

**PHOTOPHYSICAL AND PHOTOCHEMICAL
BEHAVIOUR OF
METALLOPHTHALOCYANINES: EFFECT OF
NANOPARTICLES AND MOLECULES OF
BIOLOGICAL IMPORTANCE**

A thesis submitted in fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Of

RHODES UNIVERSITY

By

MOPELOLA ABIDEMI IDOWU

January 2009

DEDICATION

To

Olufemi

Ogooluwa

Inioluwa

and

Olaoluwa

for their love, support and understanding

ACKNOWLEDGEMENTS

“Not by might, nor by power but by the spirit of the Lord of Hosts” Zechariah 4:6

To Him who has made all things possible through Christ, giving me strength, intuition, wisdom and understanding; be glory, honour and adoration.

My sincere gratitude goes to my supervisor, Prof. Tebello Nyokong for the opportunity to do research under her supervision. Prof., thank you for selflessly giving of your knowledge, time and guidance; your patience, support, encouragement and enthusiasm which has made this work a reality, cannot be quantified. Thank you Prof., for the opportunity of going to do part of my research at Justus-Liebig University, Germany.

My thanks go to my host at Justus-Liebig University, Germany, Prof. Dr. Derck Schlettwein and his research group for their support while I was there.

I also express my thanks to Prof. J.Y. Chen, Dr. O. Ogunsipe and Dr. E. Lamprecht for their numerous contributions in the course of this work.

I am especially thankful to my husband, for always being there for me, your love carried me through. To my children; thank you for the sacrifices, allowing me towards the quest for knowledge. To my family and friends, I acknowledge your prayers, love and support.

Many thanks to S22 research group, it was fun while it lasted; the Chemistry Department of Rhodes University, her staff members and postgraduate students for their assistance in numerous ways.

Financial support from Rhodes University, National Research Foundation (NRF) of South Africa and Andrew Mellon Foundation are gratefully acknowledged.

Thank you all!

ABSTRACT

Syntheses, spectral, photophysical and photochemical studies of some neutral, anionic and cationic metallophthalocyanine derivatives are presented. The effects of central metal ions, solvents, aggregation, surfactant, nanoparticles and bovine serum albumin on the photophysical and photochemical behaviour are investigated.

Mercaptocarboxylic acid stabilized CdTe quantum dots (QDs) were used as energy donors to anionic water-soluble MPcs through Förster resonance energy transfer (FRET). Energy transfer (ET) from the QDs to the MPcs occurred upon photoexcitation of the QDs. An enhancement in efficiency of ET with the nature of the cappings on the QDs was observed with few occurrences of a non-Förster type ET. QDs were found to improve the photophysicochemical behaviour of the MPcs, with the possibility of indirect production of singlet oxygen (Φ_{Δ}) via FRET mechanism. Interaction of the QDs with cationic water-soluble MPcs produced ion-pair complexes resulting in aggregates due to strong electronic coupling. The stoichiometry of the reaction and association constants are evaluated by the continuous variation method.

Improved photophysicochemical behaviour with no spectral alterations was observed in MPcs in the presence of magnetic fluid. Complexes showed high triplet quantum yields with corresponding long lifetimes and high photostability.

Elucidation of the results of the interaction of bovine serum albumin (BSA) with MPcs or QDs is presented. Increased efficiency of Φ_{Δ} generation of MPcs in the presence of BSA coupled with large binding constants, suggesting strong interaction of the MPcs with BSA was observed. Enhanced emission intensity of QDs when linked to or in a mixture with BSA due to radiationless recombination at the surface vacancies was also observed.

The study revealed positive deviation from Stern-Volmer relationship suggesting the occurrence of static and dynamic mechanisms of quenching together.

Fluorescence quenching of the MPcs by benzoquinone, analysed by Stern-Volmer relationship is also presented; the results were employed in determining fluorescence lifetimes of the complexes.

Photoelectrochemical characteristics of MPc-sensitized electrodeposited ZnO thin films were studied; ZnOCPC / ZnO films have been improved to an incident photon-to-current conversion (IPCE) value of 31.1 % with an absorbed photon-to-current conversion (APCE) of 59.6 %. The best obtained so far with phthalocyanine-type sensitizers on nanocrystalline ZnO films.

Fluorescent-magnetic nanocomposite with excellent photophysical properties which can be exploited for combined photodynamic and hyperthermia therapies is also presented.

CONTENTS

Title page	i
Dedication	ii
Acknowledgments	iii
Abstract	iv
Contents	vi
List of Abbreviations	xii
List of Symbols	xvi
List of Figures	xix
List of Schemes	xxiv
List of Tables	xxvi
 Chapter 1:	
INTRODUCTION	1
1.1 Nanoparticles	2
1.1.1 Semiconductor quantum dots	2
1.1.1.1 Absorption and fluorescence spectra of QDs	5
1.1.1.2 Syntheses	9
Water-soluble colloidal nanocrystals	10
1.1.2 Magnetic Iron Oxide Nanoparticles	12
1.1.2.1 Synthesis and stabilization of magnetic iron nanoparticles	14
1.1.2.2 Applications of magnetic iron oxide nanoparticles	16
1.1.3 Characterization of nanoparticles (QDs and magnetic nanoparticles)	18
1.2 Metallophthalocyanines (MPcs)	21
1.2.1 Structure of phthalocyanines	23
1.2.2 Syntheses of phthalocyanines	26
1.2.2.1 Unsubstituted phthalocyanines	26

1.2.2.2	Ring substituted phthalocyanines	28
1.2.2.3	Water-soluble phthalocyanines	29
1.2.3	Electronic absorption spectra of phthalocyanines	35
1.2.3.1	Aggregation in MPcs	39
1.2.3.2	Spectral studies of interaction of MPcs with QDs	43
1.3	Fluorescence studies	45
1.3.1	Fluorescence spectra	45
1.3.2	Quantum yields and lifetimes	48
1.3.3	Fluorescence quenching	52
1.3.3.1	Benzoquinone (BQ) as a quencher	57
1.3.3.2	Serum albumin fluorescence quenching	58
	Interaction between BSA and MPcs	58
	Interaction of BSA and QDs	60
1.3.4	Förster Resonance Energy Transfer (FRET)	61
1.4	Triplet state absorption	64
1.5	Singlet oxygen generation and photodegradation in MPcs	69
1.5.1	Singlet oxygen	69
1.5.2	Photodegradation	74
1.6	Summary of Aims of Thesis	77
 Chapter 2:		
	EXPERIMENTAL	79
2.1	Materials	80
2.2	Instrumentation/ Equipment	81
2.3	Methods	84
2.3.1	Absorption and fluorescence studies	84
2.3.2	Fluorescence quenching	85
2.3.2.3	Quenching of the fluorescence of MPcs by BQ or QDs	85
	BQ as fluorescence quencher	85
	QD as fluorescence quencher	86
2.3.2.2	Quenching of the fluorescence of BSA by QD or MPcs	86

2.3.2.3	Quenching of the fluorescence of QD by MPcs	86
2.3.3	Triplet quantum yields and lifetimes	86
2.3.4	Singlet oxygen and photodegradation quantum yields	87
2.3.5	Photoelectrochemical measurements	88
2.4	Synthesis	89
2.4.1	Synthesis of Quantum dots	89
	Conjugation of CdTe QDs to BSA.	91
2.4.2	Synthesis of magnetic iron oxide nanoparticles (MN)	91
	Mixed MNH (2a) and MPcs	92
2.4.3	Synthesis of unsubstituted MPcs	92
2.4.4	Synthesis of metallocarboxyphthalocyanines	94
2.4.4.1	Tetracarboxymetallophthalocyanines (MTCPC)	94
2.4.4.2	Octacarboxymetallophthalocyanines (MOCPC)	96
2.4.5	Synthesis of substituted phthalonitriles	97
2.4.6	Synthesis Aryloxy tetra-substituted phthalocyanines	100
2.4.6.1	Metal-free aryloxy tetra substituted phthalocyanines	100
2.4.7	Synthesis of aminoalkanethio-substituted phthalocyanines	103
2.4.8	MOCPCs-QD-MNS (3-in-one photosensitizer conjugate)	106
	RESULTS AND DISCUSSION	109
	PUBLICATIONS	110

Chapter 3:

	SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION	113
3.1	Synthesis and characterization of nanoparticles	116
3.1.1	Mercaptocarboxylic acid capped CdTe quantum dots (QDs)	116
3.1.2	Magnetic iron oxide nanoparticles	121
3.2	Metallophthalocyanines	125
3.2.1	Unsubstituted and tetrasulfonated MPcs	125
3.2.2	Carboxy MPcs	133
3.2.3	Aryloxy and aminoalkanethio-substituted metallophthalocyanine	138

3.2.3.1	Phthalonitriles	138
3.2.3.2	Aryloxy substituted tin (IV) metallophthalocyanines	140
3.2.3.3	Aminoalkanethio-substituted zinc (II) Pcs	147
3.3	Conclusions	154

Chapter 4:

PHOTOPHYSICAL, PHOTOCHEMICAL AND PHOTOELECTROCHEMICAL PROPERTIES		155
4.1	Fluorescence Spectra and quantum yields	156
4.1.1	Nanoparticles (QDs and MN)	156
4.1.2	Phthalocyanines	159
4.1.2.1	Monomeric water-soluble metallophthalocyanines	159
4.1.2.2	Aggregated water-soluble metallophthalocyanines	163
4.1.2.3	Monomeric non-water-soluble metallophthalocyanines	167
4.1.3	Fluorescence quenching of MTCPcs and MOCPCs by benzoquinone	169
	Determination of MPcs fluorescence lifetimes from quenching data	172
4.2	Triplet state quantum yields and lifetimes	174
4.3	Singlet oxygen and photodegradation quantum yields	183
4.3.1	Singlet oxygen quantum yields	183
4.3.2	Photodegradation (photobleaching) quantum yields	189
4.4	Photoelectrochemical processes	193
4.4.1	Electrodeposition of ZnO-Eosin-Y (ZnO-EY) hybrid films	193
4.4.2	Dye loading and arrangement on ZnO	196
4.4.3	Photoelectrochemical measurements	200
4.4.3.1	Time-resolved photovoltage	200
4.4.3.2	Time-resolved photocurrent	201
4.5	Conclusions	208

