PHOTOPHYSICAL AND PHOTOELECTROCHEMICAL PROPERTIES OF WATER SOLUBLE METALLOPHTHALOCYANINES

A thesis submitted in fulfilment of the requirements

for the degree of

MASTER OF SCIENCE

Of

RHODES UNIVERSITY

By

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January 2010

DEDICATION

To

My Mother

GLADYS NKHOSI

For your unconditional love and support since birth, may God be with you "wena wekunene, wena lomuhle".

My Sisters

BUSISIWE, BONGIWE AND ZANDILE

My Brothers

MTHUNZI, BONGINKOSI AND NHLANHLA

Thank you very much "bo Mvungandze" may God live on you all.

My Son

Thandolwami Siboniso Fortune

Who past on when finishing this program, may you rest in peace "mfana wam", And to My girlfriend HELEN "ZOLA" SIYO thank you for being there at all times.

ACKNOWLEDGEMENTS

"In him there's time for everything" *Ecclesiastes 3:1-15*

To him; who created man, heaven and earth, the creator of the universe, the true source of light and wisdom. I will like to thank the **Almighty God** for life and protecting me since I was born. For strengthening me in all things, for me to reach this far is not by intelligence but it's your will.

My deepest gratitude's goes to my supervisor, **Professor Tebello Nyokong**. Thank you so much Prof for your guidance, fruitful discussions and time which has lead to the success of this work. Thank you Prof., for giving me the opportunity of going to do part of my research twice at Justus-Liebig University, Germany. I would also like to thank **Prof. Derck Schlettwein** my host surpervisor and his research group at Justus-Liebig University, Germany. For making my stay a memorable one, thank you so much Prof., for all your guidance and support. My gratitude's also goes to **Dr Mopelola Idowu**, for the guidance, prayers and support.

To my family, my mother Gogo Nkhosi thank you so much Dlamini, "*wena lowacedza lubombo ngekuhlehletela*", and to my sisters thank you for your financial support at all times.

Thanks to the Department of Science and Technology (DST) and National Research Foundation (NRF), South Africa through DST/NRF South African Research Chairs Initiative for Professor of Medicinal Chemistry and Nanotechnology and Rhodes University for financial support.

Thank you my brothers and sisters at S22 research group, thank you for your prayers, love and support. And thanks to all my friends, too numerous to mention, thank you very much for all your support.

ABSTRACT

This work presents the synthesis, characterization, photophysicochemical and photoelectrochemical properties of anionic octa-caboxylated (MOCPcs), tetra-sulfonated (MTSPcs) and quaternized cationic (Q(T-2-Py)MPcs) water soluble aluminium, gallium, silicon, titanium and zinc phthalocynines. The peripherally tetra-substituted cationic (O(T-2-Py)MPcs) and anionic (MTSPcs) were found to be aggregated in aqueous media, yet the octa-carboxylated (MOCPcs) counterparts were monomeric in solution. Cremophor EL (CEL) was used as a disaggregating agent, all the aggregated complexes disaggregated partially or completely in the presence of CEL. The photophysicochemical properties of aggregated complexes were investigated both in the presence of CEL and in aqueous media of pH 11 alone. Low triplet, singlet oxygen and fluorescence quantum yield were obtained in aqueous media (especially for the aggregated complexes) but a high improvement was achieved upon addition of CEL. The gallium complexes ((OH)GaOCPc and (OH)GaTSPc) showed good photophysicochemical properties with higher triplet and singlet oxygen quantum yields.

For photoelectrochemistry the (MPcs) dyes were adsorbed to nanoporous ZnO, electrodeposited in the presence of eosin Y as structure directing agent (SDA) on FTO substrates by refluxing or soaking the films in a solution containing the dye of interest such that a full surface coverage was achieved. Quaternized cationic (Q(T-2-Py)MPc) and tetrasulfonated (MTSPcs) phthalocyanines formed strong aggregates when deposited on the surface of FTO/ZnO substrate leading. High external (IPCE) and internal (APCE) quantum efficiencies of up to 50.6% and 96.7% were achieved for the OTiOCPc complex. There was a lower overall cell efficiency for quaternized and tetrasulfonated metallophthalocyanines because of the strong aggregates when they were on the surface of the electrodes. Among the studied materials, OTiOCPc gave the highest overall cell efficiency of phthalocyanine electrodeposited on ZnO of so far $\eta = 0.48\%$.

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LIST OF SYMBOLS

ΔΑ	-	Change in absorbance following laser pulse
Ι	-	Intensity of light
I _{abs}	-	Intensity of light absorbed
E _{mpp}	-	Potential at a maximum power point
I _{mpp}	-	Current at a maximum power point
V _{oc}	-	Open cecuirt voltage
I _{sc}	-	Short secuirt current
F	-	Fluorescence intensity
k _F	-	Fluorescence rate constant
α	-	Non-peripheral position
β	-	Peripheral position
3	-	Molar extinction coefficient
ε _s	-	Singlet state extinction coefficient
ε _T	-	Triplet state extinction coefficient
η_e	-	Photovoltaic cells efficiency
k _I	-	Internal conversion rate constant
k _{ISC}	-	Intersystem crossing rate constant
λ_{abs}	-	Wavelength of absorption spectrum maximum
λemi	-	Wavelength of emission spectrum maximum
λεχεί	-	Wavelength of excitation spectrum maximum
λmax	-	Wavelength maximum
Ν	-	Refractive index
Φ_Δ	-	Singlet oxygen quantum yield
Φ_{F}	-	Fluorescence quantum yield
$\Phi_{\rm IC}$	-	Internal conversion quantum yield
Φ_p	-	Photodegradation quantum yield
ΦT	-	Triplet state quantum yield

$ au_{ m F}$	-	Fluorescence lifetime
$ au_0$	-	Natural lifetime
τ_{T}	-	Triplet state lifetime
$^{1}\mathrm{O2}\left(1\Delta_{\mathrm{g}}\right)$	-	Excited long-lived singlet state oxygen
$^{1}\mathrm{O2}\left(1\Sigma\mathrm{g}\right)$	-	Excited short-lived singlet state oxygen
O2 (3Σg)	-	Ground state molecular oxygen
S 0	-	Ground singlet state
S 1	-	Excited singlet state
S 0	-	Ground singlet state
T1	-	First excited triplet state
T2	-	Second excited triplet state
Epa	-	Anodic peak potential
Epc	-	Cathodic peak potential
Е	-	Potential
E1/2	-	Half-wave potential
Ep	-	Anodic-to-cathodic peak potential separation
Ipa	-	Anodic peak current
Ipc	-	Cathodic peak current

LIST OF ABBREVIATIONS

А	-	Absorbance
ADMA	-	Tetrasodium α , α -(anthracene-9,10-diyl) dimethylmalonate
APCE	-	Absorbed photon-to-current conversion efficiency
CD-RW	-	Rewritable optical media (compact disc)
СТ	-	Charge-transfer transitions
CEL	-	Cremophor EL
DBU	-	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	-	Dichloromethane
DMF	-	N,N-dimethylformamide
DMSO	-	Dimethylsulphoxide
DSSCs	-	Dye-sensitized solar cells
ET	-	Energy transfer
EY	-	Eosin-Y
FF	-	Fill factor
FTO	-	Fluorine-doped tin oxide glass
ITO	-	Indium-doped tin oxide glass
H ₂ Pc	-	Metal-free phthalocyanine
НОМО	-	Highest occupied molecular orbital
IPCE	-	Incident photon-to-current conversion efficiency
IC	-	Internal conversion
IR	-	Infrared
ISC	-	Intersystem crossing
LMCT	-	Ligand-to-metal charge transfer
LUMO	-	Lowest unoccupied molecular orbital
MLCT	-	Metal-to-ligand charge transfer
MOCPc	-	Octacarboxy metallophthalocyanine
MPc	-	Metallophthalocyanine
³ MPc*	-	Excited triplet state species of metallophthalocyanines

MPcSmix	-	Differently sulfonated metallophthalocyanine
MTSPc	-	Tetrasulfonated metallophthalocyanine
MTCPc	-	Tetracarboxy metallophthalocyanine
PBS	-	Phosphate buffered solution
Pcs	-	Phthalocyanines
PDT	-	Photodynamic therapy
TBAI	-	Tetrabutylammonium Iodide
THF	-	Tetrahydrofuran
SCE	-	Saturated calomel electrode
SEM	-	Scanning electron microscope
SDAs	-	Structure directing agent
SOC	-	Spin-orbit coupling
UV/Vis	-	Ultraviolet/visible
VR	-	Vibrational relaxation
QMPc	-	Quaternized metallophthalocyanine
UnQMPc	-	Unquaternized metallophthalocyanine
Q(T-2-Py)MPc	-	Quaternized tetra- 3,2-(2-pyridyloxy) metallophthalocyanine
UnQ(T-2-Py)MPc	-	Unquaternized tetra- 3,2-(2-pyridyloxy) metallophthalocyanine

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CHAPTER ONE

INTRODUCTION

1.1 Phthalocyanines

1.1.1 History and discovery

The first phthalocyanine complex was reported in 1907. The complex was discovered accidentally by Braun and Tcherniac as a by-product during the synthesis of *o*-cyanobenzamide from phthalamide [1-3].

This complex was first observed as an unknown insoluble bluish compound which was later identified as a metal-free phthalocyanine. Then in 1927, the first copper phthalocyanine was synthesized by de Diesbach and coworkers when they tried to convert o-dibromobenzene into phthalonitrile but it was not correctly formulated [4]. The structural elucidation was later done by Linstead [5]. Iron Pc was also accidentally discovered in 1928, when a blue product was found in a reaction flask where only white product was expected at the Scottish Dyes Ltd [6-8]. At a later stage its structure was confirmed by X-ray crystallography in 1935 by Robertson showing that the phthalocyanine molecule is a rather planar molecule with a chemical formula C₃₂H₁₈N₈ for the unmetallated phthalocyanine [9, 10].

1.1.2 Structure and some applications of phthalocyanines

A phthalocyanine is conjugated, aromatic and symmetrical molecule that consists of 32 carbon, 8 nitrogen atoms and 16 hydrogen atoms and 2 hydrogens in the center of the ring that can be substituted upon addition of a central metal ion [11]. The Pc molecule consists of four isoindole units that are linked by four nitrogen atoms and they have a two-dimensional 18π electron conjugated system, in which more than 70 different metals and non-metals can be incorporated Fig. 1.1. The 18π electron system that surrounds the core center of these heterocyclic compounds

renders them chemical and thermal stability. This extended conjugation of the electron π system is known to be responsible for their blue-green color.



Figure 1.1: The structure of metallophthalocyanine

Phthalocyanines complexes can be engineered for many applications since they possess 16 available sites on their ring structure where many substituents can be introduced to modify the chemical properties for different technological applications. Substitution with different substituents either at the peripheral (β) or at the non peripheral positions (α) enhance solubility of these complexes [12-16].



Figure 1.2: The molecular structures of metallated (MPc) and unmetallated (H₂Pc) phthalocyanines

Metallated phthalocyanines (MPcs) Fig. 1.2 are of D_{4h} geometry while their unmetallated (H₂Pc) counterparts exhibit a D_{2h} symmetry. The variation on the geometry between MPcs and H₂Pc is a result of insertion of a metal ion to the cavity of the H₂Pc without disturbing the planarity. Replacing the two hydrogen atoms with a metal leads to an increase in symmetry from D_{2h} to D_{4h} . However some metal ions (such as Pb, Sb and Ta) do not perfectly fit in the cavity because of their larger ionic size. The size of the Pc cavity or the distance between the two adjacent nitrogen atoms is known to be 396 pm [17], large metal ions tent to distort the geometry of Pcs leading to a change in planarity to a square pyramidal and a reduction of the symmetry from D_{2h} to a C_{4v} symmetry [18-21]. Since their discovery, phthalocyanines have drawn much attention for a wide variety of applications due to their diverse and excellent structural, electronic,

chemical and optical properties [6]. Because of their bright beautiful blue-green color and their considerable thermal and photochemical stability, they have been widely used for coloring of clothes, e.g for dying blue jeans and other clothings, paints for plastics, inks in pens, and for contact lenses [16]. They are also used in ink jet printing [6], electrophotography and photocopying machineries [6, 22]. Emerging applications of phthalocyanines include their use in catalysis [23-26], photovoltaic or dye sensitized solar cells (DSSCs) [27-30], fuel cells [31], liquid crystal display devices [32,33], electrochemical sensors [34-37], electrochromic display devices [38-40], optical computer re-writable discs (CD-RW) [41,42], molecular electronics [43] and semi-conductor devices [43,44]. Water soluble Pcs have been considered as candidates for photodynamic therapy of cancer (PDT) since they can be easily injected into human blood stream [45-49] and they have been successfully used in Russia for PDT and cancer diagnosis in particular the aluminium sulfonated phthalocyanine (AlPcS_{mix}) [50], containing a mixture of differently sulfonated Pcs.

1.1.3 Synthesis of water soluble phthalocyanines

The synthesis of phthalocyanines in general can be achieved by either cyclotetramerisation of phthalonitriles precursors in the presence of a metal salt (for MPcs) and a catalyst. MPcs can also be obtained by the use of phthalimides, phthalic acids and other precursors such as phthalic anhydrides in the absence of a metal for unmetallated Pc and in the presence of a metal for the metallated counterparts [21, 51]. Water solubility in phthalocyanines can be achieved by direct introducing hydrophilic substituent such as carboxylic [52-54], sulfonic [55,56] and phosphonic [57,58] acids groups on the periphery of the Pc ring either for octasubsitiution or tetrasubstitution.

1.1.3.1 Negatively charged phthalocyanines

The first negatively charged phthalocyanine complexes to be synthesized were the tetrasulfonated copper phthalocyanines (CuTSPc in 1929 [59].

1.1.3.1.1 Sulfonated MPcs



Scheme 1.1: The synthesis of tetrasulfonated metallophthalocyanine (MTSPc) [56]

Tetrasulfonated anionic phthalocyanines (MTSPcs) can be synthesized using the well known Weber and Bush [56] method Scheme. 1.1, by heating under reflux the monosodium salt of 4-sulfonic acid, urea and appropriate metal salt in nitrobenzene, in the presence of ammonium molybdate as catalyst. Water solubility in MPcs can also be achieved by direct sulfonation of any unsubstituted Pc by heating it under reflux in the presence of ~30 % oleum at temperatures of about ~100°C [60]. A mixture of mono-, di-, tri- and tetra- sulfonated MPcs represented as

 $MPcS_{mix}$ are obtained since the degree of sulfonation is uncontrollable during the preparation of these complexes. It has been observed that the temperature, reaction time and the central metal ion plays a vital role in the control of the formation of sulfonates on the ring [61].



1.1.3.1.2 Carboxylated MPcs

Scheme 1.2: Synthesis of water soluble octacarboxy metallophthalocyanine (MOCPc) [52, 62]

Octasubstituted phthalocyanines have been found to be isomerically pure compared to their tetrasubstituted counterparts, this makes octasubstituted Pcs to be easily purified.

The presence of isomers for tetrasubstituted phthalocyanines is known to enhance solubility; the unsymmetric rearrangements of the substituents at the periphery makes the tetra-substituted to be soluble than the octa-substituted phthalocyanines [63-65]. Octacarboxy more metallophthalocyanine complexes (MOCPc), Scheme. 1.2, can be obtained from a tetra-amide (tetra-amido metallophthalocyanine (MTAPc)) that is formed as an intermediate product of the reaction of benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride), urea (as a solvent and a source of nitrogen) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (as a catalyst) with appropriate amount of a metal salt [52, 62]. The amido groups are easily hydrolyzed and converted to carboxylic groups resulting to a water soluble MOCPc complex.





Scheme 1.3: Quaternization of tertiary amines to water soluble MPcs

Another way that has shown to be important in making phthalocyanines water soluble is by quaternization of tertiary amines resulting in positively charged water soluble complexes [66-68], Scheme 1.3. The quaternization of phthalocyanines (Scheme 1.3) can be achieved by first introducing substituents containing a tertiary amine at the periphery of the unquaternized MPc (UnQMPc). Then the tertiary amines are simply converted to quaternary nitrogen groups by methylation, this is achieved using methyl iodide or dimethyl sulfate (DMS), yielding a positively charged (cationic) water soluble quaternized MPc (QMPc).

1.1.3.3 Examples of known water soluble aluminium, gallium, silicon, titanium and zinc phthalocyanines of interest in this thesis

Molecular structure	Metal (M)	Abbreviated as:	Ref
	(OH)Al	(OH)AlPcS _{mix}	69
	(OH) ₂ Si	(OH) ₂ SiPcS _{mix}	69
R	ОТі	OTiPcS _{mix}	70
$R = SO_3$ or H	Zn	ZnPcS _{mix}	69

Table 1.1: Example of some known water soluble sulfonated mixed Pcs (MPcS_{mix})

The synthesis of sulfonated mixed phthalocyanines (Table 1.1) from unsubstituted phthalocyanines to form $AlPcS_{mix}$, $SiPcS_{mix}$, $TiPcS_{mix}$ and $ZnPcS_{mix}$ has been reported [69, 70]. The photophysicochemical properties of $AlPcS_{mix}$, $SiPcS_{mix}$, $TiPcS_{mix}$ and $ZnPcS_{mix}$ are known [69,70] and these complexes exhibit excellent photosensitizing behavior. The presence of a mixture of complexes that result due to random sulfonation is the major limitation, however these type of sulfonated mixed phthalocyanines are still preferable since they are easy to make regardless of the lack of selectivity and specificity upon sulfonation.

Table 1.2: Examples of some known water soluble anionic tetrasulfonated phthalocyanines containing central metals of interest in this thesis

Molecular structure	Metal Abbreviated as: (M)		Ref
NaO ₃ S	(OH)Al	(OH)AITSPc	71
	(OH)Ga	(OH)GaTSPc	72
	(OH) ₂ Si	(OH) ₂ SiTSPc	73
NaO ₃ S SO ₃ Na	Zn	ZnTSPc	74

The synthesis of water soluble tetrasufonated phthalocyanines (OH)AlTSPc [71], (OH)GaTSPc [72], (OH)₂SiPc [73] and ZnTSPc [74] is also well known. But little is known about the photophysicochemical properties of (OH)GaTSPc. (OH)AlTSPc and ZnTSPc are known to form

aggregates in solution and their photophysicochemical properties have been previously explored [71, 74].

Table 1.3: Examples of water soluble tetracarboxy and octacarboxyphthalocyanines containing central metals of interest in this thesis.

