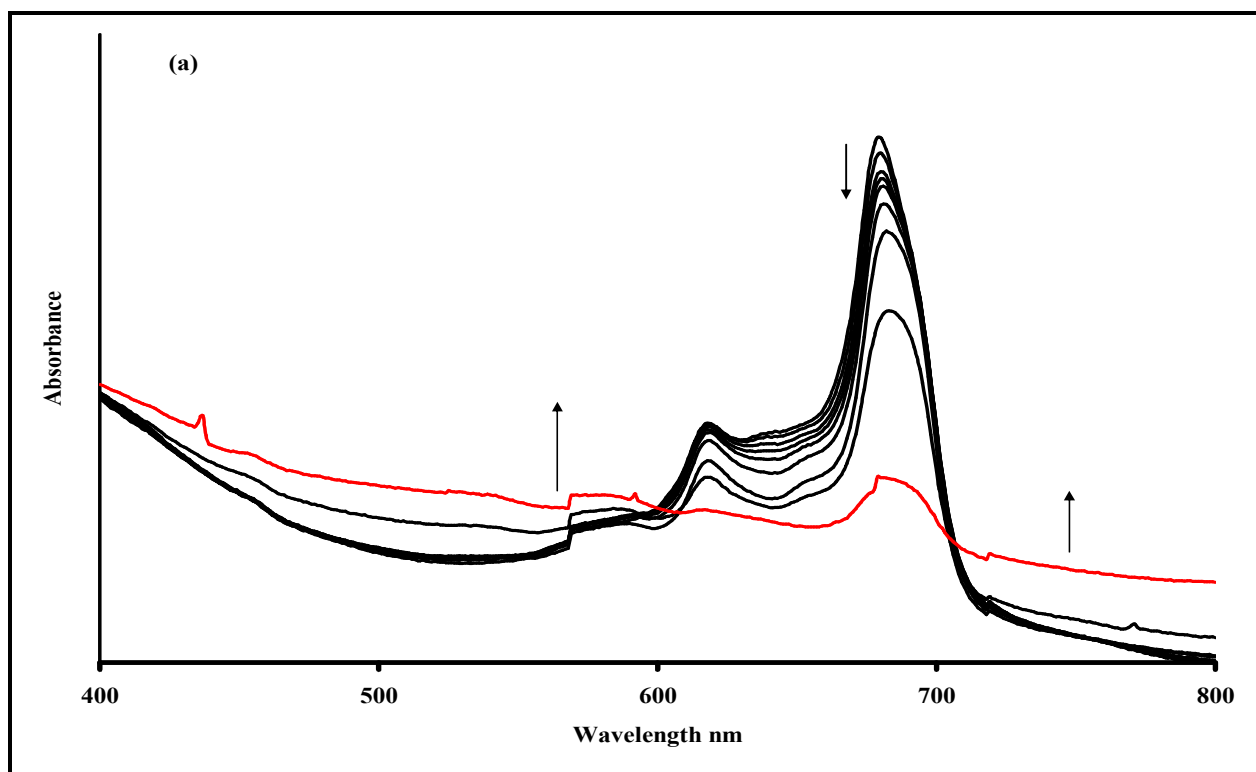
Figure 3.8: Plots of current vs, square root of scan rate; i – 21a, ii – 21b, iii-22a and iv – 22b.

To confirm that the redox processes are taking place at the phthalocyanine rings in this study, spectroelectrochemistry studies were carried out.

Spectroelectrochemical experiments were carried in an optically transparent thin-layer (OTTLE) cell. Changes in the spectra in Figs. 3.11 and 3.12 were observed on application of potential at the respective processes on the CV.

Spectral changes in Fig 3.11a are typical [115] of ring based reduction consisting of a decrease in Q band and formation of new weak bands between 500 and 600 nm This suggests that the Pc ring is being reduced $Ga^{3+}Pc^{2-}/Ga^{3+}Pc^{3-}$ (Fig. 3.11a and 3.12) and oxidized to $Ga^{3+}Pc^{1-}/Ga^{3+}Pc^{2-}$ in Fig. 3.11b.

Similar spectral changes were observed for complex **21b**, Fig. 3.12 on reduction. A decrease of the Q band at 690 nm and the emergence of new peaks at ~ 580 nm were observed, indicating that this is a ring process [146] hence the formation of $\text{Ga}^{3+}\text{Pc}^{2-}/\text{Ga}^{3+}\text{Pc}^{3-}$.



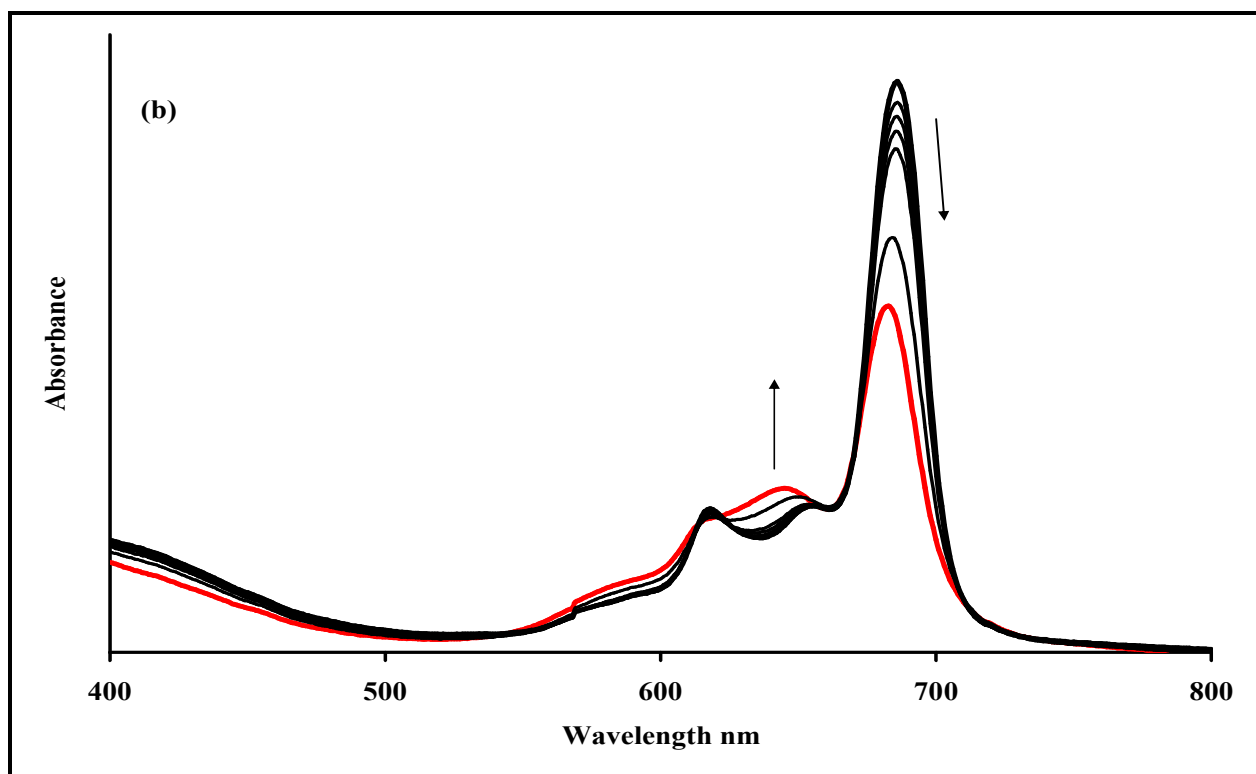


Figure 3.9: UV spectral changes observed for 21a during controlled electrolysis in DMF applied at (a) -1.20 V and (b) 1.30 V.

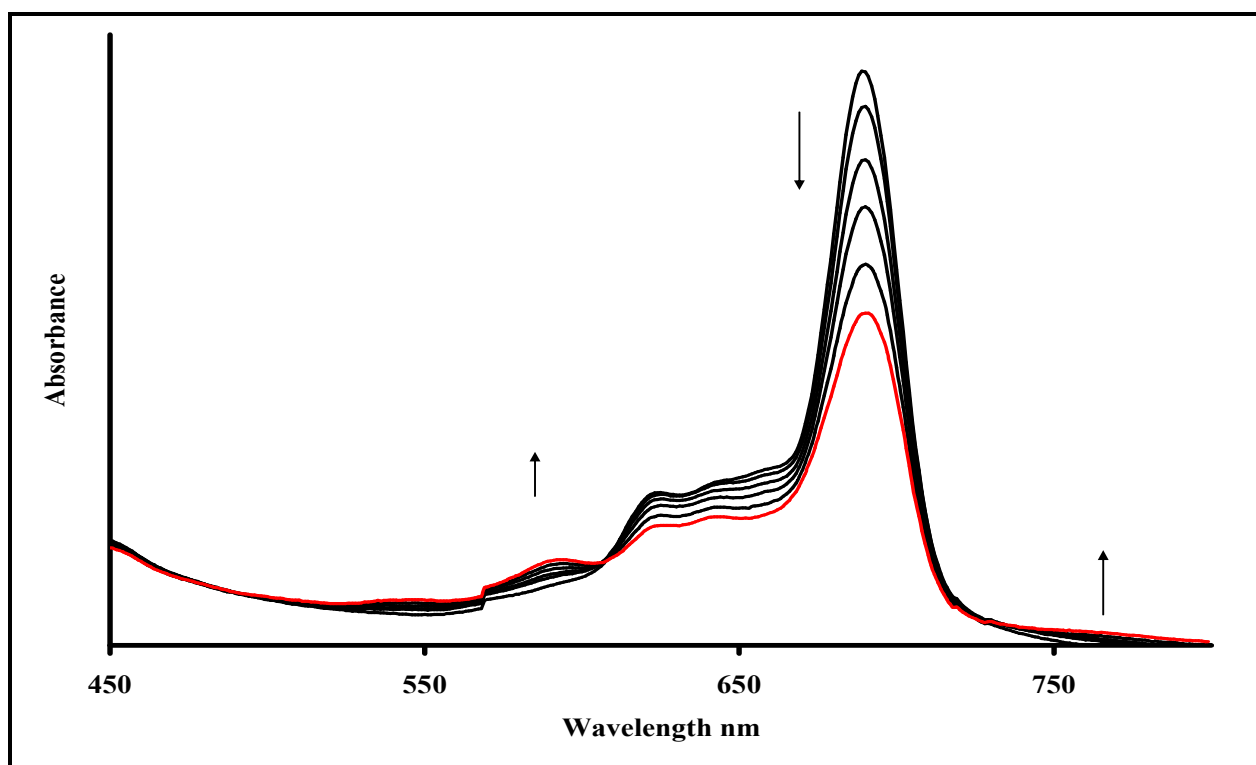


Figure 3.10: UV spectral changes observed for 21b during controlled electrolysis in DMF applied at -0.60 V.

3.2 PHOTOCHEMICAL, PHOTOPHYSICAL AND PHOTOCTALYTIC PROPERTIES

In this section, a detailed photochemical and photophysical study of the synthesized octasubstituted gallium and indium phthalocyanines is presented. Their photocatalytic competence towards the oxidation of 1-hexene to give industrially useful products is also presented.