Chapter 5:

INTERACTION OF MPcs WITH NANOPARTICLES		210
5.1	Interaction of metallophthalocyanines with quantum dots	211
5.1.1	Anionic MPcs and QDs	211

5.1.1.1	Spectral changes of MPcs in the presence of QDs	211
5.1.1.2	Fluorescence quantum yields	215
5.1.1.3	Triplet quantum yields (Φ_T) and lifetimes (τ_T)	219
5.1.1.4	Singlet oxygen production	223
5.1.1.5	Photodegradation	224
5.1.2	Cationic MPcs and QDs	224
5.1.2.1	Spectral changes of MPcs in the presence of QDs	225
5.1.2.2	Fluorescence studies	234
5.2	Förster resonance energy transfer (FRET) studies between QDs and MPcs	236
5.2.1	MPcS ₄ complexes	236
5.2.1.1	Monomeric AlPcS ₄ complex in pH 7.4 PBS	236
5.2.1.2	MPcS ₄ complexes in water: methanol solvent mixture	240
5.2.2	MOCPc complexes	245
5.2.3	Production of singlet oxygen through energy transfer	248
5.3	Interaction of metallophthalocyanines with magnetic fluid	250
5.3.1	MPcs in the presence of magnetic fluid	251
5.3.1.1	Spectral changes of MPcs in the presence of MNH	251
5.3.1.2	Effect of MNH on the photophysical behaviour of MPcs	254
5.3.1.3	Photochemical Studies	257
5.3.2	An attempted at MOCPcs-QD-MNS, a 3-in-one conjugate	258
5.3.2.1	Spectroscopic studies	260
5.3.2.2	Photophysical studies	267
5.4	Conclusions	269

Chapter 6:

INTERACTION OF BOVINE SERUM ALBUMIN (BSA) WITH METALLOPHTHALOCYANINES (MPcs) OR QUANTUM DOTS (QDs)		271
6.1	Interaction between BSA and MPcs	272
6.1.1	Binding constants and fluorescence quenching	272
6.1.2	Photophysicochemical properties of MPcs in the presence of BSA	277
6.2	Interaction between BSA and QDs	281
6.2.1	Conjugation of CdTe QDs to BSA	282

6.2.2	Spectral changes in the interaction between CdTe QDs and BSA	284
6.2.3	Quenching of BSA fluorescence by QDs	288
6.3	Conclusions	293
	GENERAL CONCLUSIONS AND FUTURE PERSPECTIVE	294
7.1	General Conclusions	295
7.2	Future Perspectives	298
	REFERENCES	299

LIST OF ABBREVIATIONS

A	-	Absorbance
AC	-	Alternating current
ADMA	-	Tetrasodium α,α -(anthracene-9,10-diyl) dimethylmalonate
APCE	-	Absorbed photon-to-current conversion efficiency
BQ	-	Benzoquinone
BSA	-	Bovine serum albumin
CHCl₃	-	Chloroform
CD-RW	-	Rewritable optical media (compact disc)
CTTs	-	Charge-transfer transitions
CEL	-	Cremophore EL
DABCO	-	1,4-diazabicyclo-octane
DBN	-	1,5-Diazabicyclo [4.3.0] non-5-ene
DBU	-	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	-	Dichloromethane
DES	-	Diethyl sulphate
DMEA	-	<i>N,N</i> -dimethylethanolamine
DMF	-	<i>N,N</i> -dimethylformamide
DMSO	-	dimethylsulphoxide
DOS	-	Density of states
DPBF	-	1,3-diphenylisobenzofuran
DSSCs	-	Dye-sensitized solar cells

ET	-	Energy transfer
EY	-	Eosin-Y
FCC	-	Face-centered cubic
FF	-	Fill factor
FRET	-	Förster resonance energy transfer
FTO	-	Fluorine-doped tin oxide glass
H₂Pc	-	Metal-free phthalocyanine
HOMO	-	Highest occupied molecular orbital
HPLC	-	High performance liquid chromatography
HRTEM	-	High resolution transmission electron microscope
HQ	-	Hydroquinone
HT	-	Hyperthermia therapy
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
LCAO	-	Linear combinations of atomic orbitals
MLCT	-	Metal-to-ligand charge transfer
MF	-	Magnetic fluid (magnetic iron oxide nanoparticles in solution)
MN	-	Magnetic iron oxide nanoparticles (magnetite)
MRI	-	Magnetic resonance imaging

MOCPC	-	Octacarboxy metallophthalocyanine
MPc	-	Metallophthalocyanine
³MPc[*]	-	Excited triplet state species of metallophthalocyanines
MPcS_{mix}	-	Differently sulfonated metallophthalocyanine
MPcS₄	-	Tetrasulfonated metallophthalocyanine
MTCPc	-	Tetracarboxy metallophthalocyanine
NIR	-	Near infrared
NR	-	Non-radiative
QD	-	Quantum dot
PBS	-	Phosphate buffered solution
PEG	-	Polyethylene glycol
Pc	-	Phthalocyanine
PDT	-	Photodynamic therapy
PL	-	Photoluminescence
PMT	-	Photomultiplier tube
TBAI	-	Tetrabutylammonium Iodide
THF	-	Tetrahydrofuran
TPPA	-	Tetrapyridinoporphyrine
TEM	-	Transmission electron microscope
TOP	-	Trioctylphosphine
TOPO	-	Trioctylphosphine oxide
TTA	-	Triplet-triplet absorption
SCE	-	Saturated calomel electrode

SEM	-	Scanning electron microscope
SDA	-	Structure directing agent
SOC	-	Spin-orbit coupling
S-V	-	Stern-Volmer
UV/Vis	-	ultraviolet/visible
VR	-	vibrational relaxation

LIST OF SYMBOLS

α	-	Non-peripheral position
α	-	Fraction of light absorbed
β	-	Peripheral position
D	-	Diffusion coefficient
e^-	-	Electron
ϵ	-	Molar extinction coefficient
ϵ_S	-	Singlet state extinction coefficient
ϵ_T	-	Triplet state extinction coefficient
Eff	-	Efficiency of energy transfer
f	-	Collision efficiency
F	-	Fluorescence intensity
F_0	-	Fluorescence intensity in the absence of a quencher
J	-	Degree of spectral overlap of donor emission and acceptor absorption spectra
K_a	-	Association constant
k_Q	-	Bimolecular quenching constant
K_b	-	Binding constant
k_D	-	Diffusion-controlled bimolecular quenching rate constant
κ^2	-	Dipole orientation factor
K_D	-	Equilibrium dimerization constant
k_F	-	Fluorescence rate constant
k_{IC}	-	Internal conversion rate constant

k_{ISC}	-	Intersystem crossing rate constant
K_{SV}	-	Stern-Volmer constant
λ_{exc}	-	Excitation wavelength of phthalocyanines
λ_Q	-	Wavelength of absorption spectrum maximum
λ_F	-	Wavelength of emission spectrum maximum
λ_E	-	Wavelength of excitation spectrum maximum
λ_{max}	-	Wavelength maximum
n	-	Refractive index
Φ_{Δ}	-	Singlet oxygen quantum yield
Φ_F	-	Fluorescence quantum yield
Φ_{IC}	-	Internal conversion quantum yield
Φ_p	-	Photodegradation quantum yield
Φ_T	-	Triplet state quantum yield
τ_F	-	Fluorescence lifetime
τ_N	-	Natural lifetime
τ_T	-	Triplet state lifetime
ΔA	-	Change in absorbance following laser pulse
I	-	intensity of light
I	-	current
I_{abs}	-	Intensity of light absorbed
$^1O_2 (^1\Delta_g)$	-	excited long-lived singlet state oxygen
$^1O_2 (^1\Sigma_g)$	-	excited short-lived singlet state oxygen

$O_2 (^3\Sigma_g)$	-	ground state molecular oxygen
r	-	Centre to centre separation distance between donor and acceptor
R	-	Radius of molecule
R_0	-	Critical distance at which efficiency of energy transfer is 50%
S_0	-	Ground singlet state
S_0	-	Excited singlet state
T	-	Temperature
T_{filter}	-	Transmittance of filter
T_{MPc}	-	Transmittance of metallophthalocyanine
T_1	-	First excited triplet state
T_2	-	Second excited triplet state
S_0	-	Ground singlet state

LIST OF FIGURES

1.1	Progression of quantum confinement and the effects on density of states	3
1.2	Schematic image of a quantum dot nanocrystal with solubilizing ligands	4
1.3	QD emission wavelength tuned by nanoparticle size or composition	5
1.4	Band gap in bulk crystals and QDs	6
1.5	Typical absorption and fluorescence spectra of QDs	7
1.6	Schematic path for fluorescence emission from a quantum dot	8
1.7	Schematic illustration of conjugation of QDs to biomolecules	11
1.8	Schematic representation of the synthesis of thiol-capped CdTe QDs	12
1.9	Schematic of a partial unit cell of a spinel ferrite structure	13
1.10	Schematic of therapeutic strategy using magnetic iron oxide nanoparticles	17
1.11	Typical transmission electron microscopic images of QDs and Fe ₃ O ₄	19
1.12	Typical powder X-ray diffraction spectra of various nanocrystals	20
1.13	Structural representation of studied nanoparticles	21
1.14	Molecular structures of porphyrin-like molecules	24
1.15	Molecular structure of metallophthalocyanines	25
1.16	Structures of studied MPcs	34
1.17	Ground state electronic absorption spectra of a typical MPc	36
1.18	Electronic transitions in MPcs	37
1.19	Ground state absorption spectra of metal-free and metallated Pc	38
1.20	Interaction between two coplanar D _{4h} metallophthalocyanine rings	40
1.21	Structure of cremophore EL	40