Molecular structure	Metal (M)	Abbreviated as:	Ref
ноос	(OH)Al	(OH)AITCPc	75
	(OH) ₂ Si	(OH) ₂ SiTCPc	76
ноос	Zn	ZnTCPc	75
соон соон	(OH)Al	(OH)AlOCPc	75
HOOC N N N N N N N N N N N N N N COOH HOOC COOH COOH	(OH)Ga	(OH)GaOCPc	This work
	(OH) ₂ Si	(OH) ₂ SiOCPc	This work
	ОТі	OTiOCPc	This work
	Zn	ZnOCPc	75

Table 1.3 shows structures of known tetra- and octa- carboxylated MPc complexes [75,76]. The photophysical and photochemical properties of the octacarboxy substituted (OH)AlOCPc and ZnOCPc are known [75]. Tetracarboxy Pcs (MTCPcs) are known to aggregate in aqueous solutions, while the corresponding octacaboxy Pcs (MOCPcs) are monomeric [75, 76]. There has been more work on MOCPcs compared to MTCPcs complexes. Even though Table 1.3 shows that MOCPcs are known, Si, Ti, Ga octacarboxy phthalocyanines are reported here for the first time.

 Table 1.4: Examples of water soluble quaternized cationic phthalocyanines

 containing central metals of interest in this thesis

Structures of nonperipheral (α) and peripheral (β) substituted MPcs





non-peripheral

peripheral

Compound	R - group	Metal (M)	ref
α-QT-3-PyClGaPc	+ CH ₃	ClGa	77
β-QT-3-PyClGaPc	+ Z CH3	ClGa	77
β-QT-2-PyZnPc	CH ₃	Zn	78

Table 1.4 lists a selection of known water soluble gallium [77] and zinc [78] phthalocyanines substituted with the quaternary pyridiloxy groups. Cationic water soluble phthalocyanines of aluminium, silicon and titanium substituted with quaternizable pyridyl groups are not known. Pyridyl groups are known to be excellent substituents to render water solubility in Pcs as they are easily converted to cationic quaternary ammonium groups which make the phthalocyanine molecule to be water soluble.

Aims of the thesis

The main aim of this work is to synthesize and design the phthalocyanine complexes that are water soluble and to explore their photophysical behavior. This works aim was also to use these water soluble phthalocyanine complexes (dyes) as photosensitizers for nanoporous ZnO films in dye sensitized solar cells (DSSCs). Previous studies have shown that other dye molecules containing substituents such as the sulfonate and carboxylate groups are preferred for dye

sensitized solar cells because they directly bind to semiconducting substrates such as ZnO or TiO_2 [79, 80] and form ester like linkages. Phthalocyanines (ZnTSPc) have been previously used as photosensitizers for ZnO based dye sensitized solar cells [81]. But the use of octacarboxy phthalocyanines or quaternized cationic phthalocyanines as photosensitizers for ZnO based solar cells has not been reported before and it is part of this thesis. Even though the photosensitizing behavior of AlTSPc, SiTSPc and ZnTSPc has been reported [81], the photosensitizing behavior of (OH)GaTSPc and OTiTSPc is reported for the first time in this thesis.

1.1.4 Electronic absoption spectra of pththalocyanines

Phthalocyanines are known to have high molar extinction coefficients of the order $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ [11, 17]. Their spectra is characterized by two main distinct absorption bands that arise as a result of π - π * transitions within the delocalized 18π electron system of the ring Fig. 1.3.



Figure 1.3: Ground state absorption spectra of metallated ((a) black) and unmetallated ((b) red) Pc

Fig. 1.3 shows a significant difference between the absorption spectra of metallated (**a**) and unmetallated (**b**) Pcs. There is a split of the Q-band in the absorption spectrum of the unmetallated phthalocyanine due to D_{2h} symmetry, and results from presence of the two protons at the core of the ring. The lowest unoccupied molecular orbital (LUMO) is non-degenerate (Fig 1.4) for H₂Pc giving rise to two allowed electronic transitions of different energies. The metallated Pc show an unsplit Q-band since there is one allowed transition, hence it has a D_{4h} symmetry and the LUMO is degenerate.



Figure 1.4: Electronic transitions in phthalocyanine complexes that results in Q and B bands

The highly intense band that is observed towards the near infrared region of the visible spectrum is known as the Q-band (Q_{00}) and is due to transitions from the a_{1u} of the highest occupied

molecular orbital (HOMO) to the e_g of the LUMO, Fig.1.4. The second band of lower intensity observed in the region between 300 to 400 nm is known as the B-band (or Soret band) and is a superimposition of B_1 and B_2 bands [16, 17, 82]. There are also three bands that are normally observed towards the UV region, the **N**, **L** and **C** bands, they are mainly observed when using transparent solvents. The charge transfer (**CT**) absorption bands Fig.1.3 are not common in all phthalocyanine complexes, and are observed only when the metal d-orbitals lie within the HOMO-LUMO gap Fig. 1.4 [83,84]. They can be assigned to either metal to ligand (MLCT) or a ligand to metal charge (LMCT) transfer.

1.1.5 Aggregation of phthalocyanines



Figure 1.5: Absorption spectra of a typical aggregated phthalocyanine; before (solid line) and after addition of a surfactant (dotted line)
Aggregation in phthalocyanines generally occurs as a result of co-planar association of phthalocyanine rings progressing from a monomer to a dimer and higher order aggregates [85-87], this can be due to high concentration of MPc complexes which brings the neighboring MPc rings in a close proximity. Fig.1.5 shows an absorption spectra of an aggregated phthalocyanine in water (solid line) and in the presence of a surfactant (dotted line), it is observed that in the presence of a surfactant there is almost complete collapse in the band due to aggregates (dimer) and the band due to the monomer is more pronounced.



Figure 1.6: Energy diagram showing the split in energy levels of the LUMO upon aggregation

Aggregation in Pcs can be due to bridging using a ligand or direct π - π interactions between two or more phthalocyanines rings [88, 89]. According to the exciton coupling theory [90, 91], Fig. 1.6, when two adjacent MPc complexes interact there is an appearance of four degenerate states leading to broadening of spectra showing that aggregates are formed. The four degenerate states arise from splitting of ¹E_u excited states, resulting in a pair of symmetry allowed transitions (solid arrows) and a pair of symmetry forbidden transitions (dotted arrows). The transitions that are symmetry forbidden will still occur to a small extent resulting in the spectral behaviors shown in Fig. 1.5, which is either broadening of the spectra or complete split in the Q-band and shifts in the Q-band to higher energies.

The nature of a solvent also plays a huge role in aggregation of Pc complexes and aggregation is highly pronounced in polar solvents such as water than in non polar solvents. When polar solvents are used there are stronger interactions that occur between Pc rings. Water soluble Pcs that have charged groups at their periphery can disaggregate in the presence of neutral surfactants [70, 78, 92-94]. The phthalocyanine complexes used in this thesis are all charged, due to substitution with cationic and anionic substituents at the peripheral positions and in some cases cremophor EL was used as a surfactant to disaggregate the Pcs.

1.2 Photophysical and photochemical parameters

1.2.1 Photophysical parameters

The photophysical and photochemical behavior of phthalocyanines can be simply explained by the Jablonski diagram Fig. 1.7 [95].



Figure 1.7: The Jablonski diagram displaying transitions of a molecule from its lower energy ground state to its higher energy excited state following irradiation with light; A = absorption, VR = vibrational relaxation, ISC = intersystem crossing, F = fluorescence, IC = internal conversion, P = phosphorescence, S₀ = singlet ground state, S₁ = singlet excited state and T₁ = 1^{st} excited triplet excited state, T₂ = second excited triplet state.

When a molecule absorbs light (A) its electrons are excited causing the overall excitation of the molecule from its lower energy singlet ground state (S_0) to the higher vibronic energy level of the first singlet excited state (S_1). The molecule will then loose energy from the higher vibronic

level through some vibrational relaxation processes (**VR**) to a lower vibronic energy level. From the lowest vibronic level of (S_1), the molecule can undergo (i) fluorescence (**F**) to the ground state (S_0), (ii) give off energy by non-radiative release of heat to its surroundings through internal conversion (**IC**) or, (iii) undergo intersystem crossing (**ISC**) to the 1st excited triplet state energy level (T_1). The change of multiplicity in **ISC** is spin-forbidden according to the selection rules, though it still occurs to some extent as a result of the spin-orbit coupling (SOC). Paramagnetic compounds or atoms with high nuclear charge (heavy atoms) such as indium [96, 97] and lead enhance (**ISC**). From the triplet state the molecules will still lose energy via **IC** or emit light through the process of phosphorescence (**P**). When the ground state molecular oxygen is present in the system the molecule can give its energy to the ground state molecular oxygen to produce singlet oxygen through photosensitization.

1.2.1.1 Fluorescence yields and lifetimes

Fig. 1.8 displays the absorption, fluorescence emission and excitation spectra of a typical MPc complex. The fluorescence of MPcs is observed at longer wavelengths compared to the absorption spectrum and is a mirror image of the absorption spectrum for non aggregated complexes. The fluorescence excitation is identical to the absorption spectrum for non aggregated Pcs [98]. For aggregated complexes the absorbance is observed as non mirror image to the fluorescence emission because dimers are known to be non photoactive [69].



Figure 1.8: The typical ground state electronic absorption (doted black), fluorescence excitation (solid red) and emission (solid black) of an MPc

The Stoke's shift in MPc complexes is estimated by calculating the distance between the Q-band absorption spectrum and the fluorescence spectrum maxima provided the molecule has exactly the same absorbance maxima to the excitation spectrum. The Stokes shifts of less than 10 nm are observed for Pc complexes, however the value of the Stokes shift can be affected significantly by the rigidity of the environment, solvent polarity or viscosity and temperature. Fluorescence quantum yields and lifetimes are photophysical properties that determine and quantify the efficiency of light emitting molecule. For phthalocyanine complexes the fluorescence quantum

yields and lifetimes can vary greatly depending on the nature of substituents, central metal, refractive indices of the solvents, pH used and temperature [99].

The fluorescence quantum yield (Φ_F) can be generally defined as the number of photons emitted relative to the number of photons absorbed and this is illustrated in Equation 1.1.

$$\Phi_{F} = \frac{\text{No. of emitted photons}}{\text{No. of absorbed photons}}$$
1.1

The fluorescence quantum yield (Φ_F) can be determined by comparative methods [100, 101] using fluorescence quantum yield of a known Pc as a standard, in this work ZnPc in DMSO has been used (Φ_F) = 0.20 [102]. The quantum yield of fluorescence is then calculated according to Equation 1.2.

$$\Phi_F = \Phi_F^{std} \frac{F.A_{std}.n^2}{F_{std}.A.n_{std}^2}$$
1.2

where *F* and F_{Std} are the areas under the fluorescence curves of the MPc derivatives and the used standard used. *A* and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, and *n* and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively.

The natural radiative (τ_0) lifetimes can be determined using PhotochemCAD program [103, 104] which uses the Strickler-Berg equation [105] by using the experimentaly obtained absorption and fluorescence emission spectra. Lifetimes of fluorescence (τ_F) can then be calculated from the radiative lifetime using fluorescence quantum yields, Equation 1.3.

$$\Phi_F = \frac{\tau_0}{\tau_F}$$
 1.3

Fluorescence lifetimes for MPc complexes are short, with a typical time scale of the order of picoseconds (ps, 10^{-12}) to nanoseconds (ns, 10^{-9}) [106] and strongly depend on the solvent used, the nature of the central metal ion, and nature of substituents on the Pc molecule.

1.2.1.2 Triplet yields and lifetimes

The triplet quantum yields can be defined as the ability of a photosensitizer to convert absorbed quanta of light to the first excited triplet state (T_1). The excited state of a photosensitizer can be studied using a technique known as laser flash photolysis. This technique provides information on the molecules that are undergoing the intersystem crossing (ISC) to the triplet state. The triplet-triplet absorption from T_1 to a higher energy state T_n of the excited molecules and the lifetime of the excited molecule are monitored [107]. A triplet decay curve from the flash photolysis experiment is obtained as a plot of change in absorbance (ΔA) versus time in seconds, following laser flash photolysis Fig. 1.9. From the triplet decay curve Fig. 1.9, lifetimes of the triplet state may be obtained. For most Pcs the triplet-triplet absorption is observed at a region of approximately 500 nm.



Figure 1.9: A typical triplet decay curve of an MPc following laser flash photolysis

The triplet lifetimes (τ_T) of the transients are conveniently determined from a software program such as OriginPro 7.5 that is used in fitting the triplet decay curve (red line shows fitting), in Fig. 1.9.

The triplet quantum yield (Φ_T) can be determined using comparative methods [102, 108], which involves the use of a known triplet yield (Φ_T) of a standard. Triplet yields are the calculated using Equation 1.4

$$\Phi_T = \Phi_T^{std} \frac{\Delta A_T \cdot \mathcal{E}_T^{std}}{\Delta A_T^{std} \cdot \mathcal{E}_T}$$
1.4

where ΔA_T and ΔA_T^{std} are the changes in triplet state absorbance of a Pc molecule and the standard respectively. ε_T and ε_T^{std} are the triplet state molar extinction coefficients for the Pc molecule and the standard, respectively. Φ_T^{std} is the triplet quantum yield of the standard. The values of ε_T and ε_T^{std} are normally determined by use of the singlet depletion method [109], using Equations 1.5a and 1.5b.

$$\varepsilon_T = \varepsilon_S \frac{\Delta A_T}{\Delta A_S}$$
 1.5a

$$\varepsilon_T^{Std} = \varepsilon_S^{Std} \frac{\Delta A_T^{Std}}{\Delta A_S^{Std}}$$
 1.5b

this involves the use of the change in absorbance of the ground singlet states of both the sample (ΔA_S) and the standard (ΔA_S^{Std}) , the changes in the triplet state absorptions of the sample (ΔA_T) and the standard (ΔA_T^{Std}) and the molar extinction coefficients of their singlet ground state for both the sample (ε_S) and the standard (ε_S^{Std}) .

Assuming no energy loss by internal conversion, the triplet state yield and fluorescence are two complementary photophysical processes and they should sum up to one. It is expected that high triplet state quantum yield (Φ_T) values be accompanied by low yields of fluorescence (Φ_F) and vice versa.

1.2.2 Photochemical parameters

1.2.2.1 Singlet oxygen



Figure 1.10: The Jablonski diagram displaying energy transfer (ET) from an excited photosensitizer (³MPc^{*}) to ground state molecular (³O₂) oxygen leading to the production of singlet oxygen (¹O₂)

The process of photosensitization is shown in Fig. 1.10. The excited triplet state molecule $({}^{3}MPc^{*})$ transfer its energy to ground state triplet molecular oxygen $({}^{3}O_{2})$, since the energy of the triplet state molecule $({}^{3}MPc^{*})$ is higher (~110 – 126 kJ mol⁻¹) than the energy required (~94 kJ mol⁻¹) for the excitation of ground state molecular oxygen [110, 111], to form excited singlet oxygen $({}^{1}O_{2})$.



Scheme 1.4: Type II mechanism for the photoreaction of MPc leading to the production singlet oxygen

The mechanisms involved in the singlet oxygen generation process include the Type II mechanism, Scheme 1.4 [112]. There are other mechanisms through which the photosensitization process could occur, these may be either via the Type I or Type III. Type I mechanism involves free radicals [113]. While in Type III, electron transfer from the substrate to the excited state sensitizer may occur [114]. The involvement of Type II mechanism is widespread in oxygen-rich and air saturated environments where the oxygen concentration is very high and it is believed that Type II mechanism is a dominant singlet oxygen production pathway in photosensitization reactions. The singlet oxygen quantum yields (Φ_{Δ}) can then be calculated Equation 1.6

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \cdot \frac{RI_{abs}^{Std}}{R^{Std}I_{abs}}$$
 1.6

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield of a known standard, R and R^{Std} are the singlet oxygen quencher (e.g tetrasodium α, α -(anthracene-9,10-diyl) dimethylmalonate (ADMA) [115]) photobleaching rates in the presence of the respective MPcs under investigation and of the standard respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the MPcs and the standard, respectively. In this method of calculating the singlet oxygen, the quencher is normally mixed with the photosensitizer solution and the mixture is irradiated. The decrease of the quencher absorption maximum is monitored spectroscopically and serves as a monitor for singlet oxygen generation.





Scheme 1.5: Photodegradation of a photosensitizer following irradiation with light in the presence of singlet oxygen

Photodegradation is the process of breakdown of a photosensitizer molecule oxidatively (on irradiation) into lower molecular weight fragments. It determines the photostability of MPc molecules and is experimentally identified by a collapse in the intensity of the Q-band absorption maxima without the appearance of new peaks in the visible region. This process is strongly influenced by the nature of the central metal, the substituents at the periphery of the photosensitizer, the solvent used and aggregation. Photodegradation of MPcs, Scheme 1.5, occurs by Diels-Alder [4 + 2] cycloaddition mechanism [116], where by singlet oxygen species ($^{1}O_{2}$) present in the system adds across the carbons of the pyrrole on the photosensitizer. Another possibility is that the singlet oxygen species may add across the carbon nitrogen bond (C=N) followed by cleavage at the meso position [117]. The main product of photodegradation is the precursor, phthalamide.

Photodegradation/photobleaching quantum yields (Φ_{Pd}) can be calculated using Equation 1.7 as the fraction of the number of MPc molecules degraded per quanta of light absorbed [69, 75, 118].

$$\Phi_{Pd} = \frac{\Delta A}{\Delta t} \cdot \frac{V}{\varepsilon} \cdot \frac{1}{I_{abs}}$$
 1.7

where ΔA is the change in absorbance of the photosensitizer, Δt is the change in time of irradiation, V is a reaction volume and ε is the ground state molar extinction coefficient of the Pc molecule under investigation. I_{abs} is the overlap integral of the radiation source intensity and the absorption of the Pc in the region of the interference filter transmittance and may be calculated using Equation 1.8.

$$I_{abs} = \frac{\alpha SI}{N}$$
 1.8

where α is the fraction of light absorbed, *I* the light intensity, *S* the irradiated cell area and N_A is the Avogadro's constant.

It is believed that the presence of electron-withdrawing substituents on the MPc ring tends to stabilize the ring resulting in difficulty of oxidation of the MPc ring and slow down in the photodegradation process [119]. The presence of electron-donating substituents has been found to speed up the photodegradation process [119]. In aqueous media, photodegradation has been found to be lower due to high concentration of aggregated MPcs [120, 121]. It has been documented that in some cases the aggregated species may transform into to monomers in some photosensitizers during the photo-irradiation [122].