3.2.1 Photochemical properties

3.2.1.1 Singlet Oxygen quantum yields

Fig. 3.13 shows the decay of DPBF (a singlet oxygen quencher) where there is no significant decrease in the Q band of the MPc for a given period of time. The decrease of DPBF was monitored at ~ 417 nm. The rate of decay of DPBF is directly related to the production of singlet oxygen species.

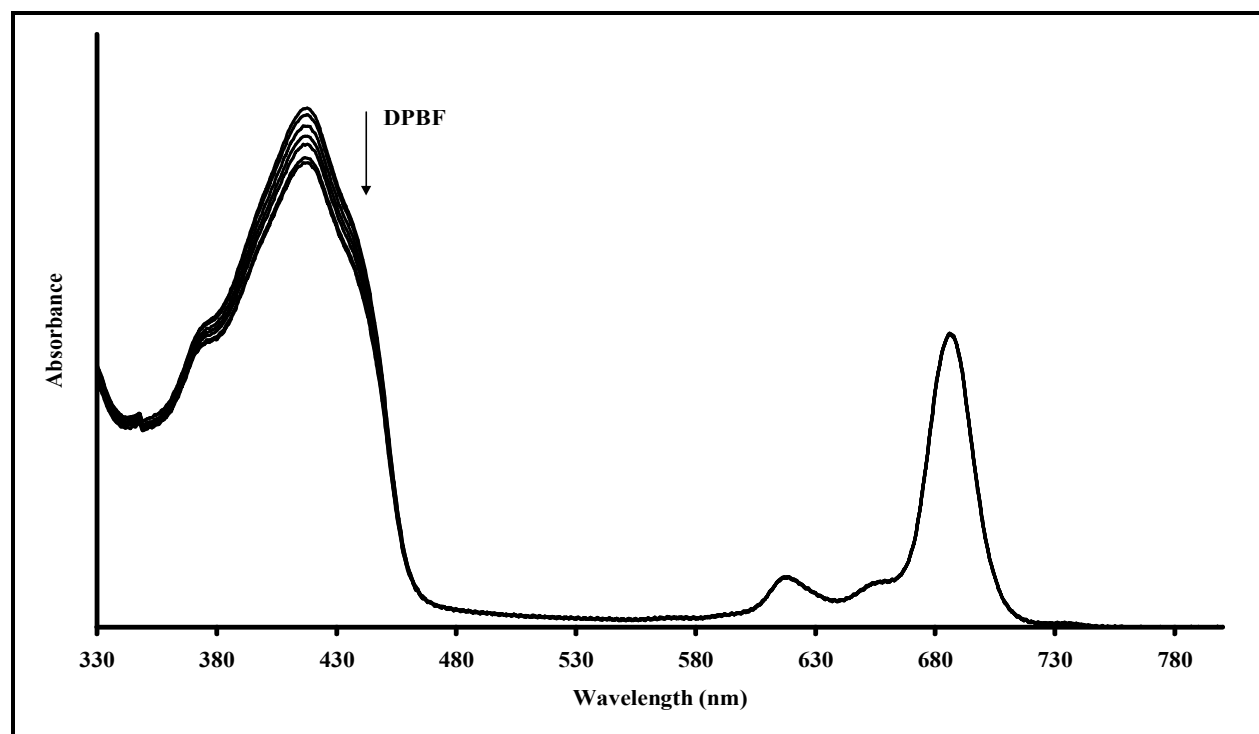


Figure 3.11: Photodegradation of DPBF in the presence of complex 21a in DMSO. [21a] = 4.8×10^{-6} M and [DPBF] = 2.5×10^{-5} M.

Singlet oxygen is formed via interaction (energy transfer) between the triplet state of a photosensitizer and ground state molecular (triplet) oxygen. As a result, the efficiency of singlet oxygen generation (quantified as singlet oxygen quantum yield, Φ_{Δ}) should depend on (i) the triplet state quantum yield, (ii) triplet state lifetime, (iii) efficiency of energy transfer, which depends on the energy of the triplet state, among other factors. Tables 3.3 and 3.4 list the Φ_{Δ} values for GaPc and InPc derivatives, respectively. The introduction of ring substituents increased Φ_{Δ} values, comparing the unsubstituted complexes **15** and **16** with corresponding substituted complexes **21a – c** (Table 3.3) and **22a – c** (Table 3.4), in DMSO. However, Φ_{Δ} values decreased in DMF for InPc derivatives (**22a – b**) when compared to complex **16**. For GaPc derivatives there was an increase in Φ_{Δ} values on substituent introduction comparing all the solvents. Solvent effects on Φ_{Δ} values are subtle for gallium complexes, as seen in Table 3.3. The values are somewhat smaller in DMSO than in DMF and toluene, Table 3.3. A different behaviour was observed for InPc complexes. Generally, higher Φ_{Δ} values were obtained for InPc complexes (**22a – c**) compared to corresponding GaPc derivatives (**21a – c**) in the same solvents, except for toluene. This is attributed to the fact that In is a larger metal than Ga and so it enhances intersystem crossing consequently resulting higher Φ_{Δ} values.

The largest Φ_{Δ} values of 0.79 and 0.78 were obtained, respectively, for **22a** and **22c** in DMSO.

Table 3.3: Photochemical parameters of GaPc derivatives in various solvents.

Solvent	MPc	Φ_{Δ}	$\Phi_{pd}/10^5$
DMSO	15	0.41	1.84
	21a	0.53	1.23
	21b	0.56	1.77
	21c	^c 0.51	^c 0.50
DMF	15	0.50	1.96
	21a	0.66	0.42
	21b	0.74	1.52
	21c	0.59	0.22
Toluene	21a	0.68	2.91
	21b	0.65	2.84
^a THF	15	-	1.49
	21a	-	3.44
	21b	-	3.93
^{a,b} CHCl ₃	21a	-	5.89
	21b	-	4.66

^a Values not obtained in THF and CHCl₃ due to lack of reference standards. ^b Complex **15** is not soluble in CHCl₃. ^c Values were from literature, Ref 108.

Table 3.4: Photochemical parameters of InPc derivatives in various solvents.

Solvent	MPc	Φ_{Δ}	$\Phi_{pd}/10^5$
DMSO	^b 16	0.61	9.90
	22a	0.79	1.39
	22b	0.72	2.35
	22c	^c 0.78	0.55
DMF	16	0.70	1.05
	22a	0.60	5.64
	22b	0.50	4.83
	22c	0.62	1.26
Toluene	22a	0.31	2.75
	22b	0.30	3.19
^a THF	^b 16	-	1.15
	22a	-	0.82
	22b	-	1.87
^a CHCl ₃	22a	-	5.96
	22b	-	6.09

^a Values not obtained in THF and CHCl₃ due to lack of reference standards. ^b Complex **16** is not soluble in CHCl₃ and toluene. ^cValues were from literature, Ref 108

3.2.1.2 Photodegradation quantum yield

The photodegradation studies for the GaPc and InPc complexes were carried out in different solvents (Table 3.3 and 3.4). This was achieved by photolysing in the region of the Q band for a certain period of time. UV/Vis spectroscopy was used to monitor

the photodegradation process which is indicated by the reduction in the Q band intensity as shown in Fig. 3.14.

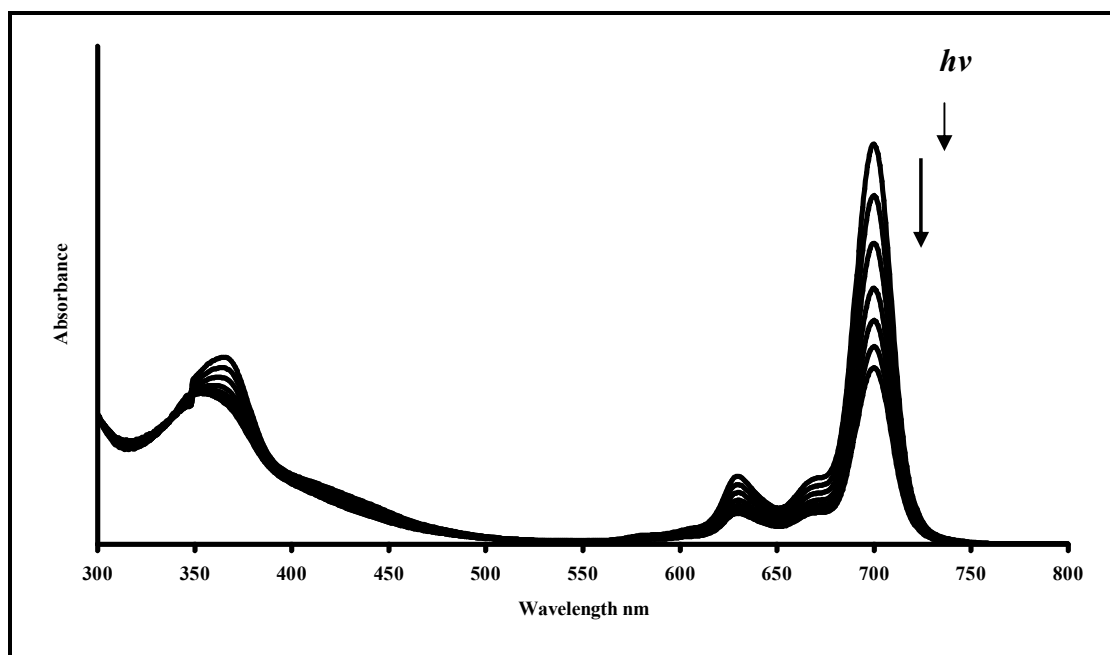


Figure 3.12: Photodegradation spectrum of complex 22a in DCM.

Photodegradation is brought about by the oxidative attack on the MPc excited triplet state by singlet oxygen [87]. The ability of singlet oxygen to react with macrocyclic metal complexes is well documented [87,153]. Singlet oxygen reacts with tetraazaporphyrin derivatives in a Diels-Alder [4+2]-cycloaddition, with the MPc ring acting as a diene and singlet oxygen as the dienophile. For MPcs, phthalimide was found to be the photo-oxidation product [40] (**Scheme 1.8**). The excited singlet state is deemed not to be a target for singlet oxygen because of its short lifetime ($\sim 10^{-9}$ s), which considerably reduces the state's probability of participating in photochemical reactions; hence the excited triplet state is being considered to be the main target for singlet oxygen. The interaction of the excited triplet state with singlet oxygen can be represented by Equation 3.1:



Therefore, the rate of photodegradation, according to the law of mass action is:

$$R = k_{pd} [^3\text{MPc}^*] [^1\Delta_g] \quad (3.2)$$

where R is the rate of photodegradation; k_{pd} , the photodegradation rate constant (a bimolecular rate constant); $[^3\text{MPc}^*]$, the concentration of the MPc excited triplet state; and $[^1\Delta_g]$, the concentration of singlet oxygen. Therefore from Equation 3.2 it could be inferred that the rate of photodegradation is directly proportional to the triplet quantum yield as well as singlet oxygen quantum yield. However in this study, there is no clear correlation between Φ_{pd} values and those of Φ_T or Φ_Δ , for the complexes. Photodegradation, Φ_{pd} values for benzyloxyphenoxy InPc and GaPc substituted complexes (**21c** and **22c**) are lower in DMSO and DMF, compared to corresponding **21a, b** or **22a, b**. Φ_{pd} values for **21a** and **21b** are lower in DMSO and DMF (coordinating and highly solvating) than in non-coordinating solvents like toluene and chloroform (Table 3.3) which implies that these complexes are more photostable in coordinating solvents than in non-coordinating solvents. This observation could be explained in terms of solvent interaction with the MPc central metal to form a complex [154]. Solvent coordination to the metal centre partly shields the MPc molecule against interaction with singlet oxygen, leading to a decrease in the rate of photodegradation.