1.22	A simplified Jablonski diagram	46
1.23	Absorption and emission spectra of a typical MPc	47
1.24	Absorption, excitation and emission of MPc with one fluorescent component	48
1.25	Typical positive deviation from and expected Stern-Volmer plot	55
1.26	Förster resonance energy transfer Jablonski diagram	61
1.27	Typical triplet decay curve of MPcs following laser flash photolysis	65
1.28	Typical differential absorption spectrum of MPcs	66
2.1	Schematic diagram of a laser flash photolysis set-up	82
2.2	Schematic diagram of a photochemical set-up	83
3.1	Electronic absorption spectra of synthesized CdTe quantum dots	118
3.2	XRD spectra of synthesized quantum dots and magnetic iron nanoparticles	121
3.3	Transmission electron microscopic images of magnetic iron nanoparticles	123
3.4	Electronic absorption spectra of magnetic iron nanoparticles	124
3.5	Electronic absorption spectra of ZnPc and ClAlPc in DMSO	125
3.6	Electronic absorption spectra of MPcS₄ complexes in aqueous medium	127
3.7	Electronic absorption spectra of SiPcS₄ and GePcS₄ at various concentrations	128
3.8	Electronic absorption spectrum of SiPcS₄ in the presence of CEL	129
3.9	Electronic absorption spectrum of GePcS₄ in the presence of CEL	129
3.10	Electronic absorption spectra of sulfonated MPc complexes in DMSO	132
3.11	Electronic absorption spectra of tetracarboxy MPc complexes in pH 10	134
3.12	Electronic absorption spectrum of ZnTCPc in the presence of CEL	135
3.13	Electronic absorption spectra of MOCPC complexes in PBS pH 7.4	137
3.14	Infrared spectra of αSnPcTbtPh (45b)	142

3.15	Electronic absorption spectra of tin (IV) MPc complexes	144
3.16	Absorption of: (a) 47a, 48a, 49a (DMSO); (b) 47b, 48b, 49b (DMSO, PBS)	150
3.17	Electronic absorption spectrum of α TZnPcQ (47b) in the presence of CEL	153
4.1	Fluorescence emission spectra of synthesized QDs	156
4.2	Absorption and fluorescence excitation spectra of CYS1	158
4.3	Fluorescence emission spectrum of magnetic iron nanoparticles	159
4.4	Absorption, fluorescence excitation and emission spectra of SiOCPC	160
4.5	Absorption, excitation and emission of 48b, 36, 47b in CEL and 39 (pH 10)	164
4.6	Absorption, fluorescence excitation and emission spectra of 46a in DMSO	167
4.7	Fluorescence emission spectral changes of AlTCPC in the presence of BQ	170
4.8	Transient absorption spectrum for α SnPcPh (45a) in DMSO	174
4.9	Spectral changes of 31 and 45a after laser irradiation	180
4.10	Photodegradation of DPBF or ADMA in the presence of MPc	185
4.11	Photodegradation curves of 45c saturated with air, oxygen or argon	190
4.12	Kinetic plots for photodegradation	192
4.13	Current measured during cathodic electrodeposition of ZnO-EY film	195
4.14	Alphastep surface profile of ZnO film	195
4.15	SEM images of ZnO-EY hybrid films	196
4.16	Images showing progress in change of colour in ZnO films	197
4.17	Absorption spectra of ZnO/MOCPC thin films	198
4.18	Time resolved photovoltage transients for ZnO/MOCPC films	200
4.19	Time resolved photocurrent transients for ZnO/MOCPC films	202
4.20	Photocurrent-voltage characteristics of ZnO sensitized with MOCPCs	205

4.21	Time resolved photocurrent of ZnO/MOCPC films at 500mW cm ⁻²	208
5.1	Spectral changes of AlPcS ₄ on addition of MPA1	212
5.2	Emission spectral changes of CYS1 in the presence of AlPcS ₄	214
5.3	Transient absorption spectrum of MOCPCs in the presence of CYS3	221
5.4	Absorption and emission of TGA2,MPA2 and cationic ZnPcs	226
5.5	Overlap of absorption spectra of cationic ZnPcs and emission of QDs	227
5.6	Absorption spectral changes of cationic ZnPcs on gradual addition of QDs	228
5.7	Continuous variation plot of cationic ZnPcs in the presence of QDs	231
5.8	Plots for determination of association constants	233
5.9	Fluorescence emission spectral changes of 47b with increasing [MPA2]	235
5.10	Overlap of absorption spectra of AlPcS ₄ and emission of QDs	237
5.11	Indirect activation of AlPcS ₄ by CYS2 through FRET	238
5.12	Overlap of absorption spectra of SiPcS ₄ and emission of MPA1, MPA2	241
5.13	Indirect activation of GePcS ₄ by TGA1 and TGA2 through FRET	242
5.14	Absorption spectra of MOCPCs and emission spectrum of CYS3	245
5.15	Indirect activation of GeOCPc by CYS3 through FRET	246
5.16	Photodegradation of ADMA in QD solution	249
5.17	Scanning electron microscopic images of MNH and AlPc	251
5.18	Spectral changes of AlPc, AlPcS ₄ and GePcS ₄ in the presence of MNH	252
5.19	Fluorescence emission of AlPc and GePcS ₄ in the presence of MNH	253
5.20	Triplet decay curve of AlPc in the presence of MNH	256
5.21	Scanning electron microscopic image of ALOCPc-QD-MNS	261
5.22	Photos of composite of ALOCPc-QD-MNS in daylight and under UV	262

5.23	Raman spectra for AlOCPc-QD-MNS	263
5.24	Electronic absorption spectra of MOCPc-QD-MNS linked and mixed	264
5.25	Fluorescence emission spectra of QD, QD-MNS and AlOCPc-QD-MNS	265
5.26	Fluorescence emission spectra of AlOCPc-QD-MNS and AlOCPc	267
6.1	Spectral changes of BSA on addition of β -TZnPcQ (48b)	273
6.2	Binding plot of BSA to β -TZnPcQ (48b) for binding constant	273
6.3	Absorption spectra of GeOCPc in the absence and presence of BSA	276
6.4	Fluorescence emission spectra of AlOCPc and in the presence of BSA	278
6.5	Triplet decay curve for ZnOCPc in the absence and presence of BSA	279
6.6	Photolysis of AlOCPc in the presence of BSA	281
6.7	Absorption and emission spectra of TGA1,MPA1 and CYS1	282
6.8	Effect of time on conjugate formation between QDs and BSA	283
6.9	Absorption spectra of BSA, MPA, BSA-MPA mixed or linked	285
6.10	Fluorescence spectra of BSA, MPA, BSA-MPA mixed or linked	286
6.11	Spectral overlap of BSA emission and MPA absorption	288
6.12	Change in fluorescence intensity of BSA with MPA	291

LIST OF SCHEMES

1.1	Reaction mechanism of formation of magnetic iron oxide nanoparticle	15
1.2	Synthesis of MPcs from typical starting materials	27
1.3	Synthesis of tetrasubstituted MPcs from monosubstituted phthalonitrile	28
1.4	Synthesis of octasubstituted MPcs from disubstituted phthalonitrile	29
1.5	Synthesis of tetrasulfonated metallophthalocyanines (MPcS ₄)	30
1.6	Synthesis of water-soluble octacarboxymetallophthalocyanine (MOCPC)	31
1.7	Quaternization of tertiary amine substituted phthalocyanines	32
1.8	Type II photoreaction mechanism in a MPc photosensitizer	70
1.9	Type I photoreaction mechanism in a MPc photosensitizer	71
1.10	Type III photoreaction mechanism in a MPc photosensitizer	71
1.11	Processes involved in the decay of singlet oxygen	73
1.12	[4+2] cycloaddition reaction of MPc with singlet oxygen	75
2.1	Schematic representation of synthesis of MOCPC-QD-MNS	107
3.1	Synthesis of CdTe quantum dots	117
3.2	Synthesis of iron oxide nanoparticles	123
3.3	Synthetic route to tetra sodium salt of tetrasulfophthalocyanine	126
3.4	Synthetic route to tetracarboxymetallophthalocyanine	133
3.5	Synthetic route to octacarboxymetallophthalocyanine	137
3.6	Synthetic routes to tin (IV) phthalocyanines	139
3.7	Synthetic route to diethylaminoethanethio-substituted phthalonitrile	140
3.8	Synthetic route to 2-diethylaminoethanethio-substituted ZnPcs	149

4.1	Mechanism of charge transfer in MPc-quinone mixture	171
4.2	Mechanism of photoreduction of MPc in the presence of light	181
5.1	Synthesis of MOCPC-QD-MNS	259
6.1	Photosensitized oxidation of BSA	280
6.1	BSA and QD linking process	283