1.2.3 Photochemical and photophysical behavior of Al, Ga, Si, Ti and Zn Pcs

The photophysical and photochemical behavior of charged water soluble Zinc complexes is well known and widely reported especially for the ZnOCPc, ZnPcS_{mix}, and ZnTSPc [69, 74, 75, 78, 123]. Shown in Table 1.5 are the photophysicochemical parameters of some MPc complexes in different solvents [69, 70, 71, 75, 78, 77, 124-126]. Interest in this thesis will be paid on the MPc studied in aqueous media for biological application purposes. The fluorescence quantum yields values are large in particular for the MPc complexes containing lighter atoms such as the Al and Si, however low fluorescence yields are seen for those MPc complexes containing heavier atoms (i.e. Ga, Ti and Zn). These behavior can be due to the fact that heavy atoms encourages intersystem crossing resulting in less fluorescing molecules [69]. Higher triplet yields for heavy atoms are then expected. MPc with diamagnetic metals or metals with closed shells such as Zn or Al are known to have high Φ_T values and long triplet lifetimes (Table 1.5)

Compond	Solvent	Φ_{F}	Φ_{T}	Φ_{Δ}	Φ_{P}	$ au_{T}$	Ref
AIPcS _{mix}	PBS DMSO	0.44 0.39	0.44 0.52	0.42 0.48	0.40 5.79	2.93 800	69 69
SiPcS _{mix}	PBS DMSO	0.34 0.29	0.45 0.58	0.49 0.52	0.71 7.35	2.90 430	69 69
TiPcS _{mix}	CH₃OH PBS DMSO	0.18 0.03 0.42	-	-	-	-	70 70 70
ZnPcS _{mix}	PBS PBS + Triton X DMSO	0.16 0.21 0.14	0.53 0.61 0.86	0.45 0.54 0.72	3.657.0213.65	2.95 2.37 530	69 69 69
AITSPc	PBS DMF	0.13 0.56	0.36 0.20	0.34	0.24	560	71 124
GaTSPc	CH ₃ OH	-	0.36	0.38	-	420	125
ZnTSPc	Aqueous DMSO	0.32 0.07	0.56 0.88	0.46	4.03	245 470	123 102
AITCPc	DMSO	0.33	0.50	-	-	340	75
SiTCPc	DMSO	0.27	0.48	0.33	-	760	76
ZnTCPc	DMSO	0.16	0.82	-	-	240	75
AlOCPc	DMSO DMSO	0.44	0.34	0.12	-	1270	75 126
ZnOCPc	DMSO pH 10	0.24	0.62	0.52	-	480	75 126
α-QClGaT-3-PyPc	DMSO Water	0.19 0.07	-	0.53 0.41	-	-	77
β-QClGaT-3-PyPc	DMSO Water	0.24 0.12	-	0.51 0.44	-	-	77
β-QZnT-2-PyPc	Water	0.11	0.43	0.29	-	10	78

Table 1.5: Photophysicochemical properties of some soluble MPc complexes

The presence of aggregates in solution is known to alter the photophysicochemical properties of MPc complexes since aggregates are known not to be photoactive [127]. In this thesis the photophysicochemical studies of the aggregated MPcs will be done in the presence of a surfactant that mimic the body fluids (i.e lipids) as disaggregating agents and compared to the studies without surfactant. No work has been reported on the photophysicochemical properties of water soluble cationic Ti complexes. Little is known on the photophysicochemical properties of water soluble silicon complexes, to our knowledge only the sulfonated negatively charged (SiPcS_{mix}) [69], SiTSPc [73] and tetracarboxy (SiTCPc) [76] are known. This work reports on the positively charged gallium (III) phthalocyanine complexes which shows good photophysical and photochemical properties [128]. Only few water soluble gallium complexes are known [77, 125]. In this thesis the photophysicochemical behavior of water soluble Al, Ga, Si, Ti and Zn in aqueous media and in the presence of a surfactant will be investigated.

1.3 Photoelectrochemical and electrochemical properties

1.3.1 Electrochemical properties

1.3.1.1 Electrochemistry of phthalocyanines in general

The reduction-oxidation (redox) properties of MPcs can be monitored using the electrochemical techniques [70, 36, 129] such as the cyclic voltammetry and square wave voltammetry, and other techniques such as photochemical [71] and spectroelectrochemical methods [129]. Fig. 1.11 shows typical simplified energy diagram of a neutral, one electron ring reduced and oxidized MPc complex.



Figure 1.11: Energy diagram displaying electronic transitions upon ring oxidation and reduction of an MPc complex

MPc exist as a dianion (MPc²⁻) in its neutral (ground) state Fig. 1.11. The redox reactions in MPc can either occur at the ring or at the metal, in some cases they can be observed on both the metal and the ring depending on the metal used. The MPc ring can undergo only two oxidation processes, due to removal (loss) of the two electrons from the $a_{1u}(\pi)$ of the HOMO resulting in (MPc¹⁻) and (MPc⁰) Fig. 1.11. There are four ring based reduction processes that can occur in MPc complexes, due to the addition (gain) of electrons to the empty $e_g(\pi^*)$ of the LUMO resulting in the formation of (MPc³⁻), (MPc⁴⁻), (MPc⁵⁻) and (MPc⁶⁻) respectively. Electron donating groups makes the MPc ring to be easily oxidized and electron withdrawing groups make MPc ease to reduce [52].

1.3.1.2 Electrochemical behavior of some Al, Ga, Si, Ti, and Zn phthalocyanines

The central metal ion in the phthalocyanine ring cavity can undergo redox processes depending where it is situated on the periodic table. For group 12 MPcs such as the ZnPcs, group 13 such as the AlPcs and GaPcs, and the group 14 such as SiPcs [130], only the ring based redox processes are observed.

Table 1.6: Half-wave potentials $(E_{1/2})$ (V vs Ag|AgCl) electrochemical data of some titanium Pc complexes in DMF using tetrabutyl ammonium fluoroborate as supporting electrolyte.

Compound	Ti ^{IV} Pc ²⁻ / Ti ^{III} Pc ²⁻	Ti ^{III} Pc ²⁻ / Ti ^{II} Pc ²⁻	Ti ^{II} Pc ²⁻ / Ti ^{II} Pc ³⁻	Ti ^{IV} Pc ¹⁻ / Ti ^{IV} Pc ²⁻	Ti ^{IV} Pc ⁰ / Ti ^{IV} Pc ¹⁻	Ref
α-ΟΤΙΤΑΡς	-0.45	-0.84	-1.30	0.75	0.91	129
β-ΟΤΙΤΑΡς	-0.42	-0.80	none	0.75	none	129
α-OTi[(SC ₆ H ₅) ₄ Pc]	-0.07	-0.37	-1.20	none	none	131
α-OTi[(SCH ₂ C ₆ H ₆) ₄ Pc]	-0.07	-0.46	-1.33	none	none	131
OTi[(SC ₆ H ₅) ₄ Pc]	-0.09	-0.42	-1.28	none	none	131
OTi[(SCH ₂ C ₆ H ₆) ₄ Pc]	-0.09	-0.40	-1.30	none	none	131

Shown in Table 1.6 are half-wave potentials of some titanium phthalocyanine complexes in nonaqueous media [129, 131]. Metal based redox properties are observed for TiPcs since the dorbital of the Ti metal have accessible energy levels that lie between the HOMO-LUMO gap of the Pc ring. Little is known on the solution electrochemistry of Al, Ga, Si, Ti and Zn phthalocyanine complexes in aqueous media. Hence in this thesis the electrochemistry of the some MOCPc in aqueous media is investigated.

1.3.2 Photoelectrochemical properties

A photoelectrochemical (photovoltaic) cell is unique in that the redox properties of a system are investigated under illumination with light.

1.3.2.1 Brief history and working principles of dye sensitized solar cell (photoelectrochemical cell)

The dye sensitized solar cell (DSSC) concept was discovered and developed in the 1960s [132]. Great attention has been paid to dye sensitized solar cells (DSSCs) as they have several advantages such as low manufacturing costs, effectiveness, flexibility and are environmentally friendly. However DSSCs suffer from low energy conversion efficiencies [133]. Over the years there has been intensive research undertaken to optimize the parameters of these photoelectrodes by using different materials such as organic dyes, which are efficient photon absorbers, and combining them with transparent metal oxides semiconductors in order to convert sunlight to useful electricity [133-139]. Recently a remarkable work by Gratzel and coworkers [140] resulted in optimization of these photo-electrodes and a conversion efficiency of approximately 11 % was achieved using the ruthenium based metal complexes.



Figure 1.12: Diagrammatic representation of working principle of a dye sensitized solar cell

A DSSC, Fig. 1.12, is a photoelectrochemical device which effectively utilizes a property of nanocrystalline wide bandgap metal oxide semiconductor such as ZnO [138, 139] or TiO_2 [140] porous electrode. The key is to employ substrates that are optically transparent with large bandgap energy to enhance the power output by increasing the cell's voltage [141]. A variety of other metal oxide substrates such as, In_2O_3 [142, 143], Fe_2O_3 [144], CeO_2 [145] and SnO_2 [142, 143] have been widely investigated for the use in DSSCs. However some substrates such as the

InSb are not suitable in DSSC applications as their bandgap energy is too small (0.17 eV) and they are optically opaque [146]. In this work ZnO will be employed since it is optically transparent and has a larger band gap of (3.4 eV). Basically the cell in Fig. 1.12 consists of a fluorine-tin oxide (FTO) deposited with nanoporous ZnO (FTO/ZnO) together with the dye of interest on working electrode, an electrolyte (I^{-}/I^{3-}) as a redox mediator and platinum (Pt) as counter electrode. Under illumination with sunlight, the dye absorbs the light and gets excited from its lower energy ground state (HOMO) to higher energy (LUMO). The excited state dye gets oxidized by an electron injection to the conduction band (CB) of the semiconductor (ZnO). Simultaneously the oxidized dye return to its ground state (HOMO) and gets regenerated (reduced) by stripping an electron from the donor in the electrolyte. The electric field inside the bulk material (ZnO/FTO) allows extraction of the injected electron in the conduction band (CB) of the semiconductor to be conducted away and flows to the external circuit. The redox mediator gets back to its reduced state by receiving an electron from the counter electrode (Pt) which completes the circuit. Through the processes occurring within the cell, radiant energy is converted into electricity [147]. The optimization of DSSC has been a demanding task as it is highly complex and there are many factors that affect the performance of a DSSC; these includes the energy level alignment between dye and substrate at the interface and also the morphology of the first mono-layer (ML). For a successful electron injection from the dye (LUMO) to the conduction band of the semiconductor, it is important that the LUMO of the dye is above the conduction band minimum of the semiconductor [148]. Previous studies have shown that organic dyes with negatively charged substituents, such as -SO₃⁻ and -COO⁻, bind directly to the nanoporous semiconductors forming self assembled linkages [138-140, 149]. In this thesis

quaternized cationic and anionic (-SO₃⁻ and -COO⁻) phthalocyanine molecules will be employed as photosensitizers for nanoporous ZnO semiconductor.

There are a variety of parameters that can be optimized to define the dye sensitized solar cell's performance. These parameters include the incident photon to current conversion efficiency (IPCE) also known as the external quantum efficiency, which determines the number of photogenerated electrons per photon absorbed. The IPCE can be determined by comparative methods using Equation 1.9 [150]:

$$IPCE = \frac{I_{p(\lambda)}}{P_{(\lambda)}\lambda} \cdot 1240 \ W \cdot nm \cdot A^{-1}$$
1.9

where $I_{p(\lambda)}$ and $P_{(\lambda)}$ are the photocurrent density (mA/cm²) and incident power density of light (mW/cm²), respectively at the absorption maxima, λ of the dye used. In conjunction with the IPCE, is the internal quantum efficiency also known as the absorbed photon to current conversion efficiency (APCE). It determines the number electrons collected to the external circuit per single absorbed photon and can be obtained using Equation. 1.10 [151]:

$$APCE = \frac{IPCE}{1 - 10^{-A}}$$
 1.10

where A is the true absorbance of the dye molecule adsorbed to the surface of the electrode.

The photovoltaic fill factor (FF) is a parameter which determines the maximum power from a solar cell. The FF is defined as the ratio of the maximum power from the solar cell to the product of V_{oc} and I_{sc} and is obtained using Equation 1.11 [151]:

$$FF = \frac{I_{mpp} \times V_{mpp}}{I_{sc} \times V_{oc}}$$
1.11

where I_{mpp} and V_{mpp} are the current and voltage at the maximum power point of the current– voltage (I-V curve) characteristics, V_{oc} is the open circuit voltage, while I_{sc} is the short-circuit current.

The photovoltaic power conversion efficiency of a DSSC (η_e) determines the overall efficiency and it can be determined by using Equation 1.12 [151]:

$$\eta_e = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}}$$
1.12

where P_{in} is the incident light power density, which is standardized at 100 mW/cm² for solar cell testing with a spectral intensity distribution matching that of the sun on the earth's surface at an incident angle of 48.2 °C, which is called the AM 1.5 (AM = air mass) spectrum [151,152]. In this thesis optimization of the parameters will be undetaken using phthalocyanines as a photon absorbers (dye).

1.3.2.2 Deposition of zinc oxide (ZnO) nanoporous substrate on FTO substrates and surface morphology of deposited films



Figure1.13: Schematic representation of the controlled growth of ZnO film on conductive substrate

ZnO nanoporous (**B**) films can be achieved by electrochemical deposition from aqueous zinc salt solutions on electrically conductive substrates (**A**) (ie FTO or ITO) Fig. 1.13. The electrodeposition of ZnO is a low temperature process; therefore the deposition is compatible with thermally sensitive substrates opening this deposition route for a variety of applications [153-155]. Structural directing agents (SDAs) such as eosin Y [139, 149] are then added to the

deposition bath to control the growth of the ZnO on the substrate by blocking the growth leading to a formation of a porous structure (**B**). The SDAs can then be easily desorbed from the surface to prepare an open sponge-like (**C**) structure resulting in a high surface area for further reloading of the dye molecules. In this thesis electrodeposition of nanoporous ZnO has been employed because of its flexibility on the control of the size growth, and its environment friendliness for industrial applications [141, 149, 156], compared to other methods that require specific conditions such as high vacuum and temperature. The electrochemical deposition of ZnO is as follows [153-156]; first is the reduction of oxygen leading to the generation of hydroxide ions at the cathode occurs by Equations 1.13

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-(E^0 = +0.16 \text{ V vs. SCE})$$
 1.13

Secondly (Equation 1.14) the hydroxide ions produced react with the zinc ions (Zn^{2+}) , zinc hydroxide is precipitated out. The zinc hydroxide is then dehydrated to form crystalline ZnO at the electrode surface.

$$\operatorname{Zn}^{+2} + 2\operatorname{OH}^{-} \to \operatorname{Zn}(\operatorname{OH})_2 \to \operatorname{ZnO} + \operatorname{H}_2\operatorname{O}$$
 1.14

1.3.2.3 Review of photoelectrochemical properties of water soluble phthalocyanines deposited on FTO/ZnO substrate

Little is known on the photoelectrochemical sensitization of nanoporous ZnO films with water soluble phthalocyanines (dyes). Phthalocyanines are good photon absorbers because of their higher intense absorption band near the infrared region of the visible spectrum and their high absorption coefficiencies. The thermal stability of phthalocyanines and their higher band gap energy of about \sim 2 eV which is a good match to the solar spectrum give an additional advantage for application in DSSCs.

Table 1.7: Some photoelectrochemical properties of AITSPc, SiTSPc andZnTSPc phthalocynine complexes deposited on FTO/ZnO substrates

Dye	Dye conc on the film (mmol.cm ⁻³)	Highest IPCE (%)	Photocurrent density (μA.cm ⁻²)	Sensitization efficiency (µA.nmol ⁻¹)	Ref
AITSPc	0.0793	0.092	1.3	0.15	81
SiTSPc	0.0119	0.389	4.8	3.40	81
ZnTSPc	0.0337	0.122	1.5	0.27	81

The photoelectrochemical properties of some tetrasulfonated Al, Si and Zn are known [28, 81, 157] (Table 1.7). Low sensitization efficiencies were observed due to high aggregation tendencies of these complexes. Other water soluble tetrasulfonated phthalocyanines such as nickel, cobalt and ion have been used on the electrodeposition of ZnO to control the morphology, although their photoelectrochemical properties have not been fully explored as photosensitizers

[158, 159]. In this thesis further optimization of electrodeposited nanoporous ZnO films sensitized with water soluble cationic and anionic dyes to improve the photovoltaic cell performance will be investigated.

1.4 Summary of Aims

The aims of this thesis are summarized as follows:

- Synthesis and spectroscopic characterization of water soluble anionic MOCPc complexes (M = Ga, Si, and Ti), MTSPc complexes (M = Ga, Si, and Ti) (Table 1.8), and quaternised water soluble cationic β-2,(3)-(tetra-2-pyridyloxy phthalocyanines (Q(T-2-Py)MPc) (M = Al, Ga, Si, and Ti) (Table 1.9).
- 2. To investigate and compare the photophysicochemical behavior (fluorescence quantum yields, triplet quantum yields and lifetimes, singlet oxygen and photodegradation quantum yields) of the MPc complexes, in water alone and in the presence of a surfactant cremophor EL.
- 3. Preparation and spectroscopic characterization of electrodeposited nanoporous ZnO films, deposited with MTSPc, MOCPc (Table 1.8) and Q(T-2-Py)MPc (Table 1.9). Furthermore to investigate the photoelectrochemical behavior (fill factors (FF), incident photon to current conversion efficiency (IPCE), absorbed photon to current conversion efficiency (APCE), current to voltage characteristics (I-V), and photovoltaic conversion efficiencies) of the MOCPcs, MTSPcs and Q(T-2-Py)MPcs complexes on the ZnO films.

Molecular structure	Metal (M)	Abbreviated as:	
соон соон	(OH)Al	(OH)AlOCPc	
	(OH)Ga	(OH)GaOCPc	
	(OH) ₂ Si	(OH) ₂ SiOCPc	
ноос (N) Соон соон соон	ОТі	OTiOCPc	
	Zn	ZnOCPc	
NaO_3S N = N N = N N = N N = N	(OH)Ga	(OH)GaTSPc	
	(OH) ₂ Si	(OH) ₂ SiTSPc	
	OTiPc	OTiTSPc	
NaO ₃ S SO ₃ Na	Zn	ZnTSPc	

 Table 1.8: Examples of water soluble octacaboxylated (MOCPc) and

 tetrasulfonated (MTSPc) anionic Pcs synthesized and used in this thesis

Table 1.9: Examples of Unquaternized (UnQ(T-2-Py)MPcs) and their quaternized (Q(T-2-Py)MPcs) cationic water soluble derivatives synthesized and used in this thesis

Molecular structure	Metal (M)	Abbreviated as:	
	CIAI	UnQ(T-2-Py)ClAlPc	
	ClGa	UnQ(T-2-Py)ClGaPc	
	Cl ₂ Si	UnQ(T-2-Py)Cl ₂ SiPc	
R	ОТі	UnQ(T-2-Py)OTiPc	
	CIAI	β-Q(T-2-Py)ClAlPc	
	ClGa	β-Q(T-2-Py)ClGaPc	
RO CH ₃ NI ⁺	Cl ₂ Si	β-Q(T-2-Py)Cl ₂ SiPc	
R 2SO ₄ ²⁻	ОТі	β-Q(T-2-Py)OTiPc	

CHAPTER TWO

EXPERIMENTAL

2.1 Materials

- For synthesis and characterization: Benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride), 4-sulfophthalic acid, aluminium trichloride, gallium trichloride, silicon tetrachloride, titanium butoxide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 2-hydroxypyridine, deuterated D₂O, DMSO-d₆, potassium carbonate (K₂CO₃), sodium chloride, zinc acetate, dimethylsulphate (DMS), urea, potassium bromide, ammonium chloride and ammonium molybdate were purchased from Sigma-Aldrich. Zinc chloride (ZnCl₂) was obtained from Chimica. Column chromatography was performed on a neutral alumina from Aldrich or silica gel 60 (0.04–0.063 mm) from Merck.
- **Photophysicochemistry:** Cremophor EL (CEL), unsubstituted zinc phthalocyanine and anthracene-9 and 10-bis-methylmalonate (ADMA) were purchased from Sigma-Aldrich
- **Photoelectrochemistry:** Acetonitrile and potassium iodide were purchased from Roth, iodine was obtained from Scharlau and ethylene carbonate was obtained from Fluka. Eosin Y, tetrabutylammonium iodide (TBAI) and potassium hydroxide were purchased from Sigma-Aldrich. The glue for electrode preparation was obtained from Araldite (Nichiban Co. Ltd.), a silver paste was obtained from DOTITE (Fujikura Kasei).
- Solvents: Sulfuric acid (98 %), nitric acid (55 %), hydrochloric acid (32 %), quinoline, dimethylsulphoxide (DMSO), methanol, n-hexane, chloroform, dichloromethane (DCM),

tetrahydrofuran (THF), acetone, ethanol and dimethylformamide (DMF) were purchased from SAARCHEM. All solvents used in this thesis were dried according to reported procedures [160] before use.