The Φ_{pd} values presented in this work fall within the reported [155] stability range ($\sim \times 10^{-5}$) for phthalocyanines.

3.2.2 Photophysical processes

3.2.2.1 Fluorescence quantum yields

Fluorescence quantum yield (Φ_F) is the fraction of molecules in the excited singlet state that are deactivated radiatively. Factors like temperature, molecular structure and solvent parameters (polarity, viscosity, refractive index and the presence of heavy atoms in the solvent molecule) are widely known to influence the values of Φ_F . Table 3.5 shows that Φ_F values do not vary much among the four gallium Pcs studied, except for complex **21c** in DMSO. The Φ_F values for **15**, **21a** and **21b** are 0.21, 0.19 and 0.22, respectively in DMSO. These values are similar (within experimental error limits) hence it is concluded that the substituent effects on Φ_F values is not significant among complexes **15**, **21a** and **21b**. Considering solvent effects on Φ_F values, chloroform gave the lowest values for GaPc derivatives, while the highest values were obtained in DMSO, except for **21c**. The low values in chloroform could be attributed to the presence of heavy atoms (chlorine) in chloroform, which could induce spin-orbit coupling, and consequently reduce the number of fluorescing molecules. On the other hand, higher Φ_F values in DMSO may be ascribed to the higher viscosity of this solvent than any of the other solvents under this study. The relatively low Φ_F values in chloroform could also be partly due to the low viscosity of chloroform. Intramolecular rotation can be inhibited if the molecule is dissolved in a fluid with low molecular free volume. Free volume is related to the fluid's viscosity [156]. Therefore, the fluorescence quantum yield is related to the viscosity (η) of the solvent. The Förster-Hoffmann equation (Equation 3.3, [157]) shows that increased viscosity results in increased Φ_F value.

$$\text{Log } \Phi_F = C + x\text{Log}\eta \quad (3.3)$$

where x is a molecule-dependent constant and C is a temperature-dependent constant. Again, the relatively high Φ_F values in DMSO could to some extent be attributed to solvation by the solvent. Solvation by DMSO makes the fluorescing MPc more rigid and therefore more fluorescent. The coordinating strength of a solvent is a function of its donor ability. DMSO has higher donor ability (1.24) than DMF (0.72) [158], which in turn is more donating than THF and toluene. This partly explains why the MPcs are more fluorescent in DMSO than in the other solvents.

Table 3.6 shows Φ_F values of InPc derivatives studied in this work. The differences of Φ_F values among the InPc derivatives is not significant, for example in DMF, Φ_F values for **16**, **22a**, **22b** and **22c** are 0.017, 0.018, 0.022 and 0.013, respectively. The Φ_F values for these InPc derivatives are low relative to their corresponding gallium counterparts (**15**, **21a – c**), which ranged from 0.053 to 0.22. 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, see discussion below.

Chloroform, unexpectedly, yielded the highest Φ_F values of 0.056 and 0.059 for **22a** and **22b**, respectively. Because chloroform contains a heavy Cl atom which promotes intersystem crossing, lower Φ_F values were expected, as was observed for GaPc derivatives above. This could be proof that it is not only the heavy atom effect that affects Φ_F values. Φ_F values in THF showed interesting behaviour in that the unsubstituted InPc ($\Phi_F = 0.076$) yielded the largest Φ_F value. High values of Φ_F in THF have been reported before [83].

Table 3.5: Photophysical and photochemical parameters of GaPc derivatives in various solvents.

Solvent	MPc	Φ_F	$^a\Phi_T$	$^a\Phi_{IC}$	τ_T	$^bS_\Delta$	Φ_Δ
DMSO	15	0.21	0.69	0.10	200	0.59	0.41
	21a	0.19	0.66	0.15	370	0.80	0.53
	21b	0.22	0.67	0.11	290	0.84	0.56
	21c	^d 0.13	0.65	^d 0.13	^d 200	0.78	0.51
DMF	15	0.12	0.78	0.10	10	0.64	0.50
	21a	0.19	0.79	0.02	20	0.84	0.66
	21b	0.15	0.74	0.11	76	1.00	0.74
	21c	0.053	0.58	0.37	20	1.02	0.59
Toluene	21a	0.14	0.65	0.21	79	1.04	0.68
	21b	0.17	0.75	0.08	10	0.87	0.65
^a THF	15	0.19	-	-	2.1	-	-
	21a	0.14	-	-	3.4	-	-
	21b	0.18	-	-	4.4	-	-
^c CHCl ₃	21a	0.12	-	-	2.9	-	-
	21b	0.12	-	-	3.4	-	-

^a Values not obtained in THF and CHCl₃ due to lack of reference standards. ^b $S_\Delta = \Phi_\Delta/\Phi_T$. ^c

15 is not soluble in CHCl₃. ^d Values were from literature, Ref 108

Table 3.6: Photophysical and photochemical parameters of InPc derivatives in various solvents.

Solvent	MPc	Φ_F	$^a\Phi_T$	$^a\Phi_{IC}$	τ_T (μs)	bS_A	Φ_A
DMSO	^d 16	0.018	0.91	0.01	50	0.67	0.61
	22a	0.025	0.84	0.14	60	0.94	0.79
	22b	0.020	0.70	0.28	50	1.03	0.72
	22c	0.013	0.88	0.12	50	0.63	^d 0.78
DMF	16	0.017	0.83	0.15	10	0.94	0.70
	22a	0.018	0.76	0.22	20	0.79	0.60
	22b	0.022	0.61	0.37	9.5	0.82	0.50
	22c	0.013	0.65	0.34	20	0.95	0.62
^c Toluene	22a	0.023	0.55	0.43	20	0.56	0.31
	22b	0.021	0.41	0.60	10	0.71	0.30
^a THF	16	0.076	-	-	8.8	-	-
	22a	0.020	-	-	7.8	-	-
	22b	0.020	-	-	30	-	-
^c CHCl ₃	22a	0.056	-	-	8.1	-	-
	22b	0.059	-	-	7.8	-	-

^a Values not obtained in THF and CHCl₃ due to lack of reference standards. ^b $S_A = \Phi_A/\Phi_T$.

^c complex **16** is not soluble in CHCl₃. ^d Value was from literature, Ref 108

3.2.2.2 Triplet quantum yield and lifetimes

Fig. 3.15 shows the triplet decay curve for **21a** in DMSO. Triplet quantum yield (Φ_T) is a measure of the fraction of absorbing molecules that undergo intersystem crossing to the meta-stable triplet excited state. Since intersystem crossing and fluorescence are two competing deactivating processes at the excited singlet state, their values for a particular species are expected to be complementary. As discussed above, Φ_F values do not vary much with the introduction of phenoxy, *t*-butylphenoxy and benzyloxyphenoxy substituents onto the (Cl)GaPc ring. This trend is also manifested in the Φ_T values (Table 3.5), which does not change much with the presence of the substituents, except for **21c** in DMF, with Φ_T values of 0.66, 0.67 and 0.65 in DMSO for **21a**, **21b** and **21c**, respectively, and between 0.74 and 0.79 for **21a** and **21b**, respectively, in DMF. The difference in Φ_T values is larger in toluene (0.65 for **21c** and 0.75 for **21b**). Solvent effects on Φ_T values are opposite to what was obtained in the case of Φ_F ; Φ_T values are lower in DMSO than in DMF and toluene, with **21c** being an exception.

Triplet lifetimes of the GaPc complexes are conspicuously higher in DMSO than in all other solvents used in this work. The longer lifetimes in DMSO are attributed to the higher viscosity of this solvent than other solvents used in this work. Molecular movements that lead to the deactivation of the excited state are impeded in viscous solvents, resulting in longer excited state lifetimes. The presence of ring substituents also lengthened the triplet lifetimes in this work (Table 3.5), comparing complexes **15**, **21a** and **21b**. The triplet lifetime for **21c** was the same as that of complex **15**. The triplet lifetimes are very low in the low viscosity solvents such CHCl₃ and THF.

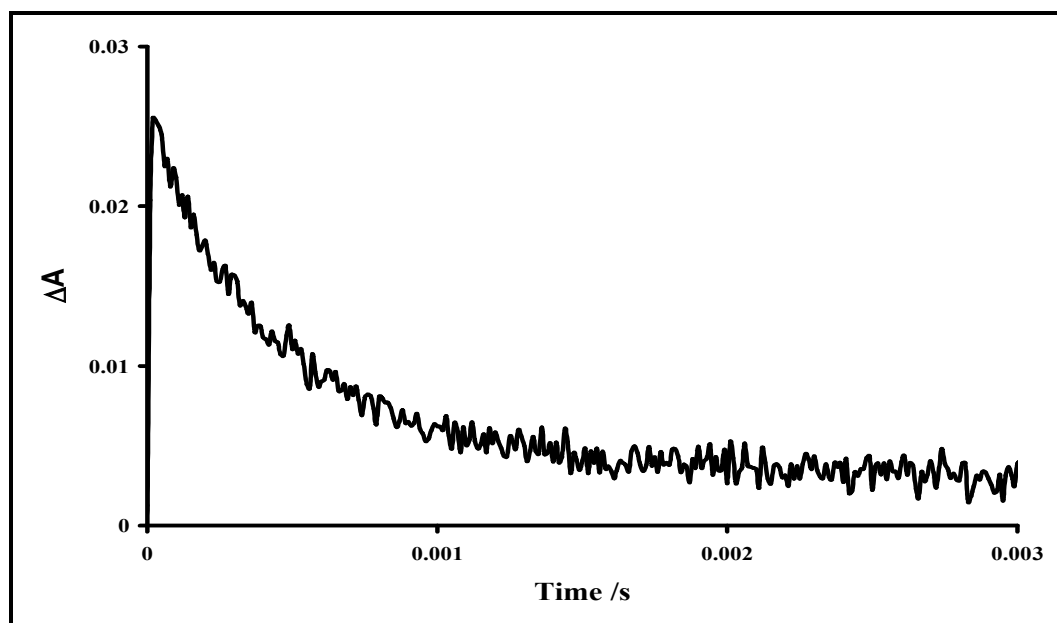


Figure 3.13: Triplet decay curve for 21a in DMSO.

Quantum yields of internal conversion (Φ_{IC}) were calculated using Equation 3.4, which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of a molecule.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \quad (3.4)$$

Internal conversion is the radiationless transition between energy states of the same spin state. The values of Φ_{IC} indicate the extent to which the excited molecules can de-excite by increasing the thermal energy of their surroundings. However in Table 3.5, the values of Φ_{IC} do not conform to any particular pattern.

Table 3.6 gives the triplet state parameters for the InPc complexes. From the results in Table 3.6, it seems both solvent and the introduction of phenoxy, *t*-butylphenoxy and benzyloxyphenoxy onto the (Cl)InPc (**16**) ring had an effect on the Φ_T values. Larger Φ_T values were obtained in highly viscous and coordinating solvents, for example in DMSO $\Phi_T = 0.91, 0.84, 0.70$ and 0.88 were obtained for **16**, **22a**, **22b** and **22c**,

respectively, and the corresponding values were smaller in DMF. Φ_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 (Φ_{IC}) were observed in toluene, Table 3.6.