LIST OF TABLES

1.1	Variation in dimerization constants of some phthalocyanines	42
1.2	Photophysical parameters of some MPcs	50
1.3	Binding and quenching data of some water-soluble MPcs with BSA	59
1.4	Photochemical parameters of some MPcs	74
3.1	List of synthesized nanoparticles with their absorption maxima and size	114
3.2	List of synthesized water-soluble MPcs	115
3.3	List of synthesized aryloxy and aminoalkanethio-substituted MPcs	116
3.4	Spectral properties of MPcS ₄ , MTCPcs, MOCPCs and quaternized ZnPCs	130
3.5	Aggregation parameters of sulfonated and cationic MPc complexes	132
3.6	Spectral data of complexes 45a-c and 46a-c in different solvents	146
4.1	Spectral properties and fluorescence quantum yields of synthesized QDs	157
4.2	Fluorescence data of studied MPcs in aqueous and non aqueous media	161
4.3	Fluorescence quenching and kinetic data for complexes in DMSO	172
4.4	Triplet quantum yields and lifetimes of studied MPcs in different solvents	176
4.5	Effect of laser energy on absorbance, triplet lifetime and yields of MPcs	182
4.6	Singlet oxygen and photobleaching quantum yields of studied MPcs	186
4.7	Spectral and photoelectrochemical data for ZnO/MOCPC electrodes	199
4.8	Spectral and photoelectrochemical data for ZnO/ZnOCPC electrodes	207
5.1	Binding and quenching data for AlPCs ₄ -QD interactions	215
5.2	Photophysical parameters of AlPCs ₄ in the presence of QDs in PBS 7.4	216
5.3	Photophysical parameters of MPcS ₄ in the presence of QDs in H ₂ O/MeOH	217

5.4	Photophysical parameters of MOCPcs in the presence of CYS3 in PBS 7.4	219
5.5	Photochemical parameters of MOCPcs in the presence of CYS3	223
5.6	Spectral and fluorescence data of cationic ZnPc in water/methanol	227
5.7	Estimated association, equilibrium and quenching constants for ZnPc-QD	234
5.8	Energy transfer parameters for AlPcS ₄ -QD interactions in PBS pH 7.4	239
5.9	Energy transfer parameters for MPcS ₄ -QD interactions in water/methanol	243
5.10	Energy transfer data for interactions of MOCPcs with CYS3	247
5.11	Indirect singlet oxygen for MOCPcs-CYS3 in aqueous solution	250
5.12	Photophysical and photochemical results for MPcs in the presence of MN	255
5.13	Photophysical properties of MOCPc-QD-MNS conjugate	268
6.1	Quenching and binding data for the interaction of MPc with BSA	274
6.2	Spectral and physicochemical parameters of MOCPcs with BSA	279
6.3	Fluorescence quantum yields of QDs in the absence and presence of BSA	290
6.4	Quenching parameters for BSA-QD interactions	292

CHAPTER 1

INTRODUCTION

1.1 Nanoparticles

Nanoparticles are generally defined as particles with sizes of a few nanometers (usually 1 to 100 nm). Their chemical and physical properties differ from those of the bulk and isolated atoms or molecules with the same chemical composition [1,2]. When there is a distinctly ordered arrangement of atoms (or ions), they are referred to as nanocrystals.

This thesis concentrates on synthesis of quantum dots (QDs) and magnetic iron oxide nanoparticles (MN) (called magnetic fluid (MF) in solution) and the study of their interaction with metallophthalocyanines. Cadmium telluride (CdTe) QDs in particular features attractive optical properties such as bright fluorescence emission and wide absorption band in the visible region and they possess the ability to act as energy donors through Förster resonance energy transfer (FRET). This will be valuable in their interaction with photosensitizers. MF is known to produce intriguing results in biomedical applications and therefore will be valuable in enhancing the effectiveness of photosensitizers in such applications. In the following section, QDs and MF will be discussed.

1.1.1 Semiconductor quantum dots

Colloidal semiconductor nanocrystals or QDs are zero dimensional inorganic semiconducting materials that are, in general, synthesized from groups 12-16 (II-VI), 13-15 (III-V) or 14-16 (IV-VI) elements of the periodic table. They are neither atomic nor bulk semiconductors; their properties originate from their physical size [3,4].

They are commonly called QDs since they have a narrow distribution density of energy states (DOS) (Figure 1.1) that are strongly dependent on the dimensions of the confining potential with electronic confinement occurring in all spatial dimensions (3-D) as

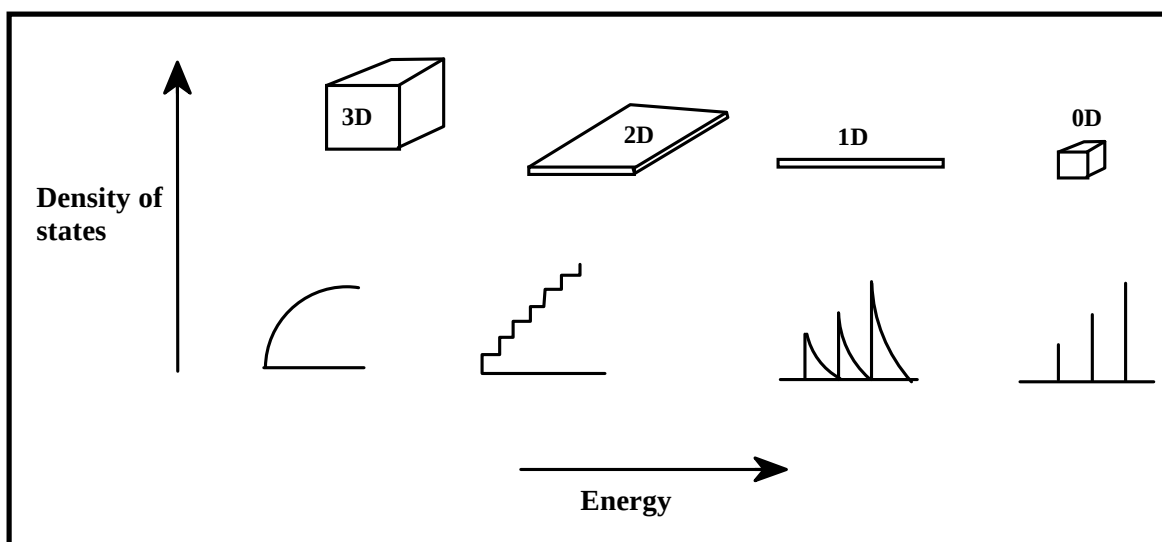


Figure 1.1: The progression of quantum confinement and the effects on the density of states. 3D represents the bulk, 2D quantum wires or fibers, 1D quantum wells and 0D the zero dimensional quantum dots [7].

opposed to 2-D (quantum wires) and 1-D (quantum wells) [5-7]. QDs show some distinct properties, such as composition- and size-dependent broad absorption which enables multiplexed imaging with a single excitation source [8], size dependent narrow and symmetrical emission peak which allow emission of pure color [9], high absorption coefficient across a wide spectral range ($\sim 10^5$ - 10^6 $\text{M}^{-1} \text{cm}^{-1}$) as well as relatively long fluorescence lifetime (dependent on size) of the order 10-50 nanoseconds, which helps in distinguishing QD signals from background fluorescence and achieving high-sensitivity detection [3]. There is a large Stokes shift between the excitation and emission spectra which allows for good separation between excitation and emission wavelengths. Their resistance to photobleaching also makes continuous or long-term monitoring of slow biological processes possible which is of advantage over conventional organic fluorophores.

QDs are somewhat spherical in shape, mostly direct-band-gap materials with the size

range of 1-10 nm in diameter [7,10,11] which is known to be smaller than the bulk Bohr excitation radius. They hold hundreds to thousands of atoms within the QD volume depending on their final size (Figure 1.2).

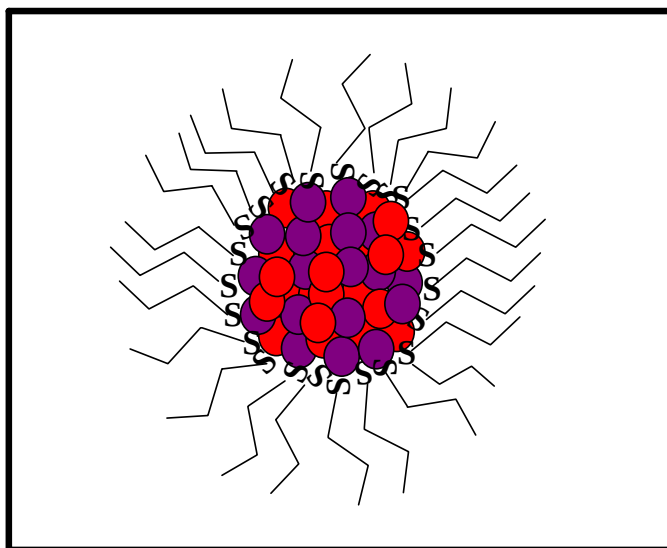


Figure 1.2: Schematic image of a QD nanocrystal core surrounded by solubilizing ligands.

Altering the QD size and its chemical composition tunes the fluorescence emission from the ultraviolet, throughout the visible, and into the near-infrared region of the spectrum spanning a broad wavelength range of 400-2000 nm [12,13]. Figure 1.3 a shows increase in emission wavelength by increasing size of a CdSe QD of constant composition while in (b) the nanoparticle size is kept constant and the composition is varied.

QDs are studied in various fields including biology, biomedics, electronics and optoelectronics [7,10]. For these applications various types of QDs have been synthesized, such as InP, InAs, GaAs, and GaN, as well as porous Si and Si/Ge dots. In addition, the family of Group 12-16 compounds with heavier atoms such as CdTe, HgSe or PbSe has been studied due to their extended optical properties into the near-infrared

region. This work focuses on CdTe QDs since it is a member of the Group 12-16 family.