Electrochemistry: Ferrocene was obtained from DBH and was recrystalized from methanol before being used as internal standard for electrochemical measurements. Sodium hydroxide (NaOH) and sodium dihydrogen phosphate (Na₂HPO₄) were purchased from SAARCHEM. Phosphate-buffered saline (PBS) solution was prepared using appropriate amounts of (Na₂HPO₄) (1.37 g) and NaOH (0.014 g) dissolved in 100 mL ultra pure water (of resistivity 18.2 MΩcm), obtained from a Milli-Q Water System (Millipore Corp, Bedford, MA, USA) and was used for all aqueous solutions.

All other reagents were obtained from commercial supplies and used as received.

2.2 Equipment and Instrumental

Proton nuclear magnetic resonance (¹HNMR) spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer, infra-red (IR) spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR spectrometer, ground state electronic absorption spectra were recorded on a Cary 500 UVVis/ NIR spectrophotometer and fluorescence (excitation and emission) spectra were recorded on a Varian Eclipse spectrophotometer using a 1cm pathlength cuvette at room temperature. Elemental analysis was performed using a Thermo Flash EA 1112 series elemental analyzer and an Elementar Vario Micro Cube CHNS Analyser.



Figure 2.1: Schematic representation of a laser flash photolysis set-up

Laser flash photolysis experiments (shown in Fig. 2.1) were performed with light pulses produced by a Quanta-Ray Nd: YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda -Physik FL3002 dye (Pyridin 1 dye in methanol). Single pulse energy ranged from 2 to 7 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses.



Figure 2.2: Schematic representation of a photochemical set-up

Photo-irradiations for photodegradation or singlet oxygen determination were performed using a General electric Quartz line lamp (300W). A 600 nm glass cut off filter (Schott) and water were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 670 nm with a band width of 20 nm or 700 nm with a band width of 40 nm depending on the Q-band maxima of the Pc) was additionally placed in the light path before the sample Fig. 2.2. Light intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter (was found to be 3.12×10^{16} photons s⁻¹ for photobleaching and to be 1.25×10^{16} photons s⁻¹ for singlet oxygen studies).

Microwave irradiations (synthesis) were carried out in a Defy DM206T microwave oven using power of 1000 W.

Scanning electron microscope (SEM) pictures and laser microscopic images were obtained at Justus-Liebig University Giessen Germany using a JEOL JSM 840 scanning electron microscope at 5KV accelerating voltage and a KENYENCE VK-9700 Laser scanning Microscope.

Maldi-TOF mass spectrometry was carried out at the University of Stellenbosch (South Africa) using an ABI Voyager DE-STR Maldi TOF instrument.

2.3: Methods

2.3.1 Fluorescence and triplet (yields and lifetimes)

Fluorescence quantum yields were determined using Equation. 1.2, with unsubstituted ZnPc in DMSO ($\Phi_F = 0.20$) used as a standard [102]. For each study at least two independent experiments were performed for the quantum yield determinations. Both the sample and the standard were excited at the same relevant wavelength.

For the laser flash photolysis experiments, the MPc solution (absorbance ~ 1.5) was bubbled with nitrogen for 30 mins in 1 cm path-length spectrophotometric cell and irradiated at the Qband maximum with laser light from a Nd:YAG laser Fig. 2.1. Triplet quantum yields (Φ_T) were calculated using Equation. 1.4, unsubstituted ZnPc in DMSO ($\Phi_T^{Std} = 0.65$) [108], in DMF ($\Phi_T^{Std} = 0.58$) [161] and ZnTSPc in aqueous solution ($\Phi_T^{Std} = 0.56$) [150] were employed as standards. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

2.3.2 Singlet oxygen and photodegradation quantum yields

For singlet oxygen (Φ_{Δ}) determination, an air-saturated with oxygen solution of the MPc under investigation (~2.0 mL) containing a singlet oxygen quencher (ADMA), was prepared in the dark (Q-band absorbance ~ 0.2 in the final solution) and were placed in a 1 cm pathlength spectrophotometric quartz cell and illuminated at the Q-band region using a 300 W General electric quartz lamp as described above Fig. 2.2.

Photodegradation (Φ_P) quantum yields were determined in the same way as Φ_{Δ} except no quencher was added, Q-band absorbance was ~ 1.0.

The wavelength of the interference filter was chosen such that it was close to the Q-band absorption of the MPc of interest. The steady reduction in the Q-band absorption intensity with irradiation time was recorded and used for the calculation of Φ_{Pd} on P29 using Eq. 1.7. For singlet oxygen, the absorbance decay of the quencher (ADMA) at 380 nm with time was monitored and used for the calculation of Φ_{Δ} according to Equation 1.6. The concentration of ADMA was kept at ~ 6 x 10⁻⁵ M to avoid chain reactions. The initial quencher concentrations (absorbance of ~ 1.0) were kept the same for both the standard and the MPc under investigation. ZnTSPc ($\Phi_{\Delta}^{Std} = 0.3$) in aqueous solution in the presence of Triton X was used as a standard for singlet oxygen quantum yields determination [162].
2.3.3 Photoelectrochemical and electrochemical measurements

Cyclic voltammetry (CV) and square wave voltammetry (SWV) data were obtained (under purified nitrogen gas) using a BioAnalytical System (BAS) model 100 B/W Electrochemical Workstation. The data were collected using a conversional three-electrode set-up with glassy carbon electrode (GCE, 3 mm diameter) as a working electrode, platinum wire as a counter electrode and Ag|AgCl wire as pseudo-reference electrode. Electrochemical experiments were performed in doubly distilled water containing 0.1 M Na₂HPO₄ and 0.1M NaOH. Prior to scans, the working electrode was polished with alumina paste on a Buehler felt pad, followed by washing with deionised water and rinsing with methanol, then with acetone and pH 10 phosphate buffer. Ultra pure water was obtained from a Milli-Q Water System (Millipore Corp, Bedford, MA, USA). Phosphate buffer saline (PBS) solution was employed for aqueous solutions.

The preparation of ZnO thin films were performed at the Justus-Liebig University, Giessen Germany. Deposition of ZnO in the presence of eosin Y, FTO doped conductive glass substrate (Asahi-Glas, Cond. $10 \Omega / cm^2$, with a transparency > 85 % in the visible region) was cut to a size of 2.5 cm x 2.5 cm. Before the substrate (FTO) was mounted to the holder for the deposition, it was cleaned ultrasonically in acetone, iso-propanol and distilled water for five minutes each. The substrate was then etched in 45 % HNO₃ for 2 min and finally rinsed with distilled water. A conversional three electrode system, consisting of a rotating disc electrode (RDE) mounted with FTO-conducting glass as a working electrode, Ag|AgCl as reference electrode and zinc rod as a counter electrode was employed. The electrochemical cell was filled with electrolyte (120 ml ultrapure H₂O containing 0.1 M KCl). The tube which supplies oxygen (99%) into the deposition cell was placed into the electrolyte and oxygen gas was allowed to

flow at a rate of 400 mL / min. This condition was maintained for approximately 10 min. The electrolyte was warmed to 70 °C using circulating thermostated water surrounding the cell. The oxygen tube was left in the electrolyte to make sure that sufficient amount of oxygen was supplied in the electrolyte. A potential of -1.06 V vs. Ag|AgCl was applied to the electrode for 30 min and RDE was set to 500 rpm. During the first 5 min, an increasing current density was observed. After the substrate activation, 1 mL each of concentrated ZnCl₂ and eosin Y (after further 5 minutes) were added to the electrolyte, resulting in the final concentration of ZnCl₂ and eosin Y of 5 mM and 50 μ M respectively. When the deposition was completed, the FTO conductive glass was then taken out from the sample holder and rinsed using distilled water and immediately dried under nitrogen flow. Then the films were soaked in a solution of KOH (pH 10.5) for 24 hours for desorption of eosin Y.

The MPc dye adsoption was done by refluxing the nanoporous ZnO thin film in a solution of KOH (pH 11) containing 1 mM (MOCPc, MTSPc and Q(T-2-Py)MPc) dye at a reflux temperature of 80 °C or at room temperature at various times in some cases for comparison. The films containing the MPc dye were rinsed with water and dried under compressed nitrogen and stored in the dark for photoelectrochemical studies.

Photoelectrochemical measurements were performed at the Justus-Liebig University, Giessen Germany. An ORIEL 1000 W xenon arc lamp (intensity = 100 mW cm^{-2}) equipped with a water filter and a UV cut off filter to restrict the illumination to the visible range (385 nm – 900 nm) was employed. The adjustment of the light intensity was carried out using a thermopile (LaserPoint). The illumination to the electrode was controlled by using a PRONTOR magnetic E/40 mechanical shutter. The shutter needed about 15 ms to reach a completely open position as measured with a SIEMENS SFH 291 silicon-PIN-photodiode and was kept open for typically 2

sec. The potential and the currents were measured with an Iviumstat potentiostat, using a conversional three-electrode arrangement in a 5 mL glass cell with the MPc/ZnO hybrid thin film as a window of the cell illuminated from the fluorine-doped tin oxide (FTO) side and used as the working electrode, a Pt as a counter electrode and a Ag/AgNO₃ as reference electrode with acetonitrile as internal solvent. A mixture of 0.5 M TBAI and 0.05 M I₂ (in a 1: 4 by volume mixture of acetonitrile with ethylene carbonate) was used as an electrolyte.

2.4 Synthesis

2.4.1 Synthesis of anionic water soluble tetrasulfo metallophthalocyanines (MTSPcs) (Scheme 3.1)

The MTSPcs (M = Ga, Si, Ti and Zn) were synthesized and purified according to the procedure for SnTSPc [163]. Briefly, a mixture of commercially available 50% aqueous 4-sulfophthalic acid solution (4 g, 8.12 mmol), urea (1.95 g, 32 mmol) and a metal salt (4.1 mmol) (GaCl₃ for hydroxy gallium tetrasulfophthalocyanine ((OH)GaTSPc), SiCl₄ for dihydroxy silicon tetrasulfophthalocyanine ((OH)₂SiTSPc), TiCl₄ for oxo-titanium tetrasulfophthalocyanine (OTiTSPc) and ZnCl₂ for zinc tetrasulfophthalocyanine (ZnTSPc)) in the presence of ammonium chloride (1.56 g, 29 mmol) and ammonium molybdate (0.17 g, 0.14 mmol) as catalysts, was irradiated in a microwave oven at 560 W for 15 min. The mixture was then added to aqueous sodium hydroxide solution (100 mL, 10 wt. %), heated until it boiled, and cooled to the room temperature. The solution was then poured into methanol (50 ml), and then *i*-propyl alcohol (100 ml) was added to precipitate the product. The complex was purified by following literature methods [163] in addition to Soxhlet extraction of impurities using methanol and ethanol. Elemental and mass spectra are only provided for the new complexes which have not been reported before.

(OH)GaTSPc:

Yield: (47%). IR (KBr, cm⁻¹): 3432(O-H), 2046, 1669, 1631(C=C), 1401, 1195, 1136(S=O), 904, 686, 584. ¹HNMR (D₂O): 8.31-8.33(4H, s, Pc-H), 8.01-8.06 (8H, d, Pc-H), 6.60-6.63(1H s-br,O-H). UV/Vis λ_{max} (nm) (log ε) (pH 11/CEL): 380 (3.74), 678 (4.96) nm. Calc. for C₃₂H₁₃N₈O₁₃S₄Na₄Ga (2H₂O): C 33.85, H 1.50, N 9.87; Found: C 34.13, H 2.06, N 9.68. MALDI-TOF MS *m/z*: Calcd: 898.4 amu. Found: (M-OH) 898.9 amu

(OH)₂SiTSPc:

Yield: 36%. IR (KBr) cm⁻¹: 3490 (O-H), 1704 (C=C), 1127(S=O), 846 (Si-O). ¹HNMR (D₂O): 8.91-9.11(4H, s, Pc-H), 8.47-8.59 (8H, d, Pc-H), 6.72-6.95(1H s-br,O-H).UV/Vis λ_{max} (nm) (log ϵ) (pH 11/ CEL): 338 (4.65), 677 (4.87).

OTiTSPc:

Yield: (47%). IR (KBr, cm⁻¹): 3467(OH), 2176, 1639, 1662(C=C), 1451, 1197, 1131, 1040(S=O), 962(Ti=O), 904, 865, 834(C-S), 686, 560. ¹HNMR (400 MHz, D₂O): 8.13-8.11(s, 8H, Pc-H), 8.05-8.03 (d, 4H, Pc-H). UV/Vis $\lambda_{max}(nm)$ (log ε) (pH10/CEL): 340 (4.30), 610 (3.67), 677 (4.98) nm.

ZnTSPc:

Yield: (38%). IR (KBr, cm⁻¹): 3428(OH), 1653 (C=C), 1035 (S=O). ¹HNMR (D₂O): 8.73-8.92(4H, s, Pc-H), 8.68-8.87 (8H, d, Pc-H), UV/Vis $\lambda_{max}(nm)$ (log ε) (pH10/CEL): 351 (4.24), 678 (4.97).

2.4.2 Synthesis of octacarboxy anionic water soluble metallophthalocyanines (MOCPc), (Scheme 3.2)

The MOCPcs (M = Al, Ga, Si, Ti and Zn) were synthesized, purified and characterized according to established literature methods [52] as follows: A mixture of benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride, 2.50 g 11.5mmol), urea (13.0 g, 0.22 mol), metal salt (23.5 mmol) (AlCl₃ for (OH)AlOCPc, GaCl₃ for (OH)GaOCPc, SiCl₄ for (OH)₂SiOCPc, titanium (IV) butoxide for OTiOCPc and ZnCl₂ for ZnOCPc) and DBU (0.1 g, 0.7 mmol) as a catalyst was heated to 250 °C in a flask until the reaction mixture was fused. The reaction products were then washed with water, acetone and 6 M hydrochloric acid (HCl). After drying, the solid obtained was hydrolyzed in 20% H₂SO₄ for a period of 72 hours. The products were purified further as explained in literature [52].

(OH)AlOCPc:

Yield: (20 %): (IR KBr, cm⁻¹): 3429 (O-H), 1724 (C=O), 1364, 1259, 1172 (C-O). ¹HNMR (400 MHz, D₂O): 8.29-8.76 (s, 8H, Pc-H), 6.93-7.14 (broad, s, 1H, (OH)-H), 3.6-3.73 (s, 8H, Carboxylic-H). UV/Vis $\lambda_{max}(nm)$ (log ε) (pH11):356 (4.87), 689 (5.15).

(OH)GaOCPc:

Yield: (34%). IR (KBr, cm⁻¹): 3423(OH), 3029 (C-H), 2781, 1724(C=O), 1466, 1398, 1399, 1283, 1186(C-O or O-H) 1054,772, 536. ¹HNMR (D₂O): 8.73-8.78 (8H, s, Pc-H), 4.81-4.86 (8H, s, carboxylic-H). UV/Vis (pH 11): λ_{max} (nm) (log ε) 360 (3.41), 688(4.52) nm. Calc. for C₄₀H₁₇N₈O₁₇Ga (18H₂O): C 37.67, H 4.16, N 8.79; Found: C 37.03, H 3.71, N 8.55. MALDI-TOF MS *m/z*: Calcd: 951.2 amu. Found: (M+1) 952.4 amu

(OH)₂SiOCPc:

Yield: (32%). IR (KBr, cm⁻¹): 3433(OH), 1752, 1631, 1574, 1403, 1282, 1024, 756 (C-S), 625, 602, 511. ¹HNMR (400 MHz, D₂O): 7.921-7.963 (s, 8H, Pc-H), 7.69-7.70 (s, 2H, (OH)₂-H), 4.63-4.64 (s, 8H, carboxylic-H). UV/Vis λ_{max} (nm) (log ε) (pH11): 346 (4.97), 618 (4.42), 690 (5.10) nm.

OTiOCPc:

Yield: (25%). IR (KBr, cm⁻¹): 3441(OH), 3029, 2782, 2357, 1725, 1644, 1469, 1399, 1283, 1054, 930(Ti=O), 772, 536. ¹HNMR (400 MHz, D₂O): 7.75-7.67 ppm (s, 8H, Pc-H), 4.13-4.15 ppm (s, 8H, Carboxylic-H). UV/Vis λ_{max} (nm) (log ε) (pH11): 338 (3.72), 620 (3.94), 693 (4.75) nm.

ZnOCPc:

Yield: (35 %). IR (KBr cm⁻¹): 3437 (O-H), 1716 (C=O), 1381, 1273, 1184 (C-O). ¹HNMR (400 MHz, D₂O): 8.56-8.82 ppm (s, 8H, Pc-H), 3.92-4.12 ppm (s, 8H, carboxylic-H). UV/Vis $\lambda_{max}(nm)$ (log ε) (pH11):350 (4.95), 689 (5.10).

2.4.3 Synthesis of 4-(2-pyridyloxy) phthalonitriles (Scheme 3.3)

The synthesis of 4-(2-pyridyloxy) phthalonitrile: 2 hydroxypyridine (7.00 g, 74 mmol) and 4nitrophthalonitrile (1, 8.50 g, 49 mmol) were suspended in dry DMSO (70 ml) in the presence of a steady flow of nitrogen. Aliquots of anhydrous K_2CO_3 (13.50 g, 98 mmol) were added and the mixture stirred at room temperature. Further aliquots of K_2CO_3 (0.63 g, 4.6 mmol) were slowly added after 4 and 24 h of stirring. After 48 h total reaction time, the mixture was poured into H_2O (250 ml), resulting in a precipitate that was recrystallized from methanol to give a brownish-yellow product (4-(2-pyridyloxy) phthalonitrile).

Yield: (80%). IR (KBr, cm⁻¹): 2267 (C≡N), 1234 (C−O−C). ¹H NMR (400 MHz, DMSO-d₆): 8.34 (s, 1H, Ar–H), 8.16–8.23 (d, 1H, Ar–H), 7.72–7. 79 (d, 1H, Ar–H), 7.01-7.28 (d, 1H, Ar'– H), 6.95 (s,1H, Ar'–H), 6.42–6.56 (d, 1H, Ar'–H), 6.04 (d, 1H, Ar'–H).