It is interesting to note that the quantum yields of triplet state (Φ_T) decrease with increase in size of substituents, in the order **16** > **22a** > **22b**. This could be due to a concept called the “loose bolt” effect [67, 159] for the *tert*-butyl phenoxy substituted **22b**. 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 σ 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 [67]. The “loose bolt” effect is expected to be less pronounced in the **22a** complex since it has less C-H bonds than **22b**. Compound **22c** was different only on the basis of size.

On the basis of the size of the central metal, the triplet quantum yields for InPc complexes were significantly larger than those for GaPc complexes in the same solvents except for toluene. This was expected as In is a heavier metal and thus enhances intersystem crossing resulting in a large population in the triplet state. The triplet lifetimes τ_T for InPc complexes listed in Table 3.6, were relatively small. The short triplet lifetimes could be due to their large triplet state quantum yields.

S_A is a measure of the efficiency of excitation energy transfer from the triplet photosensitizer molecule to ground state (triplet) molecular oxygen, $O_2(^3\Sigma_g^-)$. In Table 3.5, S_A values reveal that energy transfer to $O_2(^3\Sigma_g^-)$ is more efficient (with values closer to

unity) with the substituted GaPc derivatives (**21a – c**) than with unsubstituted (Cl)GaPc. It is possible that the substituents lower the energy of the triplet states to a level where energy transfer to $O_2(^3\Sigma_g^-)$ is easily achieved.

Listed in Table 3.6 are S_A results for InPc derivatives in this study. The results for most of the InPc derivatives in different solvents were near unity (except for **22a** in toluene) which reflects that there's an efficient quenching of the triplet state of the Pc by the molecular oxygen in its triplet state.

3.2.2.3 Determination of rate constants

Fluorescence lifetimes τ_F are listed in Table 3.7 and 3.8 for GaPc and InPc derivatives. The values do not conform to any particular trend; hence it is difficult to draw any conclusion from them. However, the values were useful for the calculation of the rate constants (discussed below) for the intrinsic processes (fluorescence, intersystem crossing and internal conversion), which jointly deactivate the excited singlet state.

Rate constants for the intrinsic processes (processes that deactivate the excited singlet state) are given in Tables 3.7 and 3.8. The values of these rate constants are a reflection of the efficiency of the respective processes, and should conform to the same trend as the corresponding quantum yields. Calculated k_F , k_{ISC} and k_{IC} for **15** and **21a – 21c** in all solvents were found to be within the reported range for MPc complexes. k_F values in DMSO and THF increased in the presence of substituents for GaPc derivatives, while k_{ISC} increased in DMSO (except complex **21c**) and DMF (except complex **21b**) suggesting that substituents encourage intersystem crossing. k_{IC} values increased on the introduction of substituents in DMSO, Table 3.7. The

photodegradation rate values (k_d) for GaPc derivatives increased with increase in substituent size for **21a** and **21b** in DMSO and the opposite was observed in DMF, where the highest k_d value was 1.96 for complex **15**. The highest k_d rates for GaPc derivatives were obtained in THF and CHCl_3 , these well complement the high photodegradation quantum yields, especially in CHCl_3 .

For InPc complexes, there was no defined trend in k_F values (Table 3.8). k_{IC} and k_{ISC} were higher in DMF than in DMSO. There was no pattern in k_d values, however higher k_d values were obtained in CHCl_3 , as was evident in GaPc derivatives.

Table 3.7: Rate constants for the excited singlet state deactivation processes for GaPc complexes.

Solvent	MPc	τ_F /ns	$^a k_F$ / $10^{-7} s^{-1}$	$^a k_{ISC}$ / $10^{-8} s^{-1}$	$^a k_{IC}$ / $10^{-7} s^{-1}$	$^a k_d/s^{-1}$
DMSO	15	3.76	5.59	1.84	2.66	0.092
	21a	2.30	8.26	2.87	6.52	0.033
	21b	2.12	10.4	3.16	5.19	0.061
	21c	^c 0.70	^c 18.6	^c 1.08	^c 18.5	0.003
DMF	15	1.94	6.19	4.02	5.16	1.96
	21a	1.34	14.2	5.90	1.49	0.21
	21b	4.00	3.75	1.85	2.75	0.22
	21c	0.30	17.8	19.3	123.3	0.11
Toluene	21a	1.49	9.40	4.36	14.1	0.36
	21b	3.82	4.45	1.96	2.09	2.84
^b THF	15	7.81	2.43	-	-	0.71
	21a	1.54	9.09	-	-	10.1
	21b	1.32	13.6	-	-	8.93
^b CHCl ₃	21a	0.96	12.5	-	-	20.3
	21b	2.02	5.95	-	-	1.37

$$^a k_F = \frac{\Phi_F}{\tau_F}; k_{ISC} = \frac{\Phi_T}{\tau_F}; k_{IC} = \frac{\Phi_{IC}}{\tau_F} \text{ and } k_d = \frac{\Phi_{pd}}{\tau_T}, ^b \text{Values not obtained in THF}$$

and CHCl₃ due to lack of reference standards. ^c Values were from literature, Ref 108

Table 3.8: Rate constants for the excited singlet state deactivation processes for InPc complexes.

Solvent	MPc	τ_F/ns	$^a k_F/$ 10^{-7}s^{-1}	$^a k_{ISC}/$ 10^{-8}s^{-1}	$^a k_{IC}/$ 10^{-7}s^{-1}	$^a k_d/$ s^{-1}
DMSO	16	0.18	10.0	0.36	0.016	1.98
	22a	0.32	7.81	26.3	43.8	0.23
	22b	0.26	7.70	27.0	107.7	0.47
	22c	0.11	^c 5.34	80.0	109.1	^c 0.038
DMF	16	0.11	15.5	75.4	136.4	1.05
	22a	0.16	11.3	47.5	137.5	2.83
	22b	0.21	10.5	29.0	176.2	5.08
	22c	0.05	26.3	130.0	680.0	0.63
Toluene	22a	0.19	12.1	28.9	226.3	1.38
	22b	0.10	21.0	42.0	600.0	3.19
^b THF	16	0.62	12.2	-	-	1.31
	22a	0.05	40.0	-	-	1.05
	22b	0.05	40.0	-	-	0.62
^b CHCl ₃	22a	0.61	9.18	-	-	7.36
	22b	0.57	10.3	-	-	7.81

^a $k_F = \frac{\Phi_F}{\tau_F}$; $k_{ISC} = \frac{\Phi_T}{\tau_F}$; $k_{IC} = \frac{\Phi_{IC}}{\tau_F}$ and $k_d = \frac{\Phi_{pd}}{\tau_T}$, ^bValues not obtained in THF and

CHCl₃ due to lack of reference standards. ^c Value was from literature, Ref 108.

3.2.3 Photocatalytic oxidation of 1-hexene

3.2.3.1 Singlet oxygen (Φ_Δ) determination

Singlet oxygen quantum yields (Φ_Δ) of GaPc and InPc complexes were determined in dichloromethane (DCM) following methods from literature [133]. DCM was chosen for its volatility for GC purposes and also because good singlet oxygen quantum yields and photocatalytic results have been reported in DCM [133]. However comparative methods used above (eq. 1.8) to determine singlet oxygen quantum yields could not be employed for DCM due to lack of standards. Hence the method described by equations 3.5 to 3.7 were employed, DPBF was used as a singlet oxygen quencher where DPBF quantum yields (Φ_{DPBF}) were calculated using equation 3.5:

$$\Phi_{DPBF} = \frac{(C_0 - C_t)V}{tI_{abs}} \quad (3.5)$$

where C_0 and C_t are respective concentrations for DPBF before and after irradiation, t the irradiation time and V is the volume of the sample in the cell. I_{abs} is determined by equation 3.6 (same as 1.10).

$$I_{abs} = \frac{\alpha SI}{N_A} \quad (3.6)$$

Singlet oxygen quantum yields in DCM were calculated using equation 3.6 [119]:

$$\frac{1}{\Phi_{DPBF}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi_\Delta} \frac{k_d}{k_a} \frac{1}{[DPBF]} \quad (3.6)$$

where k_d and k_a are the singlet oxygen decay rate constant and reaction rate constant of DPBF, respectively, in the presence of singlet oxygen. $1/\Phi_\Delta$ is obtained from the intercept of a plot of $1/\Phi_{DPBF}$ versus $1/[DPBF]$.

Listed in Table 3.9 are the singlet oxygen quantum yields values in DCM for GaPc and InPc derivatives. The singlet oxygen quantum yields (Φ_Δ) for GaPc derivatives

(**21a - c**) were lower when compared to the corresponding InPc derivatives (**22a-c**). The higher Φ_{Δ} values for InPc derivatives were attributed to the fact that In is heavier than Ga and therefore encourages intersystem crossing thus resulting in higher (Φ_{Δ}) values. The Φ_{Δ} values were highest for phenoxy derivatives and lowest were for the tert-butyl derivatives for both InPc and GaPc derivatives and the trend was as follows: phenoxy > benzyloxyphenoxy > tertbutylphenoxy. Thus, the tertbutyl derivatives gave the lowest singlet oxygen quantum yield values. Compared to the Φ_{Δ} values obtained in other solvents (Tables 3.3 and 3.4) the values in DCM were larger than for DMSO, DMF and THF for **21a**. For GaPc derivatives, on average, highest Φ_{Δ} were obtained in toluene, followed by DMF, then DCM and lastly DMSO. For InPc derivatives, the lowest Φ_{Δ} values were obtained in toluene for **22a** (0.31) and the highest in DCM (0.84).

3.2.3.2 Photodegradation quantum yields (Φ_P)

Photodegradation will affect the photocatalytic abilities of the MPc derivatives, hence the need to study it in DCM, which is the solvent that was used for the photocatalytic oxidation of 1-hexene. The photodegradation stabilities were determined by monitoring the decrease in the intensity of the Q band under irradiation with increasing time, as shown in Fig. 3.16.