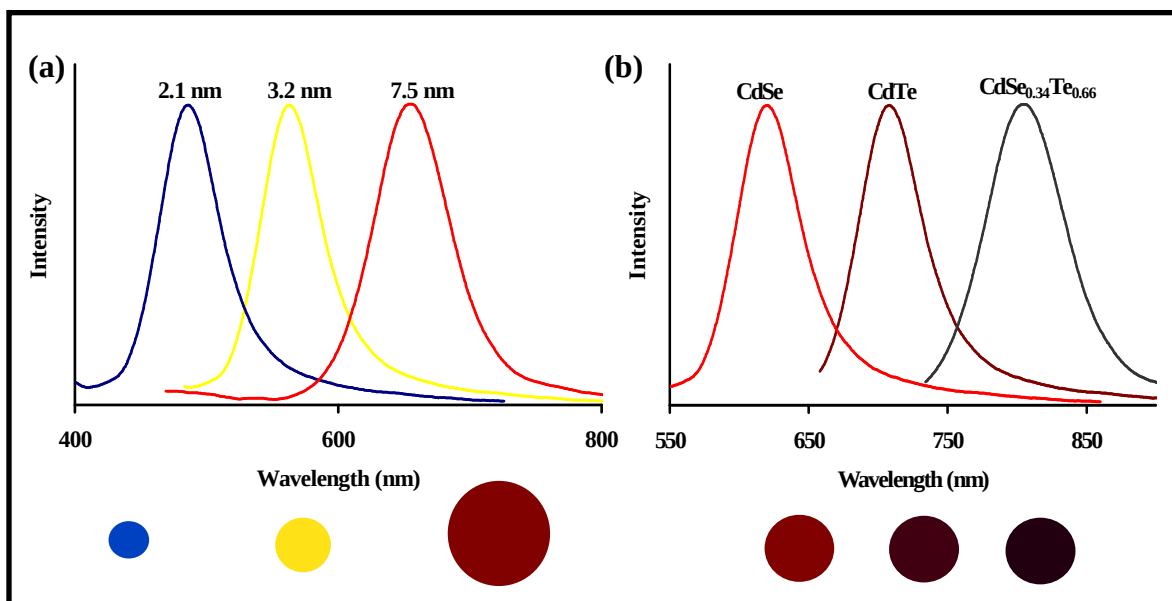


Figure 1.3: QD emission wavelength tuned by changing the nanoparticle (a) size or (b) composition. Relative sizes of the particles are shown schematically below [12].

1.1.1.1 Absorption and fluorescence spectra of QDs

One of the defining features of a semiconductor is the energy gap separating the conduction and valence energy bands. In bulk semiconductors, the gap width is a fixed parameter (Figure 1.4), determined by the material's identity and sometimes on temperature and pressure; electrons normally occupy all states up to the edge of the valence band, whereas states in the conduction band are empty. However, the situation changes, in the case of nanoscale semiconductors. At this small dimension, we begin to enter the regime of quantum confinement for which the spatial extent of the electronic wave function is comparable with the dot size [14]. As a result, the electronic structure is altered from the continuous electronic bands to discrete atomic-like states with energies that are determined by the QD radius. These states are well-separated and can be labelled

with atomic-like notations (1S, 1P and 1D) as shown in Figure 1.4 [14,15]. This

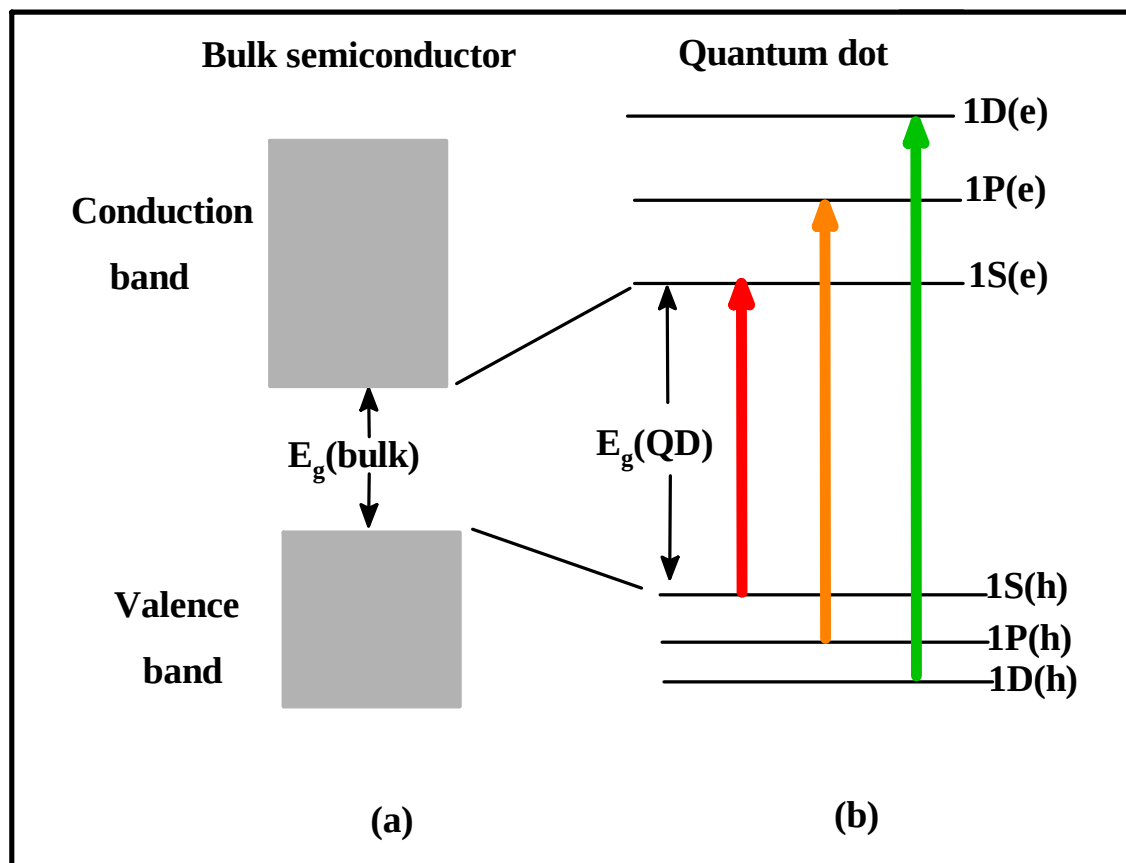


Figure 1.4: Band gap in bulk crystals and QDs showing (a) continuous conduction and valence energy bands separated by a “fixed” energy gap, $E_g(\text{bulk})$ (b) QD characterized by discrete atomic-like states with energies that are determined by the QD radius [14].

phenomenon is known as the quantum size effect. There is a close relation between the electronic structure, the optical properties and the nanocrystal size. The decrease of particle size shifts the onset of absorption from the infrared to the visible region of the electromagnetic spectrum as the band gap energy of the semiconductor increases (Figure 1.4).

The absorption spectra are sensitive to various physical and chemical effects. Line broadening in the spectra (Figure 1.5) mostly comes from the polydispersity of the

ensemble of nanocrystals, thus the absorption spectra do not show discrete lines at the different maxima as it would be expected for a single nanocrystal [16]. Even the best methods of preparation do not give nanocrystals with less than 2% deviation from the average size [17]. The absorption spectrum also depends on shape fluctuation of the nanocrystals [18], the crystalline defects, concentration and the environmental inhomogeneities.

Fluorescence emission or photoluminescence (PL) in QDs (Figure 1.5) arises from the radiative recombination of electron-hole pairs. The recombination or relaxation of the

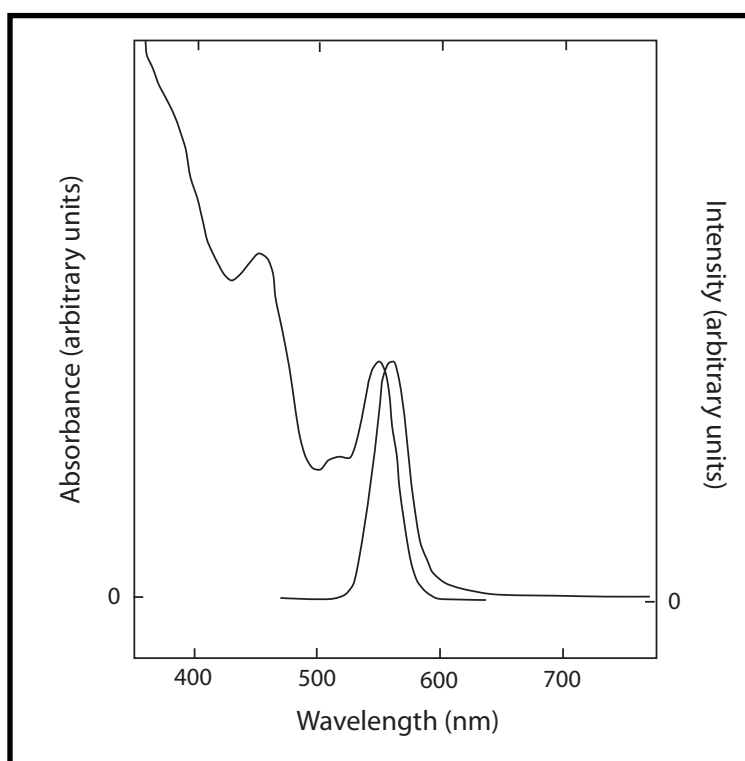


Figure 1.5: Typical absorption and fluorescence spectra of QDs [17].

charge carriers can follow different processes such as, radiative recombination (band gap emission), recombination via trap states or annihilation of the exciton or Auger processes [19]. Slight defects in the solid, such as vacancies, impurities, or adsorbates at the surface cause the formation of “trap” states (Figure 1.6) into which the photo-excited electron

can fall, or the photo-excited hole can “float.” Electron-hole recombination from these