2.4.4 Synthesis of β-2,(3)-tetra-2- pyridyloxymetallophthalocyanines (UnQ(T-2-Py)MPcs), (Scheme 3.3) [164]

A mixture of excess metal salt (3.4 mmol) (AlCl₃ for UnQ(T-2-Py)ClAlPc, GaCl₃ for UnQ(T-2-Py)ClGaPc, SiCl₄ for UnQ(T-2-Py)Cl₂SiPc and titanium (IV) butoxide for UnQ(T-2-Py)OTiPc), 2-pyridyloxyphthalonitrile (1.50 g, 6.8 mmol) and quinoline (5 mL, doubly distilled over CaH₂) was stirred at 180°C for 24 h under nitrogen atmosphere. The solution was then cooled and dropped in n-hexane. The green solid product was precipitated and collected by centrifugation and washed with n-hexane. The crude product was dissolved in DMF. After concentrating, the dark green waxy product was precipitated with hot ethanol and washed according to reported

procedure [164] with ethanol, acetone, THF, CHCl₃, n-hexane and diethylether in a Soxhlet extraction apparatus.

UnQ(T-2-Py)ClAlPc:

Yield: (57 %). IR (KBr, cm⁻¹): 3114(C-H), 1560(C=C), 1450, 1341, 1100(C-O-C), 843, 748, 610, 543. ¹H-NMR (DMSO-d₆): δ , ppm 8.74-9.02 (4H, m, Pc-H), 9.16-9.19 (4H, d, Pc-H), 9.53-9.60 (4H, m, Pc-H), 8.19-8.21 (4H, br, pyridyl-H), 8.10-8.16 (8H, m, pyridyl-H), 7.94-7.99 (4H, br, pyridyl-H). UV/Vis (DMF) λ_{max} nm (log ϵ): 354 (3.87), 676 (5.12). Calc. for C₅₂ N₁₂H₂₈O₄AlCl: C 65.98, H 2.96, N 17.76; Found: C 65.59, H 3.46 N 17.58

UnQ(T-2-Py)ClGaPc:

Yield: (64 %). IR (KBr, cm⁻¹): 3102(C-H), 1564(C=C), 1474, 1235, 1092(C-O-C), 843, 748. ¹H-NMR (DMSO-d₆): δ , ppm 8.95-9.14 (4H, m, Pc-H), 9.25-9.38 (4H, d, Pc-H), 9.64-9.67 (4H, m, Pc-H), 8.21-8.29 (4H, br, pyridyl-H), 8.10-8.14 (8H, m, pyridyl-H), 7.83-7.95 (4H, br, pyridyl-H). UV/Vis (DMF) λ_{max} nm (log ϵ): 340 (3.20), 686 (4.43). Calc. for C₅₂ N₁₂H₂₈O₄GaCl: C 63.08, H 2.83, N 16.98; Found: C 62.61, H 2.53 N 16.81.

UnQ(T-2-Py)Cl₂SiPc:

Yield: (42 %). IR (KBr, cm⁻¹): 3110(C-H), 1569(C=C), 1500, 1226, 1089(C-O-C), 837, 753, 639, 582, 524, 482(Si-Cl), 448. ¹H-NMR (DMSO-d₆): δ , ppm 8.99-9.09 (4H, m, Pc-H), 9.22-9.37 (4H, d, Pc-H), 9.56-9.61 (4H, m, Pc-H), 8.14-8.19 (4H, br, pyridyl-H), 7.97-8.11 (8H, m, pyridyl-H), 7.83-7.90 (4H, br, pyridyl-H). UV/Vis (DMF) λ_{max} nm (log ε): 347 (3.52), 674 (5.03). Calc. for C₅₂ N₁₂H₂₈O₄Cl₂Si: C 68.41, H 2.85, N 17.10; Found: C 67.95, H 3.26 N 16.98

UnQ(T-2-Py)OTiPc:

Yield: (64 %). IR (KBr, cm⁻¹): 3116(C-H), 1557(C=C), 1384, 1223, 1096(C-O-C), 981(T=O),826, 757, 645, 589, 543. ¹H-NMR (DMSO-d₆): δ , ppm 8.86-8.99 (4H, m, Pc-H), 9.22-9.34 (4H, d, Pc-H), 9.53-9.58 (4H, m, Pc-H), 8.10-8.19 (4H, br, pyridyl-H), 8.23-8.28 (8H, m, pyridyl-H), 7.68-7.75 (4H, br, pyridyl-H). UV/Vis (DMF) λ_{max} nm (log ϵ): 342 (3.34), 674 (4.82). Calc. for C₅₂ N₁₂H₂₈O₅Ti: C 65.89, H 2.95, N 17.74; Found: C 66.37, H 4.46 N 17.48

2.4.5 Synthesis of quaternized cationic water soluble β -2,(3)-Tetra-2pyridyloxymetallophthalocyanines (Q(T-2-Py)MPcs), (Scheme 3.4)

These complexes were synthesized according to the reported literature procedure [165]. The unquaternized complexes: $(UnQ(T-2-Py)ClAlPc \text{ for } Q(T-2-Py)ClAlPc, UnQ(T-2-Py)ClGaPc \text{ for } Q(T-2-Py)ClGaPc, UnQ(T-2-Py)Cl_2SiPc \text{ for } Q(T-2-Py)Cl_2SiPc \text{ and } UnQ(T-2-Py)OTiPc \text{ for } Q(T-2-Py)OTiPc)$ (0.1mmol) were heated to $120^{\circ}C$ in freshly distilled DMF (0.5 ml) and

dimethyl sulphate (0.2 ml) was added drop-wise. The mixture was stirred at 120^oC for 24 h. After this time, the mixture was cooled to room temperature and the product was precipitated with hot acetone and collected by centrifugation. The green solid product was washed successively with hot ethanol, ethyl acetate, THF, chloroform, n-hexane and diethylether under Soxhlet extraction. The resulting hygroscopic product was dried over phosphorous pentoxide.

Q(T-2-Py)ClAlPc:

Yield: (65 %). IR (KBr, cm⁻¹): 3103(C-H), 1174, 1573(C=C), 14901, 1435, 1414, 1356, 1120(S=O), 1140(S=O), 1043(C-O-C), 910, 725, 648, 623. ¹H-NMR (D₂O): δ , ppm 8.92-9.26 (28H, m, Pc-H and Pyridyl-H), 3.56-3.91 (12H, m, CH₃): UV/Vis (pH 11/CEL) λ_{max} (nm) (log ϵ): 368 (3.79), 681 (4.88). Calc. for C₅₆H₄₀N₁₂O₁₂S₂ClAl (2H₂O) : C 54.50, H 3.24, N 13.62; Found: C 54.84, H 2.95, N 13.86.

Q(T-2-Py)ClGaPc:

Yield: (75 %). IR (KBr, cm⁻¹): 3132(C-H), 1569(C=C), 1501, 1474, 1403, 1384, 1276(S=O), 1097(S=O), 1061(C-O-C), 1007, 749, 668,617. ¹H-NMR (D₂O): δ , ppm 8.84-9.46 (28H, m, Pc-H and pyridyl-H), 3.95-4.31 (12H, m, CH₃): UV/Vis (pH 11/CEL) λ_{max} (nm) (log ε): 350 (4.10), 679(4.81): Calc. for C₅₆H₄₆ClN₁₂O₁₄S₂Ga (4H₂O) : C 50.93, H 3.48, N 12.73; Found: C 50.46, H 2.97, N 13.66. MALDI-TOF MS *m/z*: Calcd: 1014.4 amu. Found: (M-Cl) 1015.3 amu.

Q(T-2-Py)Cl₂SiPc:

Yield: (70 %). IR (KBr, cm⁻¹): 3214(C-H), 1530(C=C), 1510, 1448, 1327, 1286(S=O), 1102(S=O), 1036(C-O-C), 859, 764, 622, 610, 536, 478(Si-Cl), 458. ¹H-NMR (D₂O): δ , ppm 8.79-9.13 (28H, m, Pc-H and pyridyl-H), 3.89-4.21 (12H, m, CH₃): UV/Vis (pH 11/CEL) λ_{max} (nm) (log ϵ): 348 (3.46), 675 (4.79). Calc. for C₅₆H₄₀N₁₂O₁₂S₂Cl₂Si (2H₂O) : C 52.91, H 3.15, N 13.23; Found: C 52.69, H 2.77, N 13.45.

Q(T-2-Py)OTiPc:

Yield: (60 %). IR (KBr, cm⁻¹): 3122(C-H), 1556(C=C), 1514, 1400, 1384, 1268(S=O), 1158(S=O), 1047(C-O-C), 987(Ti=O), 736, 649, 621. ¹H-NMR (D₂O): δ , ppm 8.89-9.34 (28H, m, Pc-H and pyridyl-H), 3.92-4.14 (12H, m, CH₃): UV/Vis (pH 11/CEL) λ_{max} (nm) (log ϵ): 366 (3.95), 676 (4.86). Calc. for C₅₆H₄₀N₁₂O₁₃S₂Ti : C 56.80, H 3.38, N 14.19; Found: C 57.83, H 3.62, N 13.79.

CHAPTER THREE

RESULTS AND DISCUSION

PUBLICATIONS

Part of the results presented in this thesis has been published in peer-reviewed journals and are listed below. These articles are not referenced in this thesis:

- Photophysical, photochemical and electrochemical properties of water soluble silicon, titanium and zinc phthalocyanines, Nkosiphile Masilela, Mopelola Idowu, Tebello Nyokong, Journal of Photochemistry and Photobiology A: Chemistry 201 (2009) 91–97.
- The synthesis and photophysical properties of water soluble tetrasulfonated, octacarboxylated and quaternised 2,(3)-tetra-(2 pyridiloxy) Ga phthalocyanines, Nkosiphile Masilela and Tebello Nyokong, Dyes and Pigments 84 (2010) 242–24.
- The synthesis and photophysical properties of novel cationic tetra pyridiloxy substituted aluminium, silicon and titanium phthalocyanines in water, Nkosiphile Masilela and Tebello Nyokong, submitted for publication in Journal of Luminescence.
- 4. Photoelectrochemical studies of nanoporous ZnO films sensitized with symmetrically and unsymmetrically substituted carboxy phthalocyanines, Nkosiphile Masilela, Nolwazi Nombona, Thomas Loewenstein, Tebello Nyokong and Derck Schlettwein, submitted for publication in Journal of Pophrins and Phthalocyanines.

3.1 Synthesis and spectroscopical characterization

3.1.1 Synthesis of tetrasulfo metallophthalocynaines, (MTSPcs).



Scheme 3.1: The microwave synthesis of tetrasulfo metallophthalocyanine (MTSPc) [163]

Sulfonated phthalocyanines can be obtained from commercially available 4-sulfophthalic acid through microwave synthesis as shown in Scheme 3.1. The synthesis of tetrasulfo metallophthalocyanines (MTSPcs) complexes is known and the complexes: (OH)GaTSPc [72], (OH)₂SiTSPc [73], and ZnTSPc [74] gave satisfactory spectroscopic characterization results. The synthesis of OTiTSPc is reported for the first time in this thesis and gave satisfactory spectroscopic results that are consisted with the structure. The ¹H NMR spectra of the complexes showed aromatic ring protons between 8 and 9 ppm. The peaks integrated correctly giving the expected total number (12) of protons confirming the relative purity of the complexes. From the

IR spectra the peak at 962 cm⁻¹ corresponds to the (Ti=O) confirming axial ligation of titanium to oxygen. The characteristic S=O vibrations for all the MTSPc complexes were observed in the region between 1030-1050 cm⁻¹ confirming sulfonation.



Figure 3.1: Ground state electronic absorption spactra of (OH)GaTSPc (solid green), (OH)₂SiTSPc (solid red), OTiTSPc (dotted black) and ZnTSPc (solid blue) in aqueous solution

The ground state electronic spectra of the tetrasulfonated metallophthalocyanines (MTSPcs) complexes in Fig. 3.1, shows that they are aggregated in aqueous solution with the presence of two main bands one at ~ 680 nm due to the monomeric species and the other at ~ 640 nm due to the aggregated species.



Figure 3.2: Ground state absorption spectra of ZnTSPc (a), (OH)₂SiTSPc (b), OTiTSPc (c) and (OH)GaTSPc (d) in aqueous solution (dotted line) and in the presence of CEL (solid line).

Aggregation in MPc complexes is usually depicted as a coplanar association of rings, progressing from dimer to higher aggregates, resulting in splitting and broadening of spectra, with a blue shifted peak at ~ 630 nm due to the aggregate. Tetrasulfonated phthalocyanines, exist as loosely associated species that are not chemically bonded dimers in aqueous solution which can be dissociated by surfactants or in non-aqueous solvents [17, 150]. In all the MTSPc complexes, addition of a surfactant (CEL) resulted in a decrease in the intensity of the bands due to the aggregates with an increase in the intensity of the bands due to the aggregates with an increase in the intensity of the bands due to the aggregates and presence of CEL, given in Table 3.1.

The disaggregation of (OH)₂SiTSPc and (OH)GaTSPc was total on addition of CEL, but ZnTSPc and OTiTSPc still shows some aggregation suggesting that strong forces are responsible for their aggregation or that a high equilibrium between the monomer and the aggregated species occurs in these complexes. Axial ligation sometimes play a vital role in preventing aggregation, it is observed that for non axially ligated ZnTSPc complex there was almost a complete split of the Q-band as a results of aggregation. In contrast to (OH)₂SiTSPc and (OH)GaTSPc (Fig. 3.2 (b) and (d)) with dihydroxyl and hydroxy axial ligands, they were weakly aggregated as it was judged by less pronounced absorption in the 640 nm region. There was a broadening of the spectra even after addition of CEL for the OTiTSPc complex, but the enhancement of the monomer peak confirming disaggregation of the complex. The slight red shifting of the Q-band monomer peak of the (OH)GaTSPc, OTiTSPc and ZnTSPc after addition of CEL, Fig. 3.2, Table 3.1, is probably due to changes in the media.

Table 3.1 Ground state absorption, fluorescence emission and excitationspectral parameters for various MTSPcs complexes

Complex	Solvent	Q band λ _{abs} (nm)	Excitation $\lambda_{ex}(nm)$	Emission λ_{em} (nm)	Stokes shift Δ _{stokes}
OHGaTSPc	pH 11	674	674	679	5
	pH 11 + CEL	678	675	681	6
ZnTSPc	pH 11	678,640	677	679	2
	pH 11 + CEL	678	678	680	2
OTiTSPc	pH 11	687,660	675	686	11
	pH 11 + CEL	695	694	697	3
(OH) ₂ SiTSPc	pH 11	677,639	678	684	6
	pH 11 + CEL	677	677	688	11



3.1.2 Synthesis of octacaboxy metallophthalocyanines, (MOCPcs).

Scheme 3.2: Synthesis of octacarboxy metallophthalocyanines, MOCPc [52].

Octacarboxy metallophthalocyanines (MOCPcs) can be synthesized from commercially available pyromellitic dianhydride in the presence of urea as a source of nitrogen, DBU as a catalyst and various metal salts [52] as shown Scheme 3.2. Octacarboxy metallophthalocyanines ((OH)AlOCPc, (OH)SiOCPc and ZnOCPc) complexes, are known and gave satisfactory UV-Vis, IR and NMR spectroscopic characterization. However the synthesis of (OH)GaOCPc and

OTiOCPc is presented for the first time in this thesis and their spectroscopic characterization corresponded to the structures. The FTIR data of the complexes showed characteristics bands of the complexes such as the O-H at ($\sim 3420 - 3500$ cm⁻¹), C=O ($\sim 1700 - 1750$ cm⁻¹) and C-O at ($\sim 1190 - 1200$ cm⁻¹) which are in good agreement with reported values [52]. The ¹H NMR spectra of all the complexes showed aromatic ring protons at a region between 8 and 10 ppm integrating for the 8 ring protons and 8 carboxylic acid group protons to a total number of 16 expected protons.



Figure 3.3: Ground state absorption spectra of octacarboxy metallophthalocyanines (OH)AlOCPc (dotted green), (OH)GaOCPc (solid red), (OH)₂SiOCPc (solid blue), OTiOCPc (dotted black) and ZnOCPc (solid black) in aqueous solution of pH 11.

Unlike the tetrasulfo metallophthalocyanines (MTSPcs) complexes, the ground state electronic absorption spectra of the MOCPcs (Fig. 3.3) in pH 11 showed monomeric behavior evidenced by a single narrow Q-band (~690) typical of metallated phthalocyanine complexes [52]. The monomeric nature of the MOCPcs in aqueous solutions has been found to be due to full ionization of the carboxylate groups at pH ~ 11 [166, 126]. MTSPc complexes remain aggregated in aqueous solution (at pH 11) despite being ionized, due to the presence of only four substituents. Tetra substituted MPcs (e.g MTSPcs) are a mixture of isomeric compounds [17,126, 167].



Figure 3.4: Ground state absorption spectra of (OH)GaOCPc at various concentrations: (i) = 2×10^{-6} , (ii) = 4×10^{-6} , (iii) = 6×10^{-6} , (iv) = 8×10^{-6} , (v) = 10×10^{-6} , and (vi) = 12×10^{-6} mol.dm⁻³ in aqueous solution of pH 11

Fig. 3.4 shows that as the concentration was increased for (OH)GaOCPc in pH 11, the intensity of the absorption of the Q-band also increased and there were no new bands normally blue shifted due to the aggregated species. Same trend was also observed with the rest of MOCPcs. Beer–Lambert's law was obeyed for all the MOCPcs complexes in the concentrations ranging from 2×10^{-6} to 12×10^{-6} mol dm⁻³.

Table 3.2: Ground state absorption, fluorescence emmission and excitationspectral parameters of the MOCPcs

Complex	Solvent	$\begin{array}{c} Q \text{ band} \\ \lambda_{abs} (nm) \end{array}$	Excitation λ _{exi} (nm)	Emission λ _{emi} (nm)	Stokes shift ∆ _{stokes}
OHGaOCPc	pH 11	688	687	699	12
OTiOCPc	pH 11	693	691	700	9
(OH) ₂ SiOCPc	pH 11	690	689	699	10
(OH)AlOCPc	pH 11	689	687	701	14

The OTiOCPc shows a more red shifted Q-band compared to all the MOCPc complexes Table 3.2, this is due to the heavier titanium metal compared to the Al, Si, Ga and Zn. The Stokes shifts for the complexes were between of 9 to 14 nm typical of MOCPcs in aqueous solution.