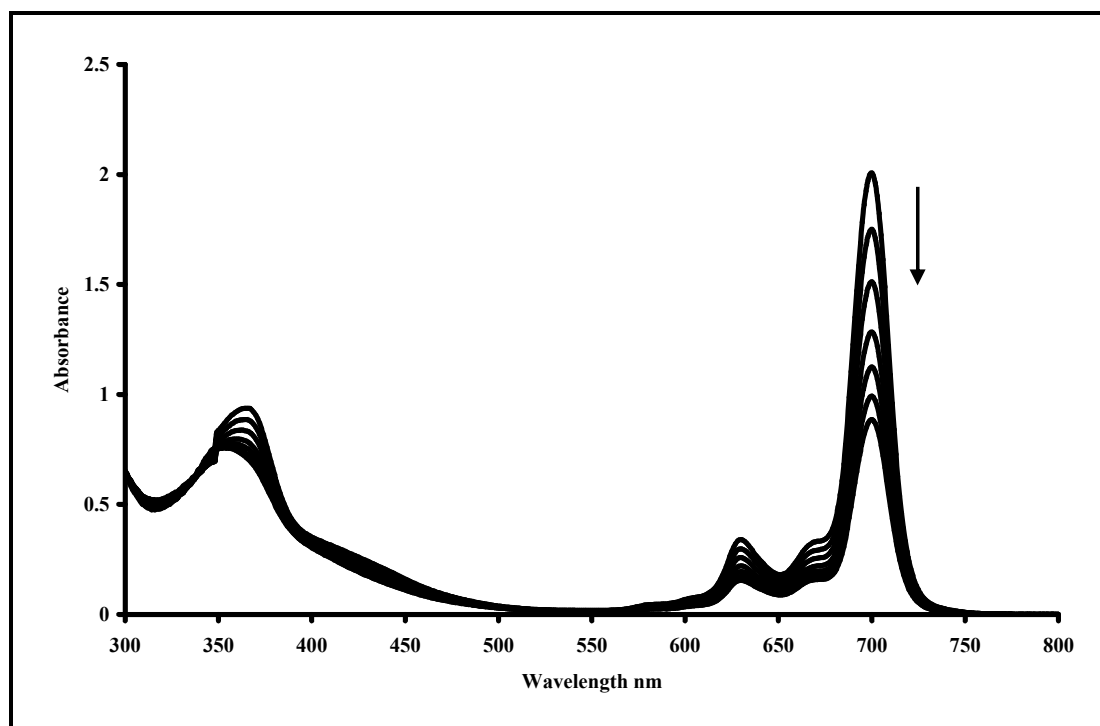


Figure 3.14: Photodegradation spectrum of complex 22a. Concentrations = 1.04×10^{-5} M.

Listed in Table 3.9 are the photodegradation quantum yields (Φ_p) for the GaPc and InPc derivatives.

Table 3.9: Singlet oxygen and photodegradation quantum yields in DCM.

Compound	Φ_{DPBF}	Φ_{Δ}	Φ_{pd}
21a	0.32	0.63	1.39×10^{-6}
21b	0.25	0.52	9.29×10^{-6}
21c	0.36	0.56	3.05×10^{-6}
22a	0.53	0.84	9.08×10^{-5}
22b	0.39	0.62	4.12×10^{-5}
22c	0.43	0.66	1.64×10^{-5}

Solvents are known to have an impact on the photodegradation rates of MPcs. For instance, as mentioned before photodegradation is faster in chlorinated solvents such as DCM and CHCl_3 due to radicals that form from C-Cl bond cleavages. These

radicals are said to aid in the photodegradation process. Also, electron releasing substituents tend to fast track the process of photodegradation due to ease of oxidation. Surprisingly given that the photodegradation studies were carried out in a chlorinated solvent (DCM) and that the substituents on the GaPc and InPc derivatives are electron releasing, the Φ_{pd} values fell within the acceptable stability range for phthalocyanines of $\sim 10^{-5}$, thus making them relatively stable. Photodegradation quantum yields for GaPc derivatives (**21a – c**) were much smaller (in the 10^{-6} range) than those for InPc (**22a - c**) derivatives, indicating that they are more stable than InPc derivatives. This could be due to the high singlet oxygen quantum yields for the InPc derivatives since photodegradation is initiated by singlet oxygen attack. Compared to the photodegradation quantum yields in other solvents (Tables 3.4 and 3.4), GaPc derivatives in DCM gave the lowest Φ_{pd} values.

3.2.3.3 Photocatalytic oxidation of 1-hexene

As mentioned before, singlet oxygen is responsible for the process of photo-oxidation of substrates such as 1-hexene. The products from the photo-oxidation of 1-hexene have been reported to be 1,2-epoxyhexane and 1-hexen-3-ol [133] and these products were obtained in this work as evidenced by the spiking with standards and by using GC-MS. Fig. 3.17 shows a GC chromatogram of complex **21a** after 6 hours of irradiation. Mass spectral peaks were observed at $m/z = 99$ amu (M-1) for 1,2-epoxyhexane and $m/z = 97$ amu (M-3) for 1-hexen-3-ol (Figs. not shown).

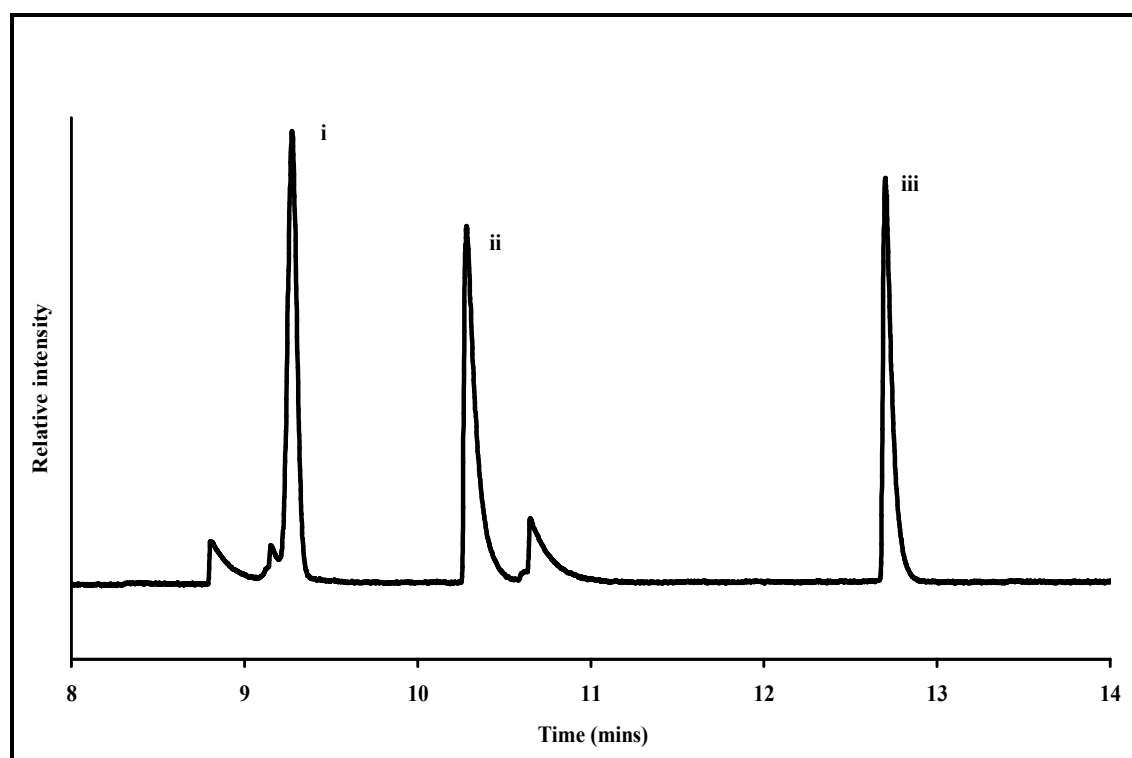


Figure 3.15: GC chromatogram of the photocatalytic reaction by complex **21c** after 6 hours of irradiation, for 1-hexen-3-ol (i), 1-hexene (ii) and 1,2-epoxyhexane (iii).

Fig. 3.18a and b (Table 3.10) show the conversion (%) of 1-hexene using GaPc and InPc derivatives. For GaPc derivatives, within the first four hours of photocatalysis, complex **21c** gave the highest conversion (%), while **21a** was the lowest throughout. Of the GaPc derivatives **21a** had the highest singlet oxygen quantum yield and was the most stable in terms of photodegradation quantum yields (Table 3.9), hence **21a** would have been expected to give the highest conversion (%) if the singlet oxygen mechanism was the only one operating. Table 3.10 shows that of the GaPc derivatives, **21b** gave the best % conversion after 6 hours

Table 3.10: Photocatalytic oxidation of 1-hexene by Ga and InPc derivatives in DCM after 6 hours.

MPc	% conversion ^a	% selectivity of 1,2- epoxyhexane ^b	% Yield of 1,2- epoxyhexane ^c
21a	38.7	37.6	1.19
21b	46.3	42.8	1.21
21c	39.9	22.3	1.08
22a	49.2	60.9	1.22
22b	49.8	65.6	1.25
22c	37.3	68.0	1.38

$$^a \% \text{ conversion} = \frac{(1 - \text{hexene}_{\text{initial}}) - (1 - \text{hexene}_{\text{remaining}})}{(1 - \text{hexene}_{\text{initial}})} \times 100$$

$$^b \% \text{ selectivity} = \frac{\text{epoxide}_{\text{obtained}}}{[(1 - \text{hexene}_{\text{initial}}) - (1 - \text{hexene}_{\text{final}})]}$$

$$^c \% \text{ yield} = (\text{Product obtained}_{1,2\text{-epoxyhexane}})/(\text{initial substrate}) \times 100$$

Fig. 3.19a shows that **21a** remained stable throughout the photocatalysis experiment because there was an insignificant decrease in the Q band. Aggregation is another factor which may affect the photocatalytic activity of the MPc complexes, however these complexes are known not to form aggregates at concentrations less than 1×10^{-5} M. The concentrations employed in the photocatalysis experiments were in the 1×10^{-6} to 1×10^{-5} mol. dm⁻³ range hence aggregation is not expected.

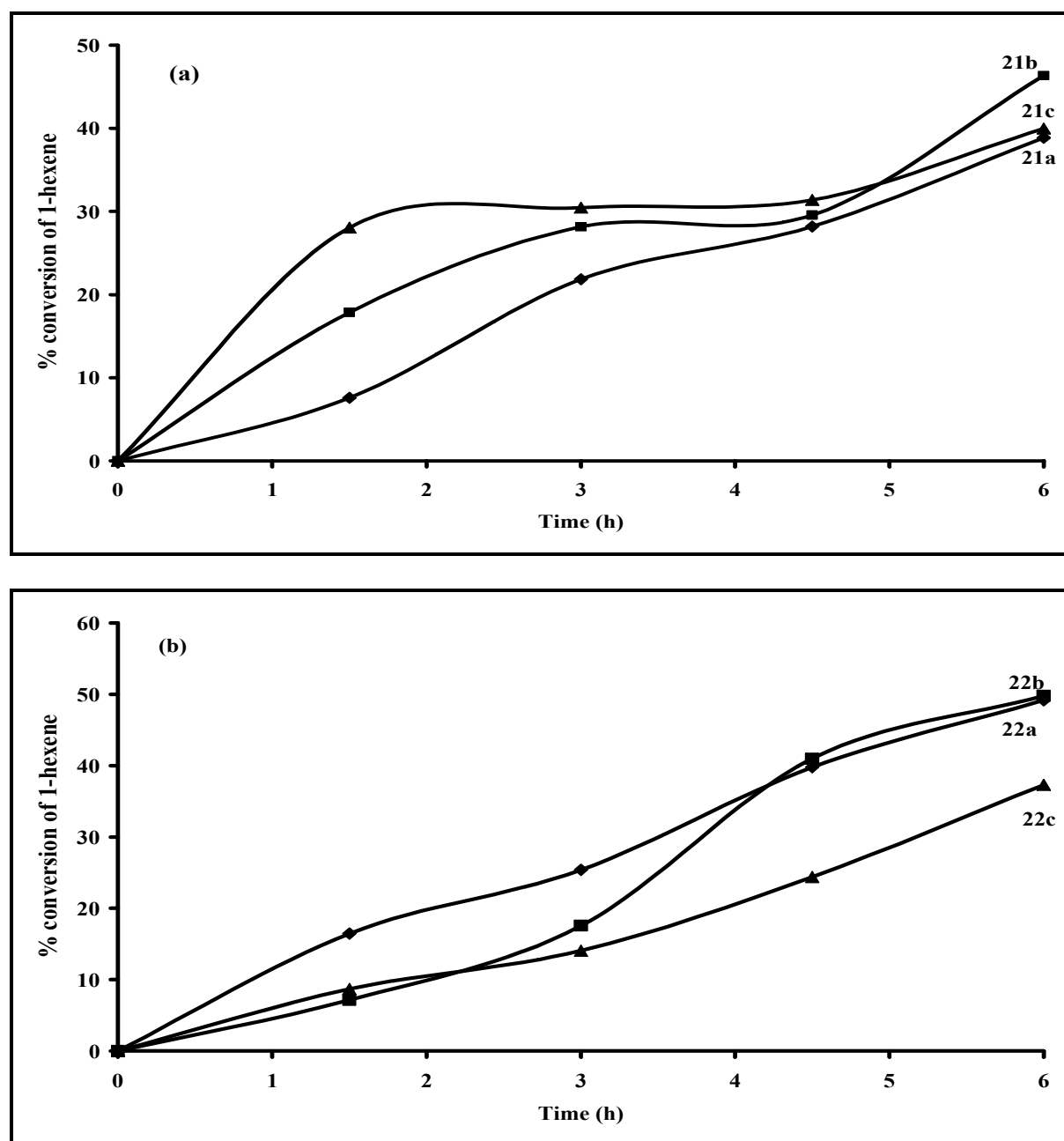


Figure 3.16: Percentage conversion plots of 1-hexene by GaPc (a) and InPc (b) derivatives in DCM.