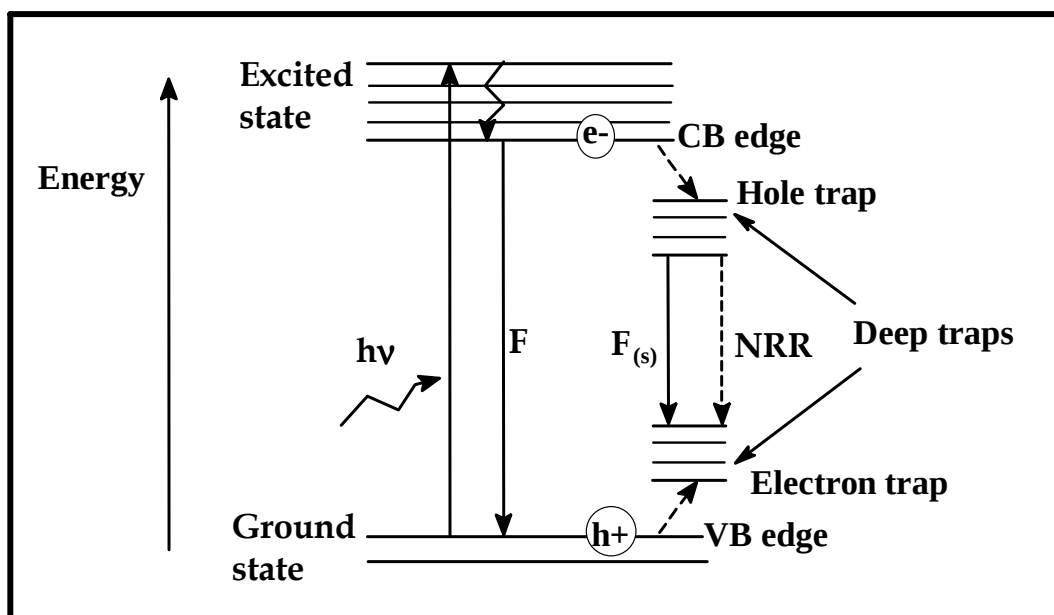


Figure 1.6: Schematic path for fluorescence emission from a QD. F or $F_{(s)}$; Fluorescence emission from radiative band-edge recombination or electron and hole recombination from surface traps respectively; NRR non radiative recombination at the surface, CB and VB; conduction and valence band respectively [20].

surface traps (defect sites) on the surface of the QD results in radiative emission of low intensity $F_{(s)}$. Some of the recombinations of the electrons and holes from surface states result in non-radiative (NR) emission [19,20]. The organic capping or stabilizer in QDs provides “electronic” passivation of the nanocrystals; by terminating dangling bonds that remain on the QDs surface. The unterminated bonds can affect the QD’s emission efficiency because they lead to a loss mechanism wherein electrons are rapidly trapped at the surface before they have a chance to emit a photon.

The emission spectrum of QDs is a symmetrical sharp peak as shown in Figure 1.5.

Fluorescence emission can show high Stokes shifts, depending on the relative energies of the trap states compared to the valence and conduction band edges.

1.1.1.2 Syntheses

Nearly all of the Groups 12-16 semiconductors have been prepared in colloidal form, in a variety of different approaches [21,22]. QDs synthesis can be tailored to specific requirements; the achievement of desired particle sizes over the largest possible wavelength range, narrow size distributions within 2% [23], good crystallinity, desired surface properties and in some cases high luminescence quantum yields, as well as adjustable electronic properties, are all results that are considered to be characteristics of a good preparation. Choice of the QDs and capping (or stabilizer) are gaining importance, as the type of QD to some extent alters the photophysical properties, whilst the capping confers properties to the QD which allow its incorporation into a desired application.

The nature and concentration of the initial materials, the capping, which keeps the particles in solution, solvent, pH value, reaction time, temperature and atmosphere, are some of the parameters that influence a colloidal synthesis of QDs nanocrystals [24]. The most successful preparations are based on the reliable separation of nucleation and growth with following size-selective precipitation.

Most procedures developed for obtaining high-quality QDs are based on variations of the high-temperature pyrolytic reaction [17] which involves the fast injection of liquid precursors (combination of an appropriate metallic or organometallic precursor (zinc, cadmium or mercury species) with a corresponding chalcogen (sulfur, selenium or tellurium species) into a coordinating solvent e.g. trioctylphosphine oxide (TOPO), trioctylphosphine (TOP) or hexadecylamine, at high temperatures under inert conditions [25-27]. The QDs obtained in this way are hydrophobic.

Water-soluble colloidal nanocrystals

In order to make QDs biocompatible, they need to be soluble in water. Bare core nanocrystals have proven impractical for two reasons. Firstly, the crystalline structure of the nanoparticle lends itself to imperfections [28], which results in emission irregularities, particularly blinking, in which single QDs switch between fluorescent and non-fluorescent states despite continuous illumination [29]. Secondly, the cores are highly reactive [28] due to their large surface area: volume ratio, resulting in a very unstable structure which is particularly prone to photochemical degradation.

QDs such as CdTe can be directly grown in aqueous solutions, [30-32] or through the procedure of organic synthesis and capping followed by surface modification [33]. Functionalization may be achieved via electrostatic interaction, adsorption, chelation or covalent bonding, as shown in Figure 1.7 [34]. Exchanging the hydrophobic TOPO surfactant molecules with bifunctional molecules that are hydrophilic on one end and that can bind to the QD with the other end results in QDs with hydrophilic surface. Commonly, thiols ($-SH$) are used as the binding groups onto the surface, and carboxyl ($-COOH$) groups are a prominent example for hydrophilic groups. Mercaptocarboxylic acids ($HS-\cdots-COOH$), such as mercaptoacetic acid, mercaptopropionic acid or mercaptodecanoic acid [4,35-37] are normally employed. Enhanced stability can be achieved by using mercaptocarboxylic acids with two thiol groups [38].

Water solubility can also be achieved by surface silanization where thiol-containing silane monomers (e.g trimethoxysilane) displace the TOPO from the surface [35,39] and create a silica capping. These thiol groups act as anchors for covalent coupling of biomolecules to the surface of the nanocrystals.

QDs can be directly grown in aqueous solutions through arrested precipitation [30-32,40]

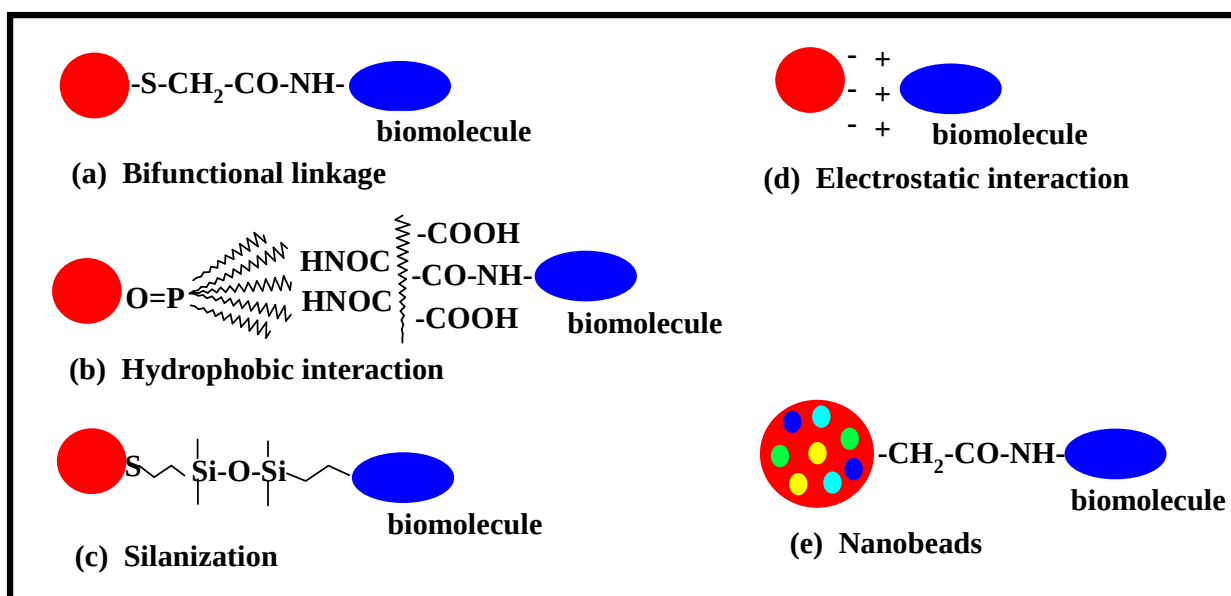


Figure 1.7: Schematic illustration of different approaches of conjugation of QDs to biomolecules: (a) Use of a bifunctional ligand to link QDs to biomolecules (b) TOPO-capped QDs bound to a modified acrylic acid polymer by hydrophobic forces (c) QD solubilization and bioconjugation using a mercaptosilane compound (d) Electrostatic attraction of positively charged biomolecules and negatively charged QDs (e) Incorporation of QDs into microbeads and nanobeads [34].

which is the most popular method and it is employed in this work. This method has been used to synthesize a wide range of QDs, including CdS, CdSe, CdTe, and HgTe. The respective cadmium salt is dissolved in water in the presence of a mercaptocarboxylic acid under inert condition to avoid the reactivity of oxygen. NaOH is added to make the solution alkaline. H_2Te gas (for CdTe QDs) is bubbled through this solution, Figure 1.8 [40]. Double replacement reaction yields CdTe QDs in solution. Additives such as thiols phosphates, and amines protect the QDs, enhance their suspension in water, stabilize the reaction, and control growth, resulting in reasonably bright and narrow PL emission. The possibility of controlling the surface charge and other surface properties of thiol-capped QDs simply by the choice of the stabilizing mercapto-compound with appropriate