3.1.3 Synthesis of unquaternized (UnQ(T-2-Py)MPc) and quaternized (Q(T-2-

Py)MPc) MPcs



Scheme 3.3 Synthesis of β -2,(3)-Tetra-2-(pyridyloxy) metallophthalocyanines (UnQ(T-2-Py)MPcs) and their quaternized (Q(T-2-Py)MPcs) water soluble derivatives of Al, Ga, Si and Ti complexes

Schemes 3.3 show the synthetic pathways for the β -2,(3)-tetra-2-(pyridyloxy) metallophthalocyanines (UnQ(T-2-Py)MPcs) and their quaternized (Q(T-2-Py)MPcs) water soluble derivatives of Al, Ga, Si and Ti complexes used in this work. Substituted phthalocyanines are normally prepared by cyclotetramerization of substituted phthalonitriles. Tetra-substituted phthalocyanines (Shceme 3.3) can be synthesized from 4-substituted phthalonitriles (4-(2-pyridyloxy)phthalonitrile). The synthesis of 4-(2-pyridyloxy)phthalonitrile has been reported before in literature [164] and gave satisfactory spectroscopic results, with a characteristic nitrile (C=N) stretch at ~2225 cm⁻¹ from the IR confirming formation of phthalonitrile. The ¹HNMR data integrated for correct number of protons corresponding to the 4-(2-pyridyloxy)phthalonitrile structure.

The synthesis of unquaternized metallophthalocyanine (UnQ(T-2-Py)MPcs) complexes derivatives were achieved by treatment of 4-(2-pyridyloxy) phthalonitrile with different salts in freshly distilled quinoline (Scheme 3.3). Inserting aluminium, gallium, silicon and titanium into the phthalocynine ring containing bulky substituents such as the pyridiloxy groups needs high energy, hence a high boiling point solvent, quinoline is employed. The UnQ(T-2-Py)MPc complexes were obtained in relatively good yields: 57 % (UnQ(T-2-Py)ClAlPc), 64% (UnQ(T-2-Py)ClGaPc), 42% (UnQ(T-2-Py)Cl_2SiPc), and 64% (UnQ(T-2-Py)OTiPc).

The compounds were then further made water soluble by quaternarization (quaternized metallophthalocyanines (Q(T-2-Py)MPcs), (Scheme 3.3)); this follows simple methylation of the tertiary ammonium groups, and converting them to quaternary ammonium moieties that renders them water solubility. Methylation was achieved by reacting each UnQ(T-2-Py)MPc with dimethylsulfate (DMS) as quaternarization agent in DMF as solvent at 120 °C for 24 h as

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shown on Scheme 3.3. The quaternized water soluble MPc (Q(T-2-Py)MPc) complexes were also obtained in good yields.

The analyses of the newly synthesized compounds were consistent with the predicted structures as shown in the experimental section. The complexes were characterized with spectroscopic techniques such as the UV-Vis, IR, NMR and mass spectra and by elemental analyses. There was a disappearance of the C=N vibrations of 4-(2-pyridyloxy) phthalonitriles at ~2230 cm⁻¹ from the IR spectra of the UnO(T-2-Py)MPc complexes confirming formation of the phthalocvanine complexes. Upon formation of quaternized water soluble phthalocyanine derivatives (Q(T-2-Py)MPcs), aliphatic C-H stretching from the IR data was observed for all the complexes, 3103 cm⁻¹ for (Q(T-2-Py)ClAlPc), 3132 cm⁻¹ for (Q(T-2-Py)ClGaPc), 3214 cm⁻¹ for (Q(T-2-Py)Cl₂SiPc) and 3122 cm⁻¹ for (Q(T-2-Py)OTiPc) cm⁻¹ respectively. There were also counter ion sulphate S=O (~1100 cm⁻¹ - 1300 cm⁻¹) stretching from the IR data of the water soluble derivatives that also suggest formation of quaternized MPc derivatives. The characteristic vibrations corresponding to ether groups (C–O–C) at 1050 -1100 cm⁻¹ was observed for all the complexes. The presence of isomers as well as phthalocyanine aggregation at the concentrations used for the ¹H NMR measurements leads to broadening of the aromatic signals [168]. The peaks integrated correctly giving the expected total number of protons for each complex, confirming the relative purity of these complexes as observed on the experimental section. The ¹H NMR spectra for all the complexes showed aromatic Pc ring protons at a region between 8 and 10 ppm. The pyridyloxy protons were observed as broad peaks in the region between 6.0 - 8.3 ppm. Some overlap of the pyridiloxy peaks and the pthalocyanine ring peaks were observed in some cases. The methyl protons for the Q(T-2-Py)MPcs were observed between 3.50 - 4.3 ppm and integrated for 12 protons in each compound, confirming quaternization.



Figure 3.5: Ground state absorption spectra of β -2,(3)-Tetra-2-(pyridyloxy) metallophthalocyanines (UnQT-2-PyMPcs) (M = ClAl (solid blue), ClGa (solid green), Cl₂Si (solid red) and OTi (dotted black)) in DMF

The ground state electronic absorption spactra for all the UnQ(T-2-Py)MPc complexes showed characteristic Q-band of typical phthalocyanine complexes (Fig. 3.5). The unquaternized complexes showed monomeric behaviour in DMF. However the UnQ(T-2-Py)ClAlPc complex (solid blue) showed broadening near 630 nm, typical of aggregation. The Q-band absorption spectra in DMF of UnQ(T-2-Py)Cl₂SiPc and UnQ(T-2-Py)OTiPc were observed at the same

wavelength of 674 nm (Table 3.3), showing no effect of the central metal on the Q-band wavelength.

Table 3.3: Ground state absorption, fluorescence emmission and excitationspectral parameters of the UnQ(T-2-Py)MPc and Q(T-2-Py)Mpc complexes

Compound	Solvent	Q-band	Excitation	Emission	Stokes shift
		λ _{abs} (nm)	λ_{exc} (nm)	$\lambda_{_{emi}}$ (nm)	Δ (nm)
UnQ(T-2-Py)ClAlPc	DMF	676	683	694	11
UnQ(T-2-Cl)GaPyPc	DMF	686	683	700	17
UnQ(T-2-Py)Cl ₂ SiPc	DMF	674	675	689	14
UnQ(T-2-Py)OTiPc	DMF	674	675	683	8
UnQ(T-2-Py)ClAlPc	pH 11	680	680	688	8
Q(T-2-Py)ClGaPc	pH 11	645, 678	680	683	3
Q(T-2-Py)Cl ₂ Si Pc	pH 11	637, 672	676	685	9
Q(T-2-Py)OTiPc	pH 11	638, 683	678	687	9
Q(T-2-Py)ClAlPc	pH 11+ CEL	681	681	690	9
Q(T-2-Py)ClGaPc	pH 11+ CEL	678	675	682	7
Q(T-2-Py)Cl ₂ Si Pc	pH 11 +CEL	675	676	685	9
Q(T-2-Py)OTiPc	pH 11+ CEL	676	674	684	10

The quaternized water soluble derivatives (Ga, Si and Ti) were aggregated in aqueous solution of pH 11, Fig. 3.6. Cationic peripherally substituted Pc complexes are known to form aggregates in aqueous media [77, 96]. Q(T-2-Py)ClAlPc did not show a distinct absorption band due to aggregated species in Fig. 3.6. The complex was essentially monomeric and such behavior has never been observed before on peripherally substituted cationic phthacyanine complexes. There was only slight broadening in the region of the absorption spectra of the aggregated species for Q(T-2-Py)ClAlPc.



Figure 3.6: Ground state absorption spectra of Quaternized β -2,(3)-Tetra-2-(pyridyloxy) metallophthalocyanines (Q(T-2-Py)MPcs) (M = CIAI (solid black), ClGa (solid blue), Cl₂Si (dotted black) and OTi (solid red)) in aqueous solution pH 11



Figure 3.7: Ground state absorption spectra of Q(T-2-Py)ClGaPc at various concentrations: (i) = 2×10^{-6} , (ii) = 4×10^{-6} , (iii) = 6×10^{-6} , (iv) = 8×10^{-6} , (v) = 10×10^{-6} , and (vi) = 12×10^{-6} mol.dm⁻³ in aqueous solution of pH 11+ CEL

Fig. 3.7 shows the concentration study for Q(T-2-Py)ClGaPc pH 11+ CEL and it was observed that as the concentration was increased, the intensity of the Q-band absorption also increased and there were no new bands blue shifted due to the aggregated species. Similar trend was also observed with the other UnQ(T-2-Py)MPcs derivatives which did not show aggregation in DMF. Beer–Lambert's law was obeyed for all the complexes, in pH + CEL for Q(T-2-Py)MPc and in DMF for UnQ(T-2-Py)MPc complexes. But Beer's Law was not obeyed in pH 11 alone especially for the Q(T-2-Py)MPcs due to aggregation.

RESULTS AND DISCUSION Normalized Absorbance 0.4 **(a)** 0 350 450 550 650 750 Wavelength (nm) 1.2 Normalised Absorbance **(b)** 0.8 0.4 0 350 450 550 650 750 Wavelength (nm) Normalized Absorbance 1.2 **(c)** 0.8 0.4 0 550 Wavelength (nm) 450 750 350 650 1.2 (d) Absorbance Normalized 0.8 0.4 0 550 350 450 650 750 Wavelength (nm)

Figure 3.8: The ground state absorption spectra of Q(T-2-Py)MPc (M = ClAl (a), ClGa (b), Cl₂Si (c) and OTi (d)) complexes in pH 11 buffer (dotted line) and in the presence of cremophor EL (CEL) (solid line).

Aggregation for the water soluble Q(T-2-Py)MPc complexes was confirmed by addition of a surfactant cremophor EL (CEL) Fig. 3.8. Surfactants like CEL are known to prevent co-planar association and charge interactions between peripherally charged phthalocyanine ring complexes in polar medium leading to pronounced monomeric absorption bands [77].

Fig. 3.8 shows the absorption spectra of the Q(T-2-Py)MPc complexes, both in the presence (solid line) and in the absence (dotted line) of CEL. It was found that the bands due to aggregates were decreased in intensity after addition CEL. There was complete disaggregation for the Q(T-2-Py)OTiPc complex (Fig. 3.8 (d)). There was incomplete disaggregation of Q(T-2-Py)ClGaPc even after the addition of CEL, as judged by the observation of some broadening in the 640 nm region in Fig. 3.8 (b). A band due to aggregation for Q(T-2-Py)Cl₂SiPc, Fig. 3.8 (c), was observed at around 630 nm even after addition of CEL suggesting that strong forces of aggregates were involved. The Q(T-2-Py)ClAIPc complex was essentially monomeric (Fig 3.8 (a)) and such behavior has never been observed before on peripherally substituted cationic phthacyanine complexes, there was no distinct change in the absorption spectra even after the addition of CEL, showing that the complex is mainly in the monomeric form.

3.2 Photophysical and photochemical properties

3.2.1 Anionic MPcs (MOCPcs and MTSPcs)

3.2.1.1 Fluorescence spectra and parameters



Figure 3.9: Normalized absorption (i), fluorescence excitation (ii) and emission (iii) spectra of (a) OTiOCPc and (b) (OH)₂SiTSPc (in the absence of CEL) in pH 10. Excitation wavelength = 630 nm.



Figure 3.10: Absorption (i), fluorescence excitation (ii) and emission (iii) spectra of (OH)GaTSPc in pH 11 (a) and in pH 11 + CEL (b), excitation wavelength = 630 nm

Figs. 3.9 and 3.10 compare the absorbance, fluorescence excitation and emission of the MOCPcs (monomeric) and the MTSPcs (aggregated) in aqueous solution. The fluorescence excitation spectra of all octacarboxy metallophthalocyanines (MOCPcs) complexes are similar to their absorption spectra and are mirror images of the fluorescence emission spectra which is usual for MPc derivatives as shown in Fig. 3.9 (a) (for OTiOCPc).

There is however a lack of agreement between the absorbance and emission spectra for the tetrasulfonated counterparts as shown in Fig. 3.9 (b) (for (OH)₂SiTSPc) and 3.10 (a) (for (OH)GaTSPc). The band around 640 nm, associated with the dimer is not seen in the fluorescence excitation spectrum of these complexes since only the monomer fluoresces. It has been documented before that dimers are non-photoactive [150]. Upon addition of CEL in Fig 3.10 (b) for the (OH)GaTSPc complex, there was an almost complete disappearance of the band due to aggregates, and hence the absorption spectrum was mirror image of the emission spectrum.

Fig. 3.11 shows the fluorescence excitation and emission spectra of the rest of MTSPc (M = Zn, $(OH)_2Si$ and OTi) complexes in aqueous medium in the presence of CEL. For ZnTSPc and OTiTSPc, the excitation spectrum still had some aggregation even in the presence of CEL as evidenced by a more clear splitting in the Q band, hence the excitation is not a mirror image of emission. For $(OH)_2SiTSPc$ there is no clear splitting, but there is broadening. Emission will be from unaggregated species for these complexes.



Figure 3.11: Normalized fluorescence excitation (i) and emission (ii) spectra of ZnTSPc (a), (OH)₂SiTSPc (b) and OTiTSPc (c), in the presence of CEL, pH 10. Excitation wavelength = 568 nm.

Tables 3.1 and 3.2 lists the ground states absorption and fluorescence emission and excitation spectral data for the anionic (MTSPc and MOCPc) MPc complexes, the Stokes' shifts for the complexes were in the range between 2 to 14 nm typical of MPc complexes. (OH)₂SiTSPc in the presence of CEL and OTiTSPc in pH 11 alone gave same highest values of the stokes shift of 11 nm for the MTSPcs. The stokes shift for the (OH)GaTSPc and ZnTSPc did not show much variation before and after the addition of CEL.

Table 3.3 shows the the ground states absorption and fluorescence emission and excitation spectral data for the quaternized cationic (Q(T-2-Py)MPcs) and unquaternized (UnQ(T-2-Py)MPcs) MPc complexes. The Stokes shifts for the complexes were in the neghbourhood of 10 nm except for the Q(T-2-Py)ClGaPc with the smallest stokes shift value of 3 nm. The UnQ(T-2-Py)ClGaPc and UnQ(T-2-Py)Cl_2SiPc complexes gave higher Stokes shift values of 17 and 14 nm.
Sample	Solvent	λ _o /nm	$\Phi_{\rm p}$.	Фю	$ au_{\pi}$	$ au_{ m E}$
Sumpre	Solvent	<i>M</i> Q/ IIII	Ψŀ	$\mathbf{\Phi}_{\mathrm{L}}$	ΨIC	C.I.	с F.
						(µs)	(ns)
ZnOCPc	pH 10	689	0.18	0.48	0.34	130	1.40
OTiOCPc	pH 10	693	0.07	0.20	0.73	70	1.59
(OH)GaOCPc	pH 11	688	0.21	0.67	0.12	80	12.8
(OH) ₂ SiOCPc	pH 10	690	0.06	0.30	0.64	70	0.54
ZnTSPc	pH 10	678,640	< 0.01	0.56 [150] ^b	0.44	190	0.02
	pH 10 + CEL	678	0.20	0.65	0.15	270	3.71
OTiTSPc	pH 10	672,660	< 0.01	0.03	0.97	50	0.01
	pH 10 + CEL	695	0.012	0.32	0.67	60	0.09
(OH)GaTSPc	pH 11	674	0.09	0.52	0.39	60	0.92
	pH 11 + CEL	678	0.15	0.63	0.22	80	3.53
(OH) ₂ SiTSPc	pH 10	677,639	0.04	0.53	0.43	40	0.28
	pH 10 + CEL	677	0.05	0.58	0.37	60	0.30

Table 3.4: Fluorescence and photophysical parameters for the MOCPc and MTSPc complexes in aqueous media and in the presence of CEL^a.

^a CEL = cremophor EL. ^b References in brackets.

The fluorescence quantum yields Φ_F of the complexes are listed in Table 3.4. The tetrasulfonated complexes (MTSPcs) have relatively low yields of fluorescence in the absence of CEL due to aggregation, but improve on addition of CEL. In this set ZnTSPc in the presence of CEL

showed the highest Φ_F of 0.20 followed by the (OH)GaTSPc with Φ_F of 0.15. Aggregation is known to dissipate the electronic energy of the excited singlet state, thereby lowering fluorescence. Monomerization of aggregates leads to enhanced fluorescence and this is noticed in the Φ_F of the complexes in the presence of CEL in aqueous medium. The Φ_F values in the absence of CEL are low compared to MPcs in general [169]. Φ_F values were relatively higher for the MOCPcs probably due to their monomeric nature as evidenced by their absorption spectra even in aqueous medium.

Lifetimes of fluorescence (τ_F) were determined using the Strickler-Berg equation from natural radiative life times as stated in chapter 1 (Equation 1.3) and are listed in Table 3.4. Using this equation, a good correlation has been [170] found for the experimentally determined fluorescence lifetimes and the theoretically determined lifetimes. Thus the values obtained using this equation are believed to be a good measure of fluorescence lifetimes. τ_F values were generally low for all the complexes, though they were higher with the MOCPcs suggesting quenching of fluorescence due to aggregation in MTSPc. The addition of the CEL slightly increased the τ_F values for the MTSPc complexes. The rate constants for fluorescence (k_F) (Table 3.5) were about the same for all the complexes except for OTiOCPc, (OH)GaOCPc, (OH)GaTSPc and ZnTSPc (the latter two in the presence of CEL).

Table 3.5 Rate constants for various excited state deactivation processes of the	
MOCPc and MTSPc complexes in aqueous media and in the presence of CEL	

Compound	Solvent	$a \mathbf{k_f} / \mathbf{s}^{-1}$	^b k _{ISC} /s ⁻¹	^c k _{IC} /s ⁻¹	$^{d}k_{d}/s^{-1}$
		(×10 ⁸)	(×10 ⁹)	(×10 ⁹)	
ZnOCPc	pH 10	1.28	0.18	0.24	3.77
OTiOCPc	рН 10	0.44	0.15	0.46	28.3
(OH)GaOCPc	pH 11	0.16	0.52	0.09	9.77
(OH) ₂ SiOCPc	pH 10	1.01	0.56	1.20	7.71
ZnTSPc	pH 10	1.44	25.5	20.0	4.96
	pH 10 + CEL	0.54	0.18	0.04	5.26
OTiTSPc	pH 10	1.11	5.42	164	12.2
	pH 10 + CEL	1.46	3.44	7.20	8.25
(OH)GaTSPc	pH 11 + CEL	0.98	0.57	0.42	4.68
	pH 11 + CEL	0.42	0.18	0.06	4.43
(OH) ₂ SiTSPc	pH 10	1.46	0.26	1.53	2.53
	pH 10 + CEL	1.64	3.22	1.25	13.2

 a k_F is the rate constant for fluorescence. Values calculated using k_F = $\Phi_F/\tau_F.$

 b k_{ISC} is the rate constant for intersystem crossing. Values calculated using $k_{ISC} = \Phi_{T} / \tau_{F}$.

 c k_{IC} is the rate constant for internal conversion. Values calculated using $k_{IC} = \Phi_{IC}/\tau_{F}$.

 d k_d is the rate constant for photodegredation. Values calculated using $k_d = \Phi_d / \tau_T.$

3.2.1.2 Triplet state spectra and parameters

Triplet quantum yield (Φ_T) is the measure of the fraction of absorbing molecules that undergoes intersystem crossing (ISC) to the triplet state. The efficiency of a phthalocyanine as a photosensitizer is determined by its triplet state quantum yield and lifetime (τ_T). The triplet quantum yields, Table 3.4, were determined using the laser flash photolysis set up shown on the experimental section (Chapter 2) and calculated using Equation 1.4 as discussed in chapter 1. The MTSPc complexes all have high Φ_T values both in the absence or presence of CEL except for OTiTSPc which shows low with or without CEL. It should be noted that the d-orbitals of the Ti metal are not fully filled and this may result in quenching of the triplet state. Φ_T values were higher in the presence of CEL since the MTSPc complexes are disaggregated in this case, monomers have greater tendencies to undergo intersystem crossing because less energy is lost through internal conversion. Of the MOCPcs, the OTiOCPc complex has the lowest Φ_T value compared to zinc, gallium and silicon as observed for the tetrasulfonated derivatives. (OH)GaOCPc gave the highest value of Φ_T among the set of the MOCPc complexes.