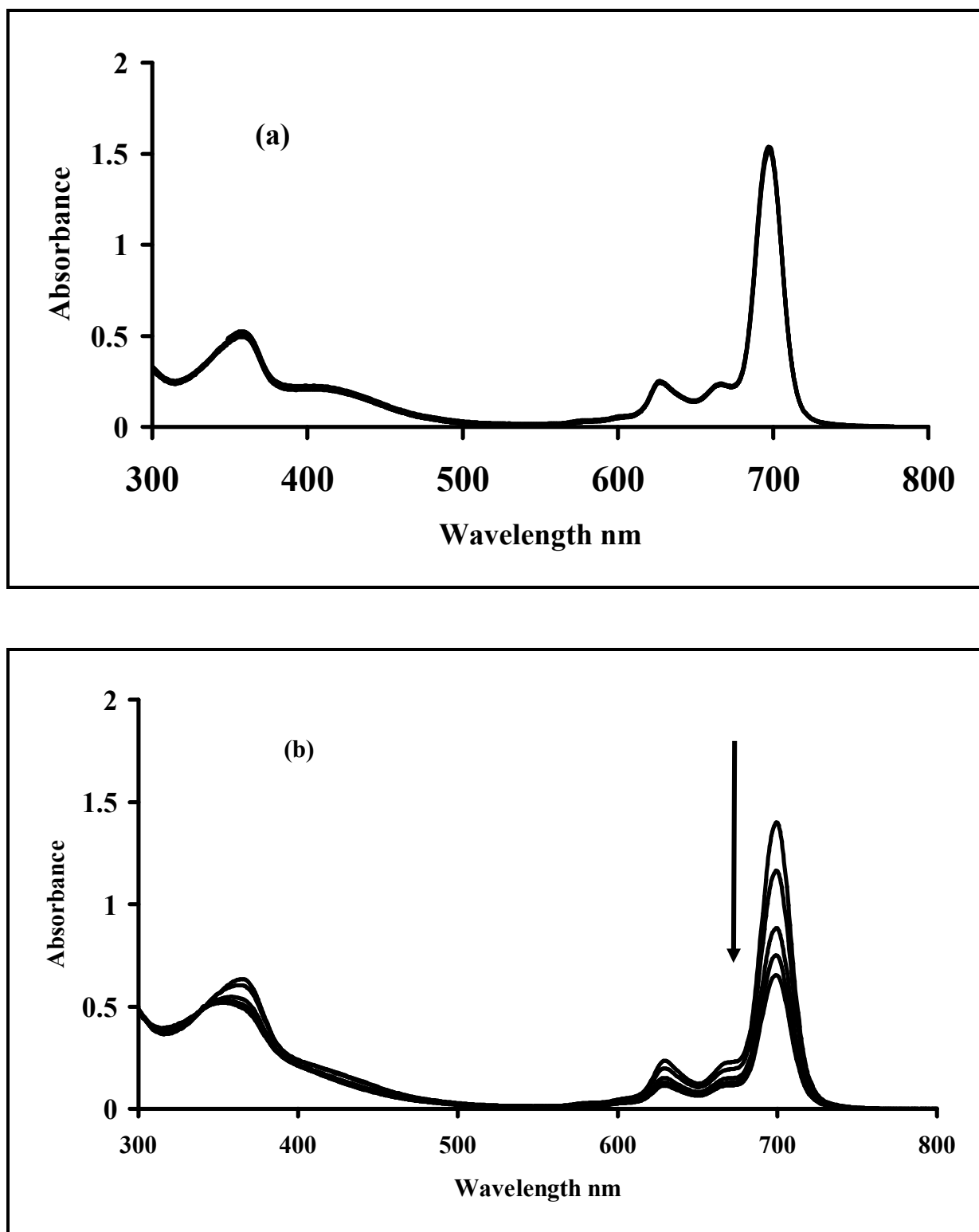


Figure 3.17: Electronic absorption spectra showing the degradation of complex 21a (a) and 22a (b) and during the photocatalytic oxidation reaction. Concentration = 5.6×10^{-5} mol dm⁻³ in DCM.

For the InPc derivatives, **22a** and **22b** gave about the same conversion (%), while **22c** was the lowest, Table 3.10. Complex **22a** was the least stable in terms of photo-bleaching quantum yields in Table 3.9, but had the highest singlet oxygen quantum yield. Fig. 3.19b shows that **22a** decomposed appreciably during the photocatalysis experiment. Thus the photocatalytic ability of the complexes towards the transformation of 1-hexene is a balance between singlet oxygen quantum yield and stability. Comparing all the complexes, Table 3.10 shows that the highest % conversions of 1-hexene were observed for **22a** and **22b**. **22a** also had the highest singlet oxygen quantum yield. This complex was also the least stable (Table 3.9). However there is no clear trend between the Φ_{Δ} values and % conversion for the complexes, suggesting that it is not only singlet oxygen mechanism in operation during catalysis.

The conversion (%) values obtained in this study are much higher than reported for TiPc complexes [133]. The % yields of 1,2-epoxyhexane were less than 2% for all MPc derivatives. This is similar to the observation for the photocatalysed transformation of cyclohexene using ZnPc [79].

Higher % selectivity values for 1,2-epoxyhexane were achieved for InPc derivatives, they range from 60.9 to 68.0 %, (Table 3.10 and Fig 3.20). % Selectivity for these derivatives increases with time, where there was a slow increase for compounds **22b** and **22c** for the first three hours and eventually a fast increase after three hours. Similar behaviour was observed for GaPc derivatives, where for all three derivatives **21a – c**, there was a slow increase in % selectivity for the first three hours (Fig. 3.21).

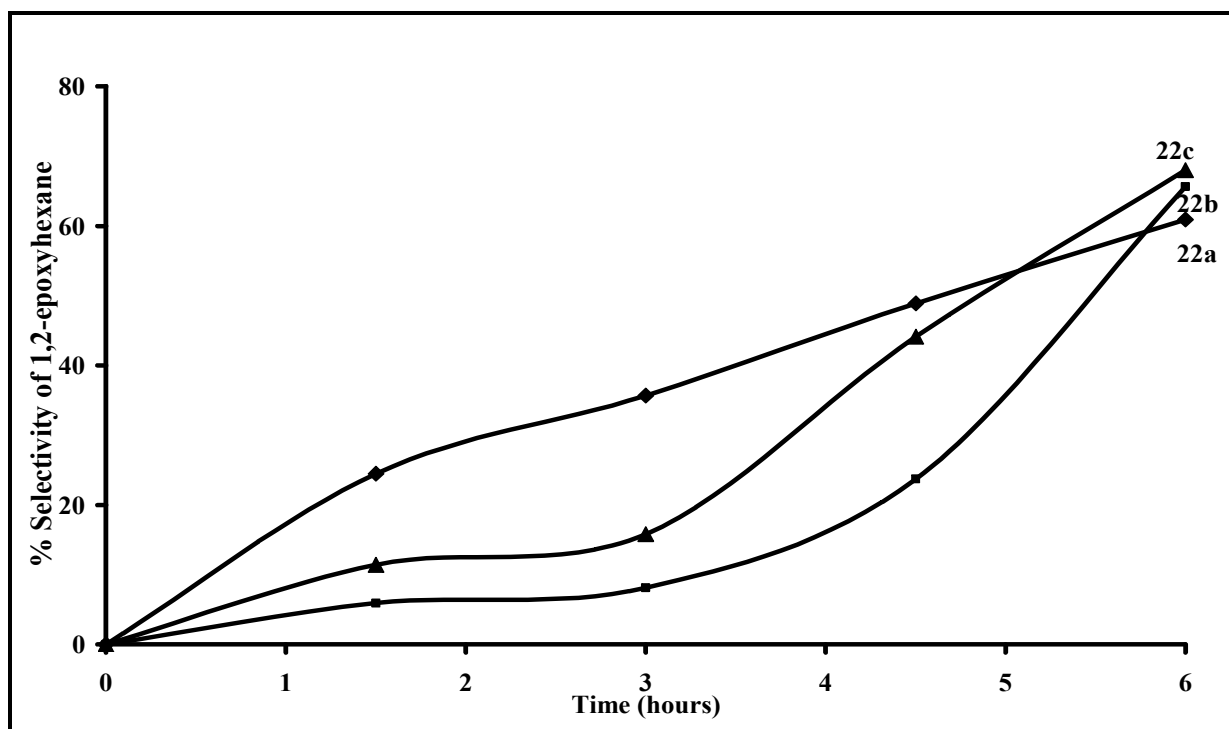


Figure 3.18: Percentage selectivity plot of 1,2-peoxyhexane in DCM using InPc derivatives.