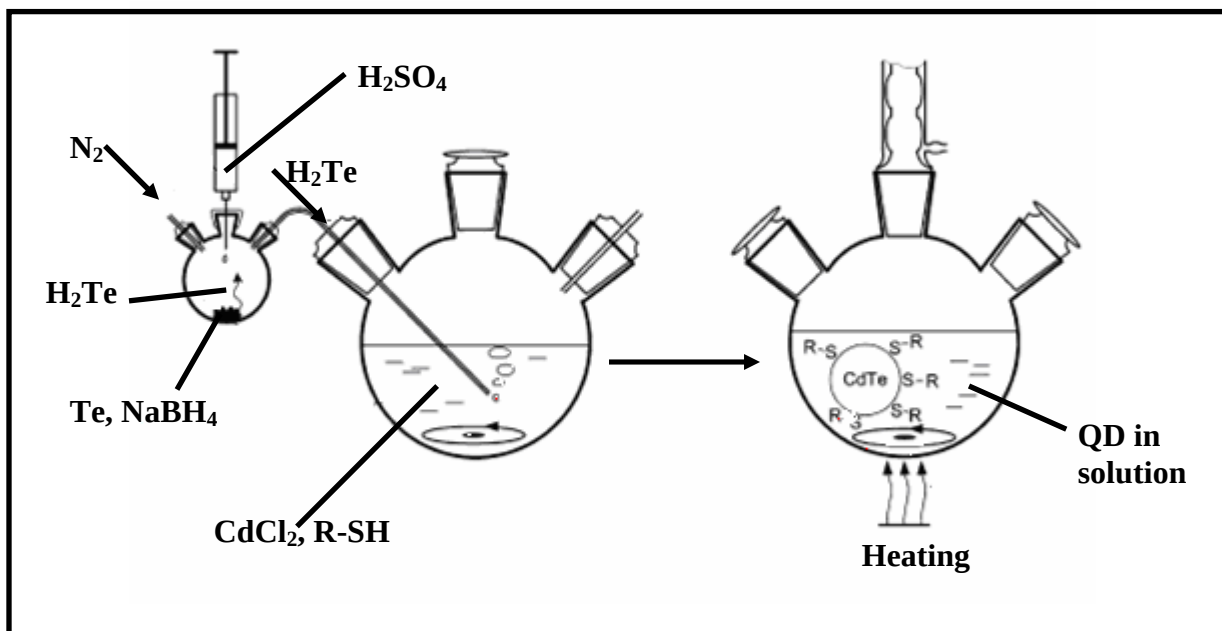


Figure 1.8: Schematic representation of the synthesis of thiol-capped CdTe QDs. First stage: formation of CdTe precursors by introducing H_2Te gas. Second stage: formation and growth of CdTe nanocrystals promoted by reflux [40].

free functional groups is definitely important, especially when water-soluble nanocrystals are needed, e.g., for fluorescence tagging applications. Mercaptoacetic acid capped water-soluble CdTe nanocrystals with stable fluorescence quantum yield up to 40% have been reported [40].

1.1.2 Magnetic Iron Oxide Nanoparticles (magnetite) (MN)

Superparamagnetic nanoparticles have been intensively developed for their fundamental scientific interest and also for many technological applications. The size reduction in magnetic materials resulting in the formation of single domain particles of about 5-20 nm in diameter gives rise to superparamagnetism. In recent years, increased investigations with several types of iron oxides have been carried out in the field of nanosized magnetic particles in single domains, among which magnetic iron oxide nanoparticle (magnetite,

Fe_3O_4 .) the focus in this work is a very promising candidate since its biocompatibility has already been proven [41].

Magnetite is a common magnetic iron oxide that has a cubic inverse spinel structure with oxygen forming a face-centered cubic (fcc) closed packing and Fe cations occupying interstitial tetrahedral and octahedral sites [42], Figure 1.9. Spinel ferrites are an ideal

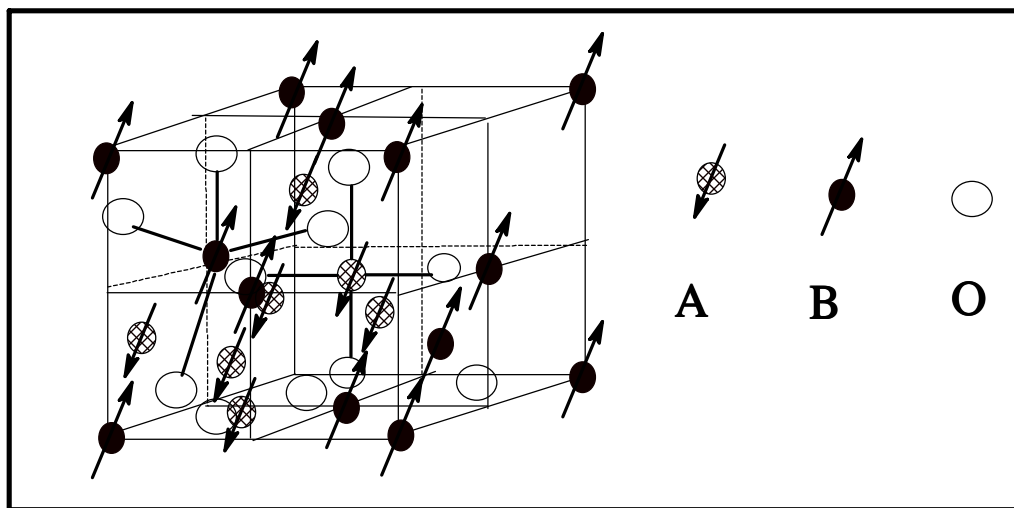


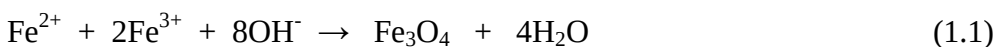
Figure 1.9: Schematic of a partial unit cell and magnetic ordering of spinel ferrite structure [42]. A and B are the two cationic sites in the spinel structure through which coordination occurs with oxygen. Fe_3O_4 as spinel ferrite is FeFe_2O_4 (AB_2O_4).

magnetic system for understanding and controlling superparamagnetic properties at the atomic level through chemical manipulations. The electrons can hop between Fe^{2+} and Fe^{3+} ions in the octahedral sites at room temperature, rendering magnetites an important class of half-metallic materials [42,43]. With proper surface capping these magnetic iron oxide nanoparticles (MN) can be dispersed into suitable solvents, forming homogeneous suspensions, called ferrofluids (FF) or magnetic fluids (MF) [44] with unique physical, chemical, thermal, and mechanical properties [45-49]. The control of the monodisperse size is very important because the properties of the nanocrystals strongly depend upon the

dimension of the nanoparticles.

1.1.2.1 Synthesis and stabilization of magnetic iron oxide nanoparticles

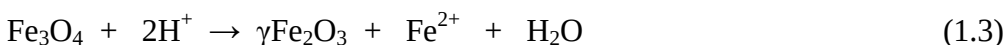
Physical methods such as gas phase deposition and electron beam lithography can be used to synthesize magnetic nanoparticles but such methods are elaborate and suffer from the inability to control the size of particles in the nanometer size range [50]. Numerous chemical methods such as microemulsions [51], sol-gel syntheses [52], hydrothermal reactions [53], hydrolysis and thermolysis of precursors [54], flow injection syntheses [55] and electrospray syntheses [56] can also be used in synthesizing magnetic nanoparticles. However, the most common and efficient method for the production of magnetic iron oxide nanoparticles is the wet chemical coprecipitation [57-60] of Fe^{2+} and Fe^{3+} (molar ratio of 1:2) aqueous salt solutions by addition of a base as shown by Equation 1.1 with a reaction mechanism shown in Scheme 1.1 [61]. The precipitated magnetite is black in colour. Appreciable control over size, composition and sometimes even the shape of the nanoparticles is possible in this method.



Complete precipitation of Fe_3O_4 should be expected at a pH between 8 and 14, with a stoichiometric ratio of 2:1 ($\text{Fe}^{3+}/\text{Fe}^{2+}$) [62], otherwise, Fe_3O_4 can be oxidized as shown by equation 1.2, or transformed into maghemite ($\gamma\text{Fe}_2\text{O}_3$) in the presence of oxygen due to

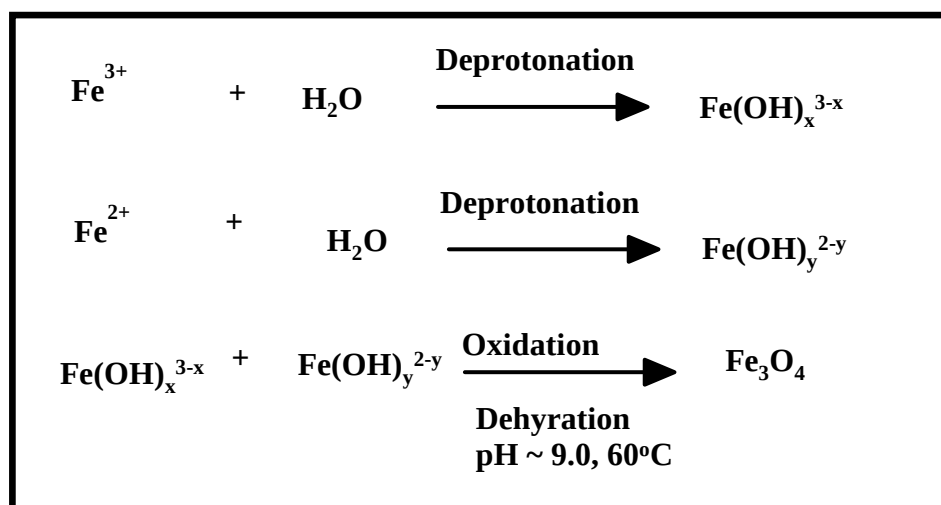


its instability and sensitivity to oxygen as shown by equation 1.3.



This can critically affect the physical and chemical properties of the magnetic particles.

In order to prevent magnetite from agglomeration and possible oxidation in air, great



Scheme 1.1: Reaction mechanism of formation of magnetite nanoparticle through precipitation.

care is taken to carry out the reaction under inert conditions so as to control the reaction kinetics, which is strongly related with the oxidation speed of iron species. This also helps in reduction of the particle size when compared with methods that are not oxygen free [60]. Fe_3O_4 nanoparticles produced by co-precipitation reaction are also usually coated with organic anions like carboxylate e.g. citric acid, polymer surface complexing agents e.g. dextran or inorganic materials like silica, gold or gadolinium [63-65] during the precipitation process. This provides stability in solution, size control and also, ideal anchorage at the nanoparticle surface for binding various biological ligands for biomedical applications. They are also known to provide better protection against toxicity. Iron oxide nanoparticles can be capped by in situ and post-synthesis cappings with much care to avoid formation of a non-magnetic surface [66].