Figure 3.12: Transient differential curve for (OH)GaOCPc in pH 11, excitation wavelength = 687 nm and triplet decay curve insert.

Fig. 3.12 shows the transient absorption spectrum of (OH)GaOCPc in pH 11. The absorption of the triplet state is at ~460–550 nm. The triplet decay curve of (OH)GaOCPc in pH 11 is shown in Fig. 3.12 (inset), and it obeyed second order kinetics. This is typical of MPc complexes at high concentrations (> 1 x 10^{-5} M) [171] due to triplet–triplet recombination. The concentrations employed in this work were in this range hence triplet-triplet recombination is expected. The triplet life times were determined from the triplet decay curve Fig. 3.12 (inset) by exponential fitting of the kinetic curves using the program OriginPro 7.5. The triplet lifetimes are highly

influenced by the presence of oxygen, however in this thesis the solutions for triplet lifetimes determinations were deaerated sufficiently before recording of flash photolysis traces.

The triplet lifetime (Table 3.4), τ_T , values range from 40-270 µs, which is a usual range for many MPc complexes. Of the tetrasulfonated complexes in Table 3.4, ZnTSPc with the highest Φ_T has the longest triplet lifetime in the absence of CEL (190µs). (OH)GaTSPc, (OH)₂SiTSPc and OTiTSPc gave shorter triplet lifetimes (60, 40 and 50 µs) in the absence of CEL. Lifetimes were longer in the presence of CEL compared to aqueous solution alone for the MTSPc complexes, which may be due to the reduction in the exposure of the phthalocyanine to the aqueous medium because of the presence of the CEL. The same trend was also observed in the τ_T values of the MOCPcs, with ZnOCPc having the longest lifetime.

The Φ_{IC} values (Table 3.4) were generally high in the MTSPcs due to the dissipation of electronic energy by the aggregates. A decrease in Φ_{IC} values in the presence of CEL was observed due to the monomerizing effect of CEL on the MTSPc complexes. Φ_{IC} values were also found to be high for the MOCPcs except for ZnOCPc and (OH)GaOCPc. The rate constants for internal conversion (k_{IC}) in in aqueous media buffer (Table 3.5) are generally higher for the MTSPcs compared to the corresponding MOCPcs, this could be due to aggregation of the former. On addition of CEL to MTSPc complexes, the k_{IC} values decrease drastically showing the effects of aggregation, Table 3.5. Larger rate constants for intersystem crossing (k_{ISC}) were observed for the MTSPc complexes compared to the sulfonic substituents may encourage intersystem crossing to the triplet state more than the carboxylic ones.

3.2.1.3 Singlet oxygen and photodegradation quantum yields

Table 3.6 Singlet oxygen and photodegradation quantum yields for the MOCPcs and MTSPcs complexes in aqueous media and in the presence of CEL. ^b References in brackets.

Sample	Solvent	λ_Q/nm	Φ_{Δ}	\mathbf{S}_{Δ}	Φ_{Pd} (×10 ⁻⁴)
ZnOCPc	pH 10	689	0.52 [150] ^b	1.0	4.90
OTiOCPc	рН 10	693	0.24	1.2	19.8
(OH)GaOCPc	рН 11	688	0.49	0.73	7.82
(OH) ₂ SiOCPc	рН 10	690	0.33	1.1	5.40
ZnTSPc	pH 10	678,640	0.03	0.05	9.42
	pH 10 + CEL	678	0.12	0.18	14.2
OTiTSPc	pH 10	672,660	0.03	1.0	4.95
	pH 10 + CEL	695	0.13	0.41	6.12
(OH)GaTSPc	pH 11	674	0.44	0.85	2.81
	pH 11 + CEL	678	0.47	0.75	3.54
(OH) ₂ SiTSPc	pH 10	677,639	0.20	0.38	1.15
	pH 10 + CEL	677	0.52	0.89	1.52

Energy transfer between the triplet state of photosensitizers and ground state molecular oxygen leads to the production of singlet oxygen, Φ_{Δ} . There is a necessity of high efficiency of transfer of energy between excited triplet state of MPc and ground state of oxygen to generate large amounts of singlet oxygen.

The singlet oxygen (Φ_{Δ}) and photodegradation (Φ_{Pd}) quantum yields values (Table 3.6) were obtained using the singlet oxygen and photodegradation set up described on the experimental section (Chapter 2). The Φ_{Δ} values were calculated using Equation 1.6 as shown in chapter 1. The singlet oxygen quantum yields are higher for the MOCPc complexes (Table 3.6) compared to MTSPc complexes in pH 11 without CEL, due to their aggregated nature, except for (OH)GaTSPc that showed the highest values of singlet oxygen quantum yields both in the absence and presence of CEL, this is because the later was less aggregated in aqueous media compared to the other MTSPc complexes. There was however an improvement in the singlet oxygen yields for all the MTSPc complexes on addition of CEL due to disaggregation. The efficiency of quenching of the triplet excited state by oxygen, S_{Δ} (= Φ_{Δ}/Φ_{T}), were near unity (Table 3.6) for the MOCPcs while they were low for the MTSPcs except for (OH)GaTSPc, OTiTSPc and (OH)₂SiTSPc (the latter in the presence of CEL).

Oxidative attack on the excited triplet state of MPcs by singlet oxygen brings about photodegradation, since the triplet state is sufficiently long lived to participate in photochemical reactions. It is believed that singlet oxygen has the ability to react with macrocyclic metal complexes [117]. Quantum yields for photodegradation were calculated using Equation 1.7 as shown in chapter 1. Photodegradation quantum yields (Φ_{Pd}) of the MPc complexes were generally within the range for MPc complexes, Table 3.6. The addition of CEL increased the photodegradation quantum yields in all the complexes. There was no clear trend with regards to the rate constants for photodegradation (k_d), Table 3.5. There was an increase in k_d values for (OH)SiTSPc and ZnTSPc on addition of CEL, but a decrease for (OH)GaTSPc and OTiTSPc , Table 3.5.

3.2.2 Quaternized cationic (Q(T-2-Py)MPcs) MPcs and their unquaternized (UnQ(T-2-Py)MPcs) derivatives

3.2.2.1 Fluorescence spectra and parameters

For all the UnQ(T-2-Py)Mpc complexes in DMF, the excitation spectra were similar to absorption spectra and both were mirror images of absorption spectra.

Fig 3.13 compares the absorption, fluorescence excitation and emission spectra of quaternized cationic water soluble MPcs (Q(T-2-Py)MPcs) in pH 11 buffer alone or pH 11 + CEL. The excitation spectra are almost similar to absorption spectra in the presence and absence of CEL only for the Q(T-2-Py)ClAlPc only Fig. 3.13 (a).

Due to aggregation in the absence of CEL for the UnQ(T-2-Py)ClGaPc, UnQ(T-2-Py)Cl₂SiPc and UnQ(T-2-Py)OTiPc (eg. Fig. 3.13 (c)) there was a lack of agreement between absorption and excitation spectra, since aggregates do not fluoresce.

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Figure 3.13: Ground state absorption, fluorescence excitation and emission spectra of (Q(T-2-Py)ClAlPc) in pH 11 alone, (Q(T-2-Py)Cl₂SiPc) in pH 11 plus CEL, (Q(T-2-Py)OTiPc) in pH 11 buffer alone.

Table 3.7: The phophysical parameters of the various MPcs; Triplet quantum yields (Φ_T), fluorescence yields (Φ_T), internal conversion (Φ_T), and triplet life times (τ_T). Values in parenthesis are for pH 11 plus cremophor (CEL).

Compound	Solvent	$\Phi_{_{\mathrm{T}}}$	$\Phi_{_{\rm F}}$	Φ _{IC}	τ _T (μs)
UnQ(T-2-Py)ClAlPc	DMF	0.65	0.12	0.23	70
UnQ(T-2-Py)ClGaPc	DMF	0.59	0.16	0.25	120
UnQ(T-2-Py)ClGaPc	DMSO	0.70	0.20	0.10	170
^a UnQ(T-3-Py)ClGaPc	DMSO	0.57	0.19	0.24	160
UnQ(T-2-Py)Cl ₂ SiPc	DMF	0.77	0.10	0.13	40
UnQ(T-2-Py)OTiPc	DMF	0.69	0.04	0.27	190
Q(T-2-Py)ClAlPc	pH 11	0.56	0.12	0.32	70
		(0.61)	(0.23)	(0.16)	(160)
Q(T-2-Py)ClGaPc	pH 11	0.55	< 0.01	0.45	60
		(0.68)	(0.04)	(0.28)	(170)
^a Q(T-3-Py)ClGaPc	water	0.61	0.12	0.27	50
Q(T-2-Py)Cl ₂ SiPc	pH 11	0.51	< 0.01	0.48	110
		(0.73)	(0.10)	(0.17)	(220)
Q(T-2-Py)OTiPc	pH 11	0.55	< 0.01	0.44	50
		(0.62)	(0.16)	(0.22)	(190)

^aValues from reference 172

Table 3.7 lists the photophysical parameters of the various MPc complexes. Higher fluorescence quantum yields (Φ_F) were obtained for the unquaternized complexes in DMF probably due to their monomeric nature compared to their quaternized water soluble derivatives in pH 11 alone, with the exception of ClAIPc derivatives.

Low fluorescence yields (<0.01) were obtained for quaternized complexes: (QT-2-PyClGaPc, QT-2-PyCl₂SiPc and QT-2-PyOTiPc, in pH 11 buffer alone due to higher aggregation tendencies of these complexes in aqueous media. Monomerization of the aggregates enhances fluorescence and this is noticed in the Φ_F of the complexes in DMF for the UnQT-2-PyMPcs and in the presence of CEL for the QT-2-PyMPcs.

The quaternized water soluble aluminium complex (QT-2-PyClAlPc) gave the higher fluorescence yield in the presence of CEL, compared to pH 11 alone, suggesting that there was some small aggregation in this complex.





Figure 3.14: Typical triplet decay curve of Q(T-2-Py)ClAlPc upon excitation in pH 11 in the presence of CEL, excitation wavelength = 681 nm

Fig. 3.14 shows the triplet decay curve for complex Q(T-2-Py)ClAlPc which obeyed second order kinetics. This is typical of MPc complexes at high concentrations due to the triplet-triplet recombination as stated already. The unquaternized (UnQ(T-2-Py)MPc) MPc complexes in DMF gave higher triplet quantum yields (Φ_T) than the corresponding quaternized complexes in the absence of CEL, Table 3.7. However there was a high improvement on the Φ_T values on addition of CEL. The Φ_T values will be affected by aggregation and also by the nature of the solvent. Water does quench the triplet state of phthalocyanine complexes. The Q(T-2-Py)ClAlPc which is not significantly aggregated in pH 11 buffer alone, gave Φ_T value which is similar to the Q(T-2-Py)OTiPc complex in both pH 11 alone and in the presence of CEL. This could be due to more enhanced intersystem crossing in the Q(T-2-Py)OTiPc complex due to its size even though the complex is aggregated in pH 11 alone. The silicon complexes in DMF and in pH 11 + CEL gave the highest triplet yields of 0.77 and 0.73, respectively.

More energy was lost through internal conversion due to aggregation for Q(T-2-Py)ClGaPc, Q(T-2-Py)Cl_2SiPc and Q(T-2-Py)OTiPc complexes in pH 11 alone, as judged by higher yield of internal conversion (Φ_{IC}) of 0.45, 0.48 and 0.44, respectively.

The τ_T values for UnQ(T-2-Py)ClGaPc reported in this work in DMSO were marginally higher than those reported for the corresponding UnQ(T-3-Py)ClGaPc [172], Table 2. Similarly for Q(T-2-Py)ClGaPc, τ_T values are slightly higher than the corresponding Q(T-3-Py)ClGaPc in aqueous media [172]. As stated above, pH 11 is employed in this thesis in order to ensure solubility of all complexes (MOCPc complexes in particular are soluble in basic media). The reported data [172] for Q(T-3-Py)ClGaPc were in non-buffered water. Lifetimes were longer in the presence of CEL compared to pH 11 (in the absence of CEL) for all the water soluble complexes which may be due to the reduction in the exposure of the phthalocyanine in the aqueous medium because of the presence of the CEL as stated already and due to monomerization. The highest triplet lifetime of 220 µs is observed for complex Q(T-2-Py)Cl₂SiPc in the presence of CEL. The unquaternized titanium complex (UnQ(T-2-Py)OTiPc) in DMF and its quaternized (Q(T-2-Py)OTiPc) water soluble derivative in the presence of CEL gave the same triplet lifetime of 190 µs respectively. Lowest triplet lifetimes were observed for the UnQ(T-2-Py)Cl₂SiPc complex. Even though water is known to quench triplet states [102], the triplet lifetimes in DMF for unquaternized complexes are similar to those of the quaternized complexes in aqueous media.

3.3 Electrochemical and photoelectrochamical properties

3.3.1 Electrochemical properties for the MOCPcs

Table 3.8: Half wave potential $(E_{1/2})$ of the MOCPc (Ti, Si and Zn) complexes in Ph 10 buffer (vs Ag|AgCl).

Complex	E _{1/2} (mV)			
	I (Pc^{-3}/Pc^{-4})	$II (Pc^{-2}/Pc^{-3})$		
OTiOCPc	-714	-512		
(OH) ₂ SiOCPc	-632	-482		
ZnOCPc	-776	-596		

Cyclic and square wave volammetry (SWV) studies (Fig. 3.15, for ZnOCPc and (OH)₂SiOCPc) were undertaken for the MOCPc complexes which were not aggregated in order to determine the relative ease of reduction of the complexes. (OH)₂SiOCPc and ZnOCPc complexes are expected to show only ring based processes. Two ring based reduction processes were observed for the complexes (including OTiOCPc) Fig. 3.15 and their redox potentials are summarized in Table 3.8.



Figure 3.15: Cyclic and square wave voltamograms of (a) (OH)₂SiTSPc and (b) ZnOCPc in a buffer solution of pH 10 at a scan rate of 50mV/s.

All the processes showed reversible to quasi-reversible behavior with cathodic to anodic peak separations (ΔE) of 90 mV to 120 mV. A ΔE of the ferrocene standard was 120 mV in the same

solvent. SWV showed reversibility of the couples (Fig. 3.15 inset). The redox processes labeled **I** are assigned to MPc⁻³/MPc⁻⁴ and **II** to MPc⁻²/MPc⁻³ according to literature [173] for water soluble and redox inactive central metals. Table 3.8 shows that the Si and Ti complexes are more easily reduced than the zinc complex due to the tetra positive nature of the central metal.

3.3.2 Photoelectrochemical properties

3.3.2.1 Preparation of nanoporous ZnO, dye (MPc) readsoption and surface morphology

Deposition of nanoporous ZnO in the presence of eosin Y as a structural directing agent (SDA) was achieved electrochemically as described in the experimental section and in chapter 1 following Equation 1.13 and 1.14.

Electrodeposition of ZnO in the presence of eosin Y was carried out at a potential of -1.0 V vs SCE. The film growth was monitored, and a plot of the observed current against time, which is typical of ZnO growth during deposition in the presence of eosin Y was obtained [138, 174,175] (Fig. 3.16). An increase in current up to 2.37 mA.cm⁻² was observed at the beginning of the transient curve from time 0 to 300 min, which was due to the substrate activation following the reduction of oxygen. A decrease in current to 1.26 mA.cm⁻² was observed during the formation of the ZnO and was constant from time 300 to 600 min. Finally a gradual increase in current was

observed from time 600 to 1800 min, as a result of the eosin Y that was added to block the ZnO gowth to induce porocity of the film.



Figure 3.16: Current vs time transient obtained during the cathodic electrodeposition of ZnO/eosin Y films from aqueous 5 mM ZnCl₂, 50 mM eosin Y, O₂ saturated 0.1 M KCl at 70 °C.

Fig. 3.17 (a) shows typical scanning electron microscope (SEM) images of nanostructured ZnO in the presence of eosin Y. Nanoporous substrates are very important in dye sensitized solar cells as they act as a sponge like structure such that a high concentration of the dye molecules can be re-adsorbed on the surface of the film.



Figure 3.17: Scanning electron microscope images (SEM) of nonporous ZnO in the presence of eosin Y (a) and after the desorption of eosin Y (b).

When the SDA was desorbed (cleaved off) from the ZnO surface by treatment with KOH, the surface area of ZnO increases significantly, with a high porous structured ZnO. A clear nanoporous ZnO structure is observed after desorption of Eyosin Y (as SDA), Fig. 3.17 (b), a single ZnO particle is shown on the inset. Such crystal shape of nanoporous ZnO SEM images has been previously reported using different SDAs [176].

Then MPc dye adsorption was done by refluxing the nanoporous ZnO (Fig. 3.18 (white)) thin film in a solution of KOH (pH 11) containing 1 mM MPc dye under investigation at a reflux temperature of 80 °C as described on the experimental section.



Figure 3.18: Images displaying films; electrodeposited ZnO in the presence of eosin Y (red), after desorption of eosin Y (white) (treatment with KOH), and in the presence of OTiOCPc (blue).

A color change from red to white was observed indicating complete desorption of eosin Y from the ZnO surface Fig 3.18. When the MPc dye molecules were readsorbed on the surface of ZnO after desorption of eosin Y, an intense blue-green color was observed suggesting complete coverage of the ZnO by the dye molecules (Fig. 3.18 (blue)). The ZnO/MPc films were then charachterised by UV-Vis spectra in order to determine whether there were changes (e.g aggregation) on the electronic structure of the dye molecules on the ZnO surface.



Figure 3.19: Electronic absorption spectra (a) (OH)GaOCPc, (b) ZnOCPc, (c) OTiOCPc, (d) (OH)₂SiOCPc and (e) (OH)AlOCPc deposited on ZnO/FTO substrate.

Fig. 3.19 shows the solid state absorption spectra of the different MOCPc complexes adsorbed on the surface of a nanoporous ZnO thin film deposited on FTO substrate. There were new bands formed due to aggregation for all complexes on the ZnO substrate, this is due to self assembly of phthalocyanines on the surface. The bands in the long wavelength region for all the complexes in the Q-band region are due to the monomeric species in these molecules and are more intense than the dimeric bands that are observed towards the short wavelength region of the Q-band absorption, suggesting weak aggregation [87,89]. All complexes were monomeric in aqueous solution as shown on the spectral characterization for the MOCPc complexes Fig. 3.3, but aggregates are expected in the solid state Fig. 3.19. It has been documented that for a better efficiency for dye-sensitized solar cells [148], there must be a full monolayer surface coverage of the dye molecules on the ZnO surface which in practice leads to interaction of dye molecules.