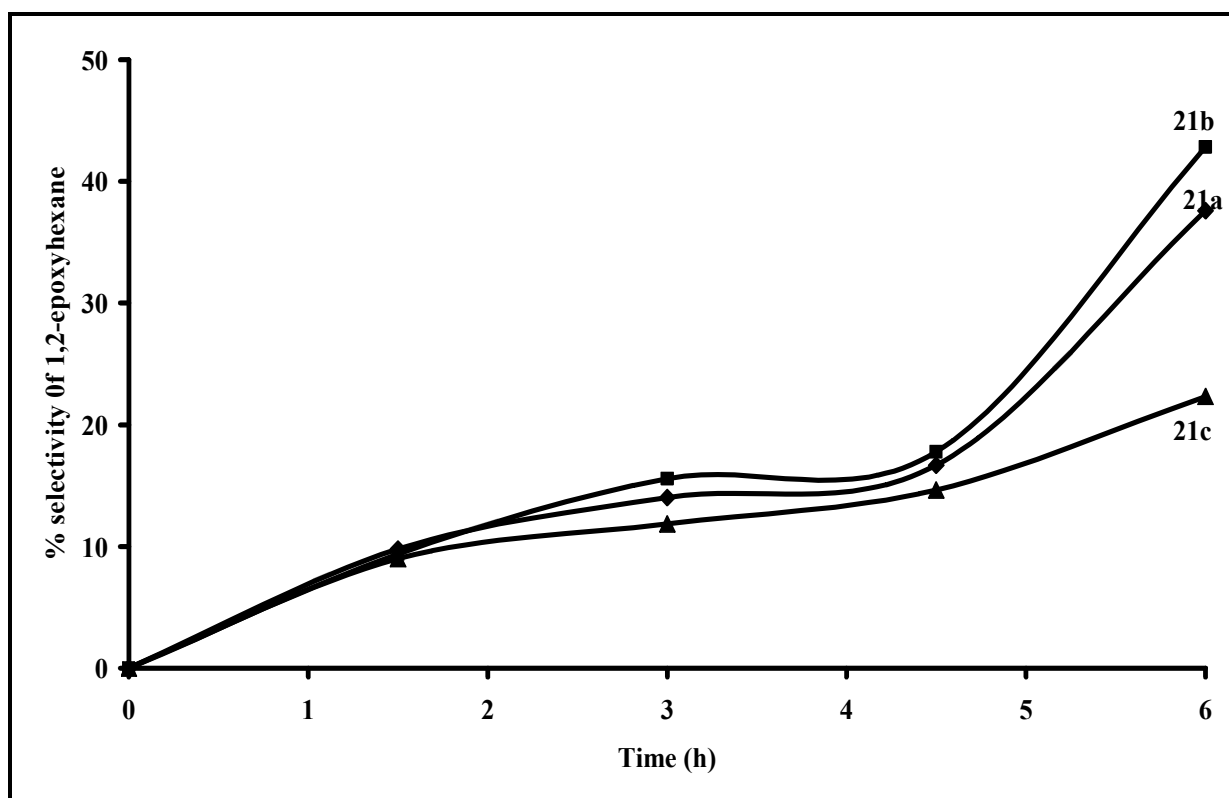
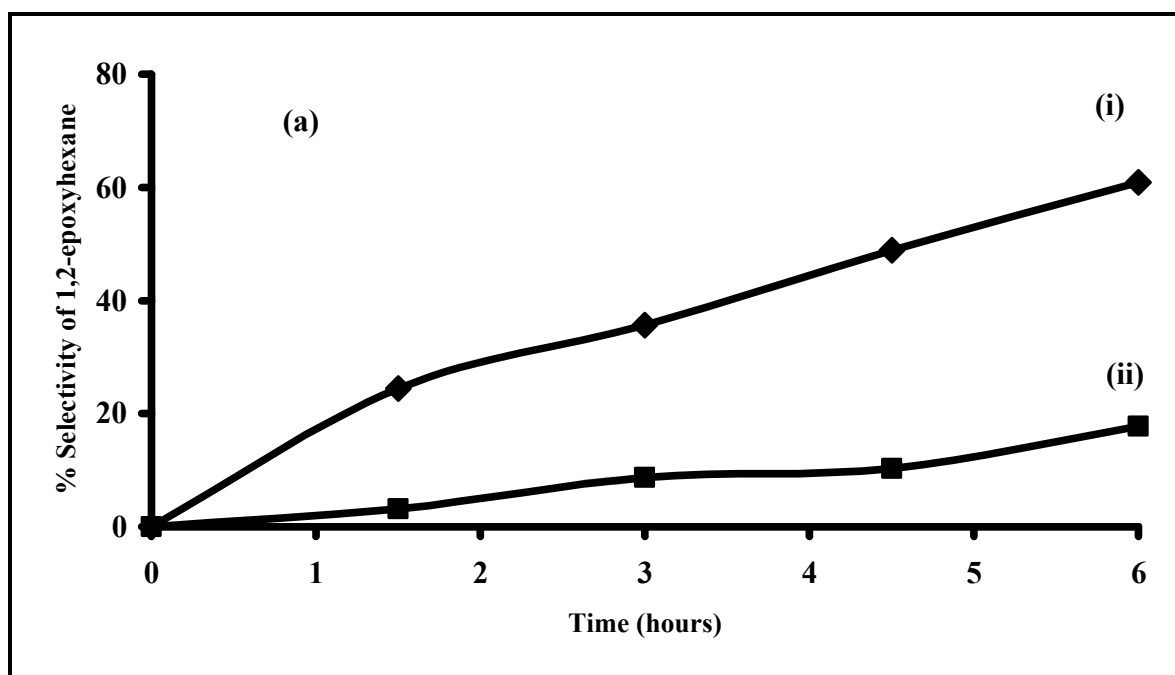


Figure 3.19: Percentage selectivity plot of 1,2-peoxyhexane in DCM using GaPc derivatives.

As mentioned before both Type I and Type II mechanisms may be involved in the photocatalytic oxidation reactions. In order to confirm if both mechanisms are involved, a singlet oxygen quencher, DABCO, was added to solutions containing the MPc derivative and 1-hexene, then the solution was photolysed. There was a significant decrease in both conversion (%) of 1-hexene and % selectivity for 1,2-epoxyhexane Fig. 3.22a and b. The fact that there was a decrease in both conversion of 1-hexene and selectivity for 1,2-epoxyhexane, shows that singlet oxygen is involved in the photocatalysis mechanism. However since there was still some activity in the presence of DABCO and the activity did not decrease any further than shown in Fig. 3.22 with increase in the concentration of DABCO, shows that it is not only singlet oxygen (Type II) which is involved in the photocatalysis mechanism and suggest the involvement of Type I mechanism.



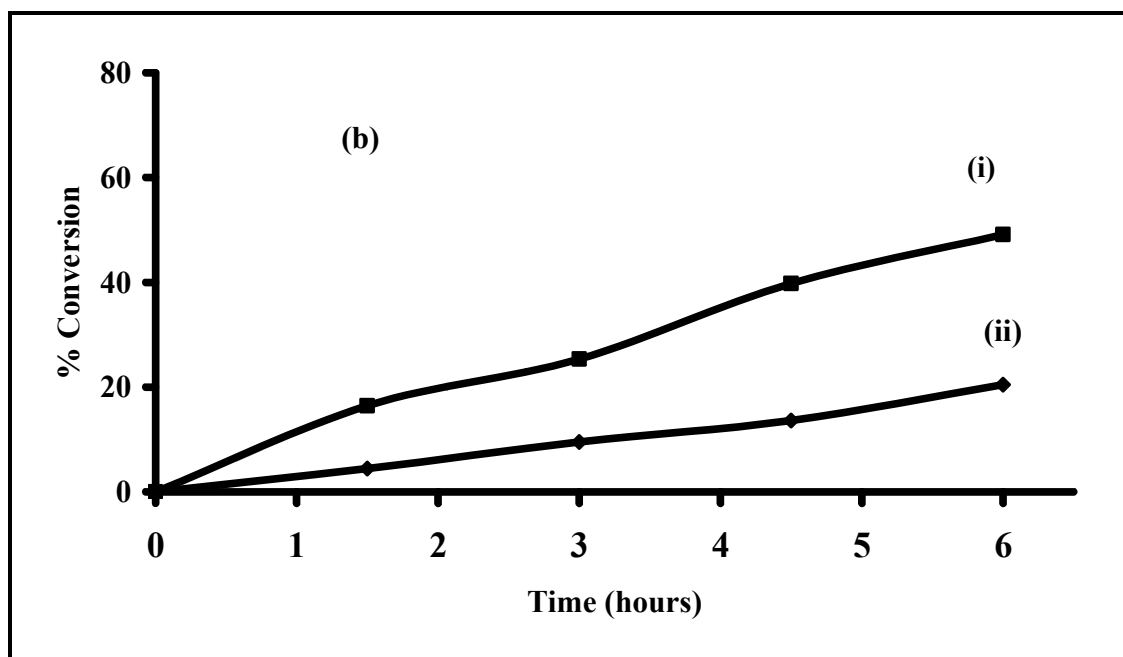
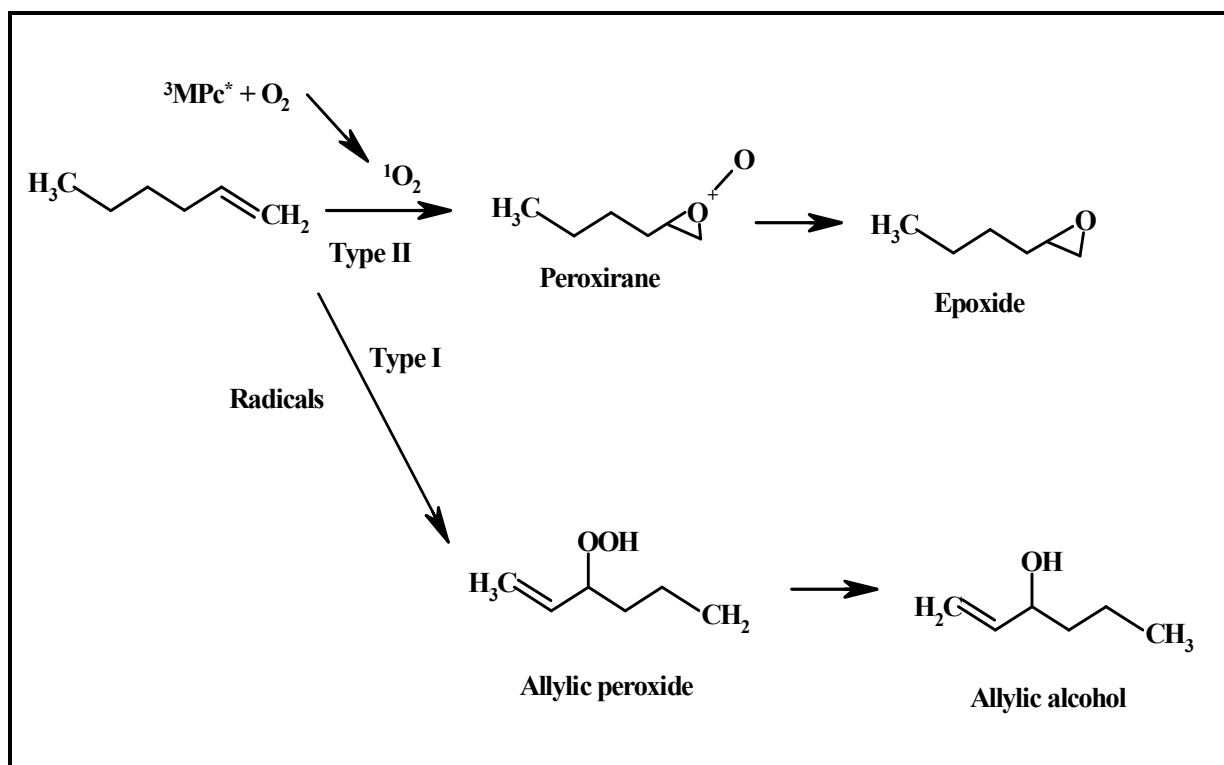


Figure 3.20: Percentage selectivity for 1,2-epoxyhexane (a) and % conversion of 1-hexene (b) plots in the absence (i) and presence (ii) of DABCO in DCM, by complex 22a.