For a full surface coverage to be accomplished dye molecules have to be in a close proximity to each other as much as possible and an interaction of the dye molecules themselves is required to form a self assembled monolayer hybrid. Nevertheless strong electronic coupling of sensitizers as observed, for example, in phthalocyanine aggregates can lead to an increased rate of non-radiative recombination and an increased rate of back- electron transfer [138, 149]. Aggregates are not photoactive [150], hence the presence of dimers will lead to a lower efficiency of the photovoltaic cells performance. The presence of axial ligands did not influence aggregation significantly. For example, Fig. 3.19 the aggregate band was almost as intense as the monomer band for axially ligated (OH)GaOCPc (a), whereas for ZnOCPc containing no axial ligand, the band due to the aggregate was much weaker than that of the monomeric species. The tetrasulfo phthalocyanines (MTSPcs) and the quaternized cationic (Q(T-2-Py)MPcs) water soluble phthalocyanine were also employed for photoelectrochemical studies despite their high

aggregation tendencies in aqueous solution (Fig 3.1 for MTSPcs and Figure 3.6 for Q(T-2-Py)MPcs).



Figure 3.20: Laser microscopic images of FTO (a) and ZnO on FTO (b), (OH)AlOCPc (c), OTiOCPc (d), (OH)₂SiOCPc (e), ZnOCPc (f), OTiTSPc (g) and QT-2-PyCl₂SiPc (h) deposited on ZnO/FTO

Shown in Fig 3.20 are laser microscopic images of various MPc thin films deposited on ZnO/FTO hybrid. Fig 3.20 (a) shows the plain FTO conducting glass substrate alone, a uniform nanoporous structure of ZnO was observed (b) after deposited of the ZnO on the FTO. Different dye molecules showed different morphologies when deposited on the ZnO/FTO hybrid film. Figure 3.20 (c), (e) and (f) displays the (OH)AlOCPc (c), (OH)₂SiOCPc (e) and ZnOCPc (f) on ZnO/FTO. Small aggregates were observed for (OH)AlOCPc, (OH)₂SiOCPc and ZnOCPc. A homogeneous morphology was observed for the OTiOCPc film (d) that might be due to the oxo axial ligand on the central metal prevening closeness of molecules to each other. Agglomerates were observed for the films deposited with aggregated MTSPcs and Q(T-2-Py)MPcs, using the OTiTSPc and Q(T-2-Py)Cl₂SiPc Fig. 3.20 films as examples. This is an indication that since the MTSPcs and QT-2-PyMPcs were aggregated even in solution, strong forces of aggregates are expected in the solid state which may lower their photoelectrochemical performance.

3.3.2.2 Photoelectrochemical measurements and parameters

The photoelctrochemical behavior of some MTSPc complexes is known [81] and studies have shown that aggregation is the limitation for these complexes. However the MOCPc which are not aggregated in solution were employed as photosensitizers for ZnO based solar cell for the first time in this thesis. Dyes with carboxylic and sulfonic substituents were selected since they are known to form an ester-like linkage with the ZnO surface [138-140].

Table 3.9: Summary of the photoelectrochemical data obtained during the study of various films at different deposition times, the photoelectrochemical data was obtained at an incident photon flux of 10¹⁶ s⁻¹ cm⁻² conditions for measuring IPCE and APCE, and 100 mW.cm⁻² white light with UV- and water filter (close to AM 1.5) for FF and efficiency.

Compound	Deposition period	% FF	% IPCE	% APCE	Abs	%η _e
ZnOCPc	150 min	25.0	23.1	25.7	0.99	0.32
(OH)GaOCPc	5 days	25.1	2.00	2.12	1.10	0.05
OTiOCPc	90 min	28.0	42.3	96.7	0.25	0.19
OTiOCPc	5 days	36.4	50.6	62.8	0.71	0.45
(OH)AlOCPc	60 min	35.6	3.66	8.40	0.25	0.16
(OH) ₂ SiOCPc	5 days	48.6	15.8	28.0	0.36	0.21
Q(T-2-Py)ClGaPc	90 min	33.6	2.5	4.7	0.31	0.06
Q(T-2-Py)Cl ₂ SiPc	5 days	39.9	16.6	18.9	0.91	0.30
Q(T-2-Py)OTiPc	180 min	38.5	0.20	0.4	0.26	0.009
Q(T-2-Py)ClAlPc	5 days	38.12	2.65	3.11	0.83	0.08
OTiTSPc	60 min	37.3	0.66	1.3	0.31	0.009
(OH)GaTSPc	4 hrs	34.24	0.81	1.40	0.37	0.05

The photelectrochemical measurements were performed at Justus-Liebig University, Germany, using the experimental set up as described on the experimental section.

Table 3.9 summarizes photovoltaic parameters; the incident photon to current conversion efficiency (IPCE), absorbed photon to current conversion efficiency (APCE), fill factors (FF) and overall cell efficiency ($\%\eta_e$) at optimum deposition time for all the complexes. And were calculated using Equations 1.9, 1.10, 1.11 and 1.12 as described on Chapter 1.

The IPCE obtained for the MOCPc complexes were quite high and a record for phthalocyanine/ZnO sensitization, with OTiOCPc giving the highest external quantum efficiency (IPCE) of 42.3% (for 90 min deposition time) and 50.6% (for 5 days deposition time), Table 3.9. This was also observed on the photocurrent transient curves Fig. 3.21 (a) where OTiOCPc/ZnO film under illumination at the Q-band wavelength gave the highest photocurrent density of 0.81 mA.cm⁻² at a photon flux of 10^{16} photons s⁻¹.cm⁻². Such high external IPCE efficiencies have not been reported before on ZnO/phthalocvanines sensitized cells. Lower IPCE were obtained for the MTSPcs and the Q(T-2-Py)MPcs which is a results of the high aggregation tendencies of these molecules in aqueous solutions. The Q(T-2-Py)Cl₂SiPc complex gave better IPCE efficiencies (16.6) among the aggregated quaternized cationic phthalocyanine complexes. ZnO/(OH)₂SiOCPc (5 days deposition time, IPCE = 15.8), ZnO/(OH)AlOCPc (60 min deposition time, IPCE = 3.66), ZnO/(OH)GaOCPc (5 days deposition time, IPCE = 2.0) and ZnO/OTiOCPc (90 min deposition time, IPCE = 23.1) films gave lower external quantum efficiencies (IPCE) among the MOCPc complexes but they were much higher compared to the MTSPcs and Q(T-2-Py)MPcs complexes. For OTiOCPc, there was an improvement on external quantum efficiencies (IPCE) for films deposited over 5 days while (OH)AlOCPc and (OH)GaOCPc were highly aggregated when left for over 5 days and agglomerates were formed.



Figure 3.21: Time dependent photocurrent transient curves under optimum deposition of OTiOCPc (a), ZnOCPc (b), (OH)SiOCPc (c), (OH)AlOCPc (d), and (OH)GaOCPc (e) deposited on ZnO/FTO under illumination at the Qband wavelength maxima (i) and under illumination with white light (ii).

The low IPCE values for the MTSPc, Q(T-2-Py)MPc complexes and in some of the MOCPc is due to aggregation, which leads to charge traps and non-radiative recombination of charges before and after electron injection from the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine molecules to the conduction band of ZnO or to increased recombination of charges already injected to the electrolyte. Low IPCE was observed for the (OH)AlOCPc due to less amount of dye molecules on the ZnO surface as was judged by its lower absorbance on Table 3.9. Lower absorbance was obtained even when the film was left longer (5 days) on the deposition bath for the (OH)AlOCPc, OTiTSPc and (OH)GaTSPc. The lower IPCE for the (OH)GaOCPc was due to very strong forces of aggregates on the surface of the electrode, which was also evident from their solid state absorption spectra Fig. 3.19 (a).

The same trend of variation on photocurrent densities for all the MOCPc complexes was observed both under illumination at the Q-band (Fig. 3.21 (i)) wavelength and under illumination with white light shown in Fig. 3.21 (ii). The time resolved photocurrent density transients were similar in shape (Fig. 3.21) for all the complexes indicating that similar relative rates of fast electron injection and reduction of dye regeneration were obtained. Hence almost rectangular photocurrent responses were obtained for the complexes, especially for the complexes with higher quantum efficiencies (IPCE) with almost no overshoot photocurrent when the light was switched on, showing that the dye molecules are in contact with the electrolyte [81] and therefore suggesting a full coverage.

The internal quantum efficiency determines the number of electrons that are photogenerated or converted to the external circuit per photon absorbed on the surface of the electrode. It is known as the absorbed photon to current conversion efficiency (APCE). The APCE is therefore an important parameter to determine the efficiencies of the internal processes like injection

efficiency, and is consequently able to show the potential sensitizing properties of a dye molecule of a given combination of materials. As shown in Table 3.9, again the ZnO/OTiOCPc gave the highest APCE of 96.7% (for 90 min deposition time) and 62.8% (for 5 days deposition time) with the absorbed light intensity at absorbance of 0.25 and 0.71, respectively. The fact that nearly almost every absorbed photon generates an electron in the external circuit after 90 minutes of dye adsorption speaks for a very efficient injection of electrons into the conduction band of the ZnO at low recombination probability showing the potential of the dye as a sensitizer. After 5 days re-adsorption for OTiOCPc, more dye molecules were re-adsorbed to the surface whose injection efficiency was decreased so as judged by the decrease in APCE. This suggests readsorption of dye molecules that are not directly connected to the ZnO. However for OTiOCPc the overall efficiency (% $\eta_{\rm o})$ increased from 0.19% (90 minutes) to 0.45% (5 days of dye adsorption), confirming a relative increase in the overall cell (%n) efficiency with a higher amount of dye (0.25 at 90 minutes, and 0.71 after a period of 5 days) absorbed to the ZnO/FTO substrate. Very low APCE and $\eta_{_{e}}$ values were obtained for the MTSPc and Q(T-2-Py)MPcs due to aggregation, except the Q(T-2-Py)Cl_2SiPc. Lower $\eta_{_{P}}$ value was observed for (OH)GaOCPc electrode due to a higher concentration of aggregates on the surface of the electrode as evident from the high-energy shoulder of the Q-band in the UV-vis spectra 3.19 (a). ZnOCPc gave the the second highest $\eta_{_{e}}\,$ value of 0.32% due to high amount of (less aggregated, absorbance $\sim 0.99)$ dye molecules absorbed on the ZnO substrate.



Figure 3.22: Power to voltage curves of OTiOCPc (a), ZnOCPc (b), (OH)₂SiOCPc (c), (OH)AlOCPc (d) and (OH)GaOCPc (e) under illumination with white light on the FTO/ZnO substrate.

Fig. 3.22 displays the photogenerated power per illuminated area of the selected MOCPc complexes deposited ZnO/FTO substrate. ZnO/OTiOCPc (a) showed the highest photogenerated power of (448 μ W.cm⁻²) under illumination with white light. Followed by the ZnO/ZnOCPc. Low photogenerated power were observed for ZnO/(OH)AlPc (d) and ZnO/(OH)GaOCPc (e). The MTSPcs and QT-2-PyMPcs gave very low power as judged by their overall cell efficiencies, Table 3.9, such low performance or low photogenerated power are a result of recombination of

charges upon electron injection to the conduction band of ZnO due to higher concentration of aggregated species on the electrode surface for these complexes.



Figure 3.23: Time dependent photovoltage curves of OTiOCPc (a), ZnOCPc (b), (OH)AlOCPc (c), (OH)SiOCPc (d), and (OH)GaOCPc (e) deposited on ZnO/FTO substrate under illumination with white light.

Fig 3.23 shows the time- resolved photovoltage curves for the different films under illumination with white light, Fig. 3.23 (a) with ZnO/OTiOCPc film giving the highest photovoltages of 0.41 V. $(OH)_2SiOCPc$ (d) showed fast photovoltage decay immediately after the shutter was closed. ZnO/(OH)GaOCPc and ZnO/(OH)_2SiOCPc films gave lower photovoltages of 0.25 V

and 0.31 V among the MOCPc complexes Fig. 3.23. The MTSPcs and QT-2-PyMPcs gave lower photovoltages as a result of strong forces of aggregates of these complexes on the films and the ZnO is not fully covered as was evident with their laser microscopic pictures (Fig. 3.20) because aggregates are too bulky to cover the surface efficiently. Therefore, the amount of charge is low then resulting in lower photovoltages.



Figure 3.24. Photocurrent density to voltage curves (I-V) of nanocrystalline ZnO sensitized with (OH)₂SiOCPc under illumination with AM 1.5 simulated sunlight (dotted black) and in the dark (dotted blue).

Shown in Fig. 3.24 is a typical current to voltage curve (I-V) characteristics under illumination with white light (dotted black) and in the dark (dotted blue) for the $ZnO/(OH)_2SiPc$ film giving the short circuit photocurrent (I_{se}) of 1.22 mA.cm⁻² and open circuit voltage (V_{oc}) of 0.35 V. The fill factor (FF) values are determined by the area of the largest rectangle under the illuminated curve. Faradaic characteristics were observed for the films also reflected in higher power fill factors shown in Table 3.9. The ZnO/(OH)₂SiOCPc films gave the highest fill factors of 48.6%, ZnO/ZnOCPc, ZnO/(OH)GaOCPc gave similar values of fill factor of 25% with the ZnO/OTiOCPc giving 36% fill factor. The fill factor being so low for all the complexes (MOCPc, MTSPc and QT-2-PyMPc) is a decisive factor that is limiting the cell efficiency, these is due to the fact that the electrolyte is less shielded from the ZnO substrate by the dye molecules as a result of aggregation. The fill factor can then be improved by additives in the redox solution of the cell, these studies were not done in this work, for the simplicity of the experiments. In this work the focus was to compare the dyes only in the absence of additives. Further optimization of the experiments for the promising dyes found in this work should improve the efficiencies.

CHAPTER FOUR

CONCLUSIONS

4.1 General conclusions

In conclusion, there was a success in the synthesis and characterization of a series of novel UnQ(T-2-Py)MPcs (M = aluminium, gallium, silicon, and titanium) peripherally tetra-substituted with 2-pyridiloxy groups. The coumpounds were effectively quaternized to give new watersoluble cationic Q(T-2-Py MPcs. This work also presented the synthesis and characterization of water soluble anionic gallium, silicon, titanium and zinc tetra-substituted with sulfonic groups (MTSPcs) and octa-substituted with carboxylic groups (MOCPcs). All the complexes presented in this thesis gave satisfactory spectroscopic results confirming their purity. All the MOCPc complexes exhibited a monomeric behavior in aqueous solution as was evident by their UV-vis spectra characteristic of a high intense monomeric Q-band absorption. The tetra-substituted anionic (MTSPc), and cationic (Q(T-2-Py)MPcs) were aggregated in aqueous solutions, as was evidenced by their UV-vis showing split and broadening of absorption spectra. The aggregated complexes were partially or completely disaggregated upon addition of a surfactant (cremophor EL). The photophysical and photochemical properties of anionic (MOCPcs and MTSPcs) water soluble of gallium, titanium, silicon and zinc were investigated and compared. Triplet quantum yields ranged from 0.20 to 0.67 for MOCPcs and 0.32 to 0.65 for MTSPcs in aqueous solution and in the presence of CEL. High triplet lifetimes were observed for the zinc complexes ZnTSPc (270 µs, in the presence of CEL) and ZnOCPc (130 µs). The gallium complexes gave highest triplet yields (OH)GaTSPc (0.63 in the presence of CEL) and (OH)GaOCPc (0.67) which resulted in the production of higher singlet oxygen. Singlet oxygen quantum yields were very low for the tetrasulfo phthalyanines in aqueous solution except for gallium, but a high improvement was observed in the presence of CEL. Overall the MOCPc gave higher singlet oxygen quantum yields than the MTSPcs.

Higher triplet yields were obtained for the quaternized cationic water (Q(T-2-Py)MPcs) soluble phthalocyanines compared to the anionic (MTSPcs and MOCPcs) counterparts, since the pyridiloxy groups have an ability to enhance intersystem crossing more that the sulfo- and caboxy- groups. A remarkable improvement in triplet and fluorescence yields including the triplet lifetimes was achieved for the aggregated Q(T-2-Py)MPc complexes when they were studied in the presence of CEL. The photophysical behavior of all the complexes can be summerised as follows; Q(T-2-Py)MPcs > MOCPcs > MTSPcs. Based on the water solubility and the excellent photophysicochemical behavior of these molecules, therefore they have a potential to be used in areas such as photodynamic therapy of cancer (PDT).

Electrochemical studies showed that OTiOCPc and (OH)₂SiOCPc derivatives were more easily reduced than the ZnOCPc derivatives. Ease of reduction is a requirement for possible use of these complexes in photoelectrochemistry.

Photoelectrochemical studies of water soluble metallo-octacarboxy (MOCPcs) phthalocyanines compared with (MTSPcs and Q(T-2-Py)MPcs) shows that these molecules (especially the MOCPcs) incorporated with ZnO are promising candidates for the next renewable energy systems. Oxotitanium octacarboxy phthalocyanine (OTiOCPc) was the best sensitizer for ZnO with an IPCE value of 50.6% and an APCE of up to 96.7% and such values have not been achieved before on phthalocyanine/ZnO based dye sensitized solar cells. There was a poor efficiency of cells that were sensitized with MTSPcs and Q(T-2-Py)MPcs due to the ability to aggregate even in aqueous solution. The results obtained for the MOCPcs as sensitizers for nanoporous ZnO can therefore be seen as a very promising first step in the study of this group of sensitizers. To an appreciable extent OTiOCPc gave the best external and internal quantum
efficiency of phthalocyanines as sensitizers for electrodeposited nanoporous ZnO achieved so far.

4.2 Future perspective

Further optimization of electrodes for photoelectrochemistry based on these sensitizers (Q(T-2-Py)MPcs, MOCPcs and MTSPcs) appears very promising in particular because of high quantum efficiencies. Octacarboxy phthalocyanine molecules with bulky axial ligands to prevent aggregation on the other hand need to be synthesized and tested for photoelectrochemistry. Low symmetry phthalocyanines with only one sulfo- or carboxy- either axially ligated or on the periphery binding to the ZnO which may also reduce chances of aggregation can further be investigated.

A mixture of phthalocyanines with nanoparticles such as quantum dots may be employed as sensitizers to accomplish a full surface coverage and to harvest all the light in a broad spectrum of wavelength.

Here in this thesis the main focus was to experimentally use half-cells in testing varous MPcs for the sensitization of nanoporous ZnO substrates. In practice the results observed for the half-cells may differ in complete DSSCs. In future, fabrication of complete DSSCs using the studied MPc complexes as photosensitizers for nanoporous ZnO substrates would be of great importance.

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