The possible mechanism taking into account both Type I and Type II mechanisms is shown by Scheme 3.4. The two processes that could be taking place are epoxidation and allylic oxidation. These take place due to the attack at the 1-hexene double bond for epoxidation and hydrogen abstraction in the allylic oxidation process. These processes may occur at the same time (Scheme 3.4. [133, 160]).



Scheme 3.4: Proposed mechanism for the formation of the photooxidation products.

3.3 NONLINEAR OPTICAL PARAMETERS

This section compares the nonlinear parameters of tetra- and octasubstituted gallium and indium phthalocyanines.

3.3.1 Threshold limit (I_{lim}) and absorption cross section ratio (k) values

These parameters were calculated for complexes **21a** - **c** and compared with the corresponding **22a** - **c** and to the peripherally and non-peripherally tetrasubstituted InPc (**17,19**) and GaPc (**18,20**) derivatives. Triplet absorption cross sections for InPc and GaPc derivatives occurred in the region between 400 and 600 nm, Fig. 3.23.

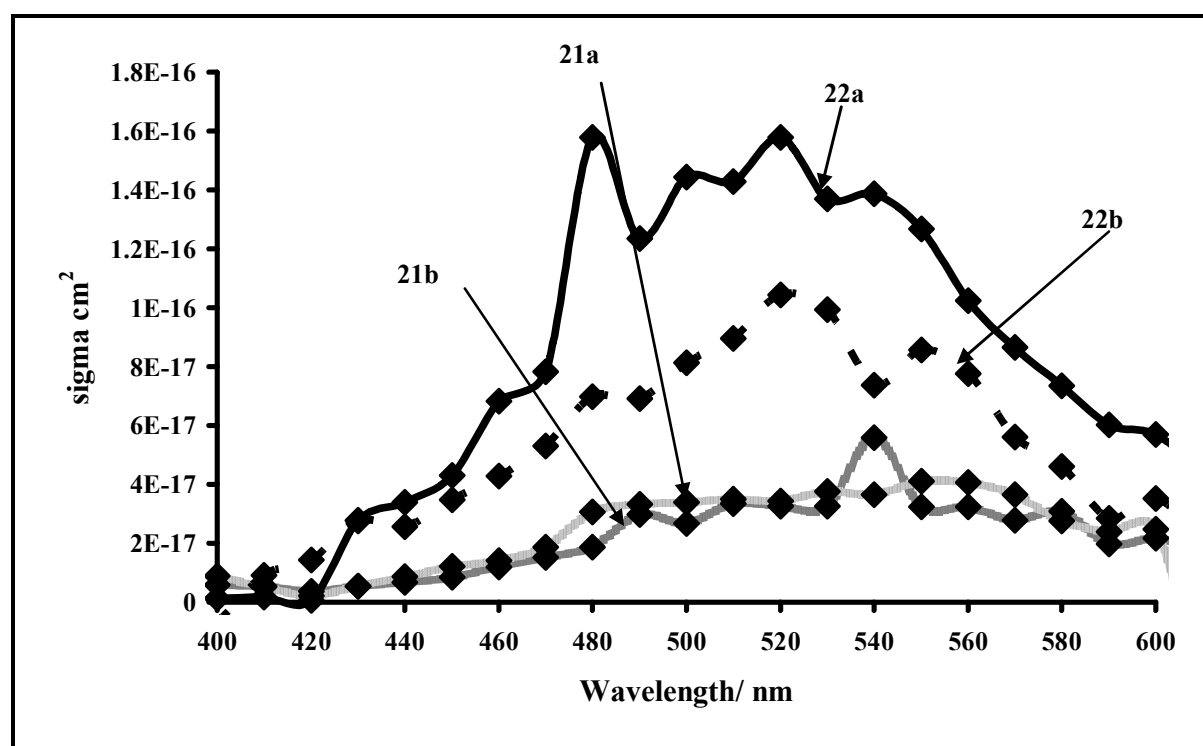


Figure 3.21: Absorption cross sections for the excitet triplet state for gallium and indium phthalocyanine derivatives.

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 non-linear optical studies. Table 3.11, gives the I_{lim} values for the octa-substituted InPc derivatives and compares them with the corresponding octa-substituted GaPc complexes. Compound **21a** has the lowest value of 0.15 W cm^{-2} , followed by **21b** with 0.20 W cm^{-2} and **21c** with 0.47 W cm^{-2} . It seems the limiting intensities increase with the size of the substituents for GaPc derivatives. 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 [37]. Thus the I_{lim} values obtained in Table 3.11 for octasubstituted GaPc and InPc derivatives show that the derivatives are good optical limiters, with phenoxy substituted gallium and indium octasubstituted Pcs showing better non-linear optical behaviour than *tert*butylphenoxy and benzyloxyphenoxy substituted 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 in terms of I_{lim} , Table 3.11.

Among the tetrasubstituted compounds, the GaPc derivatives (**18** and **20**) show better optical limiting behaviour than the corresponding InPc derivatives, Table 3.12. Peripherally (β) substituted complexes (**19**, **20**) showed better optical behaviour than the corresponding non-peripheral (α) substituted complexes (**17**, **18**) in Table 3.12 in terms of I_{lim} . For example, complex **19a** gives a smaller I_{lim} value than **17a** and the same applies to complexes **17b** and **19b**, and **18b** and **20b**. Comparing octa with tetra substitution, showed that the former are better optical limiters than the latter, in that I_{lim} values are observed at lower values for the former considering the same substituents, Tables 3.11 and 3.12.

The excited state (σ_{ex}) to ground state (σ_{g}) absorption cross section ratio ($k = \sigma_{\text{ex}} / \sigma_{\text{g}}$) is also an excellent indicator of limiting power. The values of k are listed in Table 3.11 and 3.12. As with I_{lim} values, the k values are highest for InPc derivatives, showing that these complexes are good optical limiters in terms of k but not in terms of I_{lim} discussed above. The k values for GaPc derivatives (**21a – c**) are within the range of the values reported in the literature for MPc containing metals including Ga, Zn, Co, Cu, Ni, Si and In [106, 161 - 164] ranging between 3 and 15. The k values for InPc peripherally substituted with *tert*-butyl groups were however found to be much higher. The values obtained for **22a**, **22b** and **22c** in this study were 41.4, 53.4 and 9.4, respectively, which are slightly larger than reported in the literature [37]. Compared to octa-substituted derivatives, the tetra-substituted counterparts gave lower k values, (Table 3.12) suggesting that octa-substitution improves optical limiting characteristics.

3.3.2 Third order susceptibility ($I_{\text{m}}[\chi^{(3)}]$) and second hyperpolarizability (γ)

The values of third order susceptibility ($I_{\text{m}}[\chi^{(3)}]$) and second hyperpolarizability (γ) for InPc and GaPc derivatives are listed in Tables 3.11 and 3.12. The $I_{\text{m}}[\chi^{(3)}]$ values were well within expected ranges for phthalocyanines ($\sim 10^{-11}$ to 10^{-9}) [37, 100, 165]. The $I_{\text{m}}[\chi^{(3)}]$ are larger for octasubstituted GaPc derivatives compared to corresponding InPc complexes. There is a general increase in $I_{\text{m}}[\chi^{(3)}]$ of the tetrasubstituted derivatives compared to the corresponding octasubstituted ones, Tables 3.11 and 3.12, with the exception of (**21a** and **21b**). In general, peripheral substitution decreases the $I_{\text{m}}[\chi^{(3)}]$ values.

The γ values are listed in Tables 3.10 and 3.11 for the octa- and tetra-substituted derivatives, smaller γ were obtained for benzyloxyphenoxy substituted GaPc (**21c**) and InPc (**22a**) derivatives, compared to 4-tertbutylphenoxy and benzyloxyphenoxy. In general, tetra substitution increases γ values for InPc derivatives and decreases the values for GaPc complexes, whereas peripheral (β) substitution decreases the values. The γ values are within the range reported for MPc complexes [37, 100].

Table 3.11: Optical limiting parameters for octa substituted GaPc and InPc derivatives in DMSO.

MPc (in DMSO)	λ (nm)	τ_T (μ s)	$I_m[\chi^{(3)}]$ (esu)	γ (esu)	$(k) \sigma_{ex}/\sigma_g$	I_{lim} (Wcm^{-2})
21a	530	370	7.99×10^{-11}	3.49×10^{-35}	9.96	0.15
21b	540	290	1.12×10^{-10}	4.88×10^{-35}	3.13	0.20
21c	540	^a 200	7.80×10^{-11}	3.40×10^{-35}	2.41	0.47
22a	520	60	4.59×10^{-11}	2.00×10^{-35}	41.4	1.16
22b	520	50	2.87×10^{-11}	3.07×10^{-35}	53.4	1.92
22c	540	50	6.81×10^{-11}	2.97×10^{-35}	9.44	1.47

^a Values were from literature, Ref 108

Table 3.12: Optical limiting parameters for tetrasubstituted GaPc and InPc derivatives in DMSO.

MPc (in DMSO)	λ (nm)	τ_T (μ s)	$I_m[\chi^{(3)}]$ (esu)	γ (esu)	$(k)\sigma_{ex}/\sigma_g$	I_{lim} (Wcm^{-2})
17a	550	40	1.12×10^{-10}	4.83×10^{-35}	2.21	2.11
17b	540	40	8.40×10^{-11}	3.66×10^{-35}	5.24	1.81
18a	520	230	6.44×10^{-11}	2.81×10^{-35}	1.11	0.22
18b	540	350	4.67×10^{-10}	2.04×10^{-35}	3.76	0.26
19a	510	50	9.19×10^{-11}	4.01×10^{-35}	2.58	1.93
19b	510	50	3.23×10^{-11}	1.41×10^{-35}	1.24	1.71
20b	520	340	4.85×10^{-11}	2.12×10^{-35}	3.19	0.20

4 CONCLUSION

4.1 CONCLUSION

This work has demonstrated that gallium(III) phthalocyanine derivatives are well-suited for applications that require metastable excited states. The photophysical and photochemical parameters of the complexes reveal that the complexes would find use as photosensitizers in PDT and other applications. The photochemical and photophysical parameters of complexes **15**, **21a – c** have been reported in different solvents. It was concluded that fluorescence quantum yields vary in different environments. The yields are higher in solvents that are of a highly viscous nature. It was also found that substituents do not have major effects on the results.

From the results obtained for InPc derivatives (**16**, **22a – c**) in this work, it can be concluded that the substituted complexes **22a – c** gave large triplet state (Φ_T) and singlet oxygen quantum yields (Φ_Δ) due to the heavy atom effect of the In central metal, which also resulted in short triplet lifetimes (τ_T). The Φ_T values ranged from 0.70 to 0.91 and Φ_Δ from 0.61 to 0.79 in DMSO. The lowest Φ_Δ were obtained in toluene. The good performance of these complexes in producing singlet oxygen shows that they are suitable candidates for 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 in terms of I_{lim} but not in terms of k . The I_{lim} values obtained were far less than 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.

For the photocatalytic oxidation of 1-hexene, singlet oxygen quantum yields were determined in DCM and InPc derivatives had better Φ_{Δ} values relative to GaPc (**21a – c**) derivatives. The % conversion of 1-hexene was highest for InPc derivatives (**22a** and **b**), which had the largest singlet oxygen quantum yield, suggesting Type II mechanism. However, addition of singlet oxygen quencher showed that Type I mechanisms may also be involved. The products of the photooxidation are 1,2-epoxyhexane and 1-hexen-3-ol.

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