The relative success in the control of size, shape, growth process and composition of nanoparticles depends on the type of salts used (e.g. chlorides, sulphates, nitrates, perchlorates, etc.), Fe^{2+} to Fe^{3+} concentration ratio, pH, temperature and ionic strength of

the media [67-69]. Studies have shown that magnetic nanoparticles prepared with $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions having an optimum concentration between 39 and 78 mM are effective enough to be used as contrast agents [69-71]. It has also been documented that the higher the pH and ionic strength, the smaller the particle size, size distribution and width, because these parameters determine the chemical composition of the crystal surface and consequently the electrostatic surface charge of the particles [72].

1.1.2.2 Applications of magnetic iron oxide nanoparticles

Magnetic nanoparticles are applied in magnetic storage media [72], biosensing applications [73] and magnetic inks for jet printing [74].

Magnetic iron oxide nanoparticles in solution (also represented as magnetic fluid) can interact with an external magnetic field and be positioned to a specific area of the body, facilitating magnetic resonance imaging (MRI) for medical diagnosis [75,76], alternating current (AC) magnetic field-assisted cancer therapy (hyperthermia (HT)) [76], tissue repair [77], magnetofection, immunoassay, detoxification of biological fluids, drug delivery, cell separation and cellular therapy (such as cell labeling or targeting) [61]. These biomedical applications require that the nanoparticles have high magnetization values, a size of about 100 nm [48], and a narrow particle size distribution so that the particles have uniform physical and chemical properties. Functionalized magnetic nanoparticles can bind to drugs or antibodies and be directed to organs or tumors using an external magnetic field [78-80].

Of interest in this thesis is the application of MF in hyperthermia. This was first envisaged in 1993 [81]. It is the use of heat of about 45°C to damage or kill cancer cells, since tumor cells are sensitive to temperature increase whereas normal cells can survive

at high temperatures [82]. It can also be used to increase the effectiveness of other cancer treatments, such as PDT, chemotherapy or radiation therapy. For the therapy to be effective, the proper amount of heat must be applied to a specific area over a given period of time to alter the cancer cells while preventing the surrounding cells from becoming damaged.

In magnetic fluid HT, magnetic particles are embedded around a tumor site and subjected to an oscillating magnetic field (Figure 1.10), some heat is generated due to magnetic

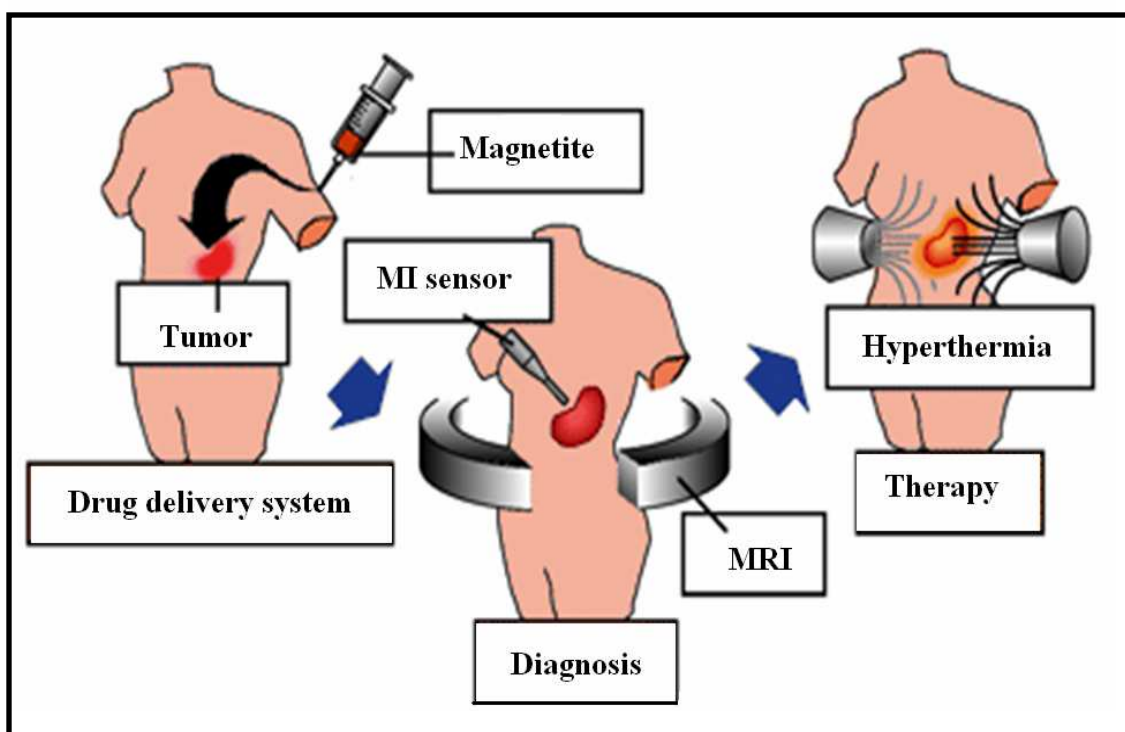


Figure 1.10: Schematic representation of the therapeutic strategy using magnetic iron oxide nanoparticles, MRI: magnetic resonance imaging and MI: magnetoimpedance [76].

hysteresis loss and the amount of heat generated is dependent on the magnetic properties of the material, the strength of the magnetic field, the frequency of oscillation and the cooling capacity of the blood flow in the tumor site. Magnetic field is not absorbed by the living tissues and can be applied to deep region in the living body. Preliminary data

indicate that the malignant cells take up nine times more MF than normal cells [83,84]. MF of the order of tenth of milligram may easily be used to raise the temperature of biological tissue locally up to cell necrosis if the magnetic particles are high powered with appropriate external magnetic field. These materials are not only biocompatible, but also bioactive and could be useful for bone tumors [85].

Scientists are unsure why HT improves the effectiveness of other cancer therapies. One theory is that higher temperatures improve blood flow to tumors and better blood flow can deliver more chemotherapy drugs to cancer cells. It can also provide increased oxygen, which can make PDT or radiation therapy more effective. Some researchers believe that high temperatures may also increase the strength of the immune system. This increased strength may potentially fight off cancer cells and tumor growth. Heat also alters the proteins that make up cells. This can render cancer cells more vulnerable to standard treatments.

The focus in this work is getting a bifunctional agent for improvements in tumor response during PDT. This can be achieved by delivering the light for PDT in a manner which would produce thermal as well as photodynamic effect i.e. simultaneous photosensitization and hyperthermic treatment. The magnetic nanoparticles can also be used in carrying the photosensitizer (drug delivery), in which magnetic particles are coated with a photosensitizer and suspended in a solution, and an external field is directed to the internal treatment site. This increases PDT's efficacy.

1.1.3 Characterization of nanoparticles (QDs and magnetic nanoparticles)

The size of the particle core of nanoparticles can be determined by transmission electron microscopy (TEM) images [40,86] as shown in Figure 1.11. This technique reports the

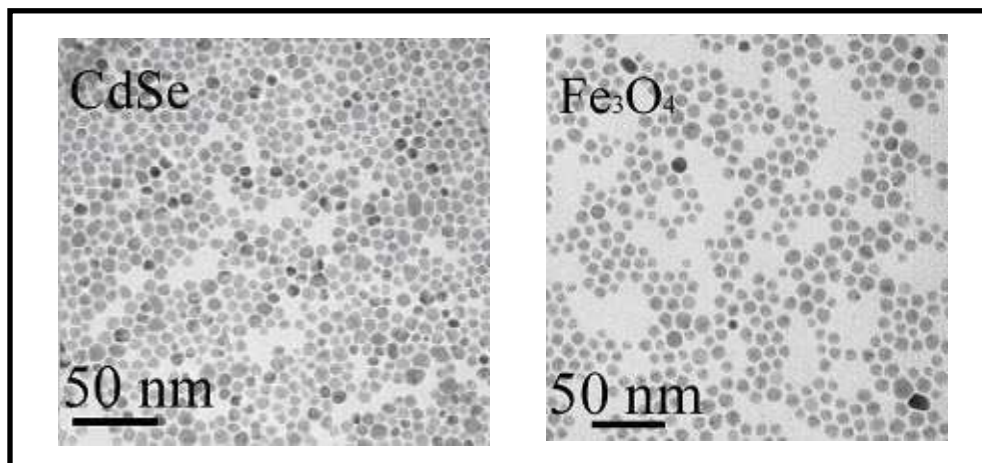


Figure 1.11: Typical TEM images of QDs and magnetic iron oxide nanocrystals [86].

total particle size of the core (crystalline and amorphous parts) and gives access to a number-weighted mean value. It provides details on the size distribution and the shape. However, this technique needs an analysis by image treatment, and it has to be performed on a statistically significant number of particles. Moreover, the sample preparation can induce aggregation of the colloids, and the TEM measurements may consequently not reflect the size and the distribution in solution; aggregates of smaller particles can be discerned [87]. High-resolution transmission electron microscopy (HRTEM) gives access to the surface atomic arrangement. It can be used to study local microstructures (such as lattice vacancies and defects) of crystalline nanoparticles [40,86,87].

X-ray powder diffraction (XRPD) can be performed to obtain the crystalline structure of the particles. In a diffraction pattern, the intensity can be used to quantify the proportion of nanoparticles formed in a mixture by comparing experimental peak and reference peak intensities [17,88] as shown in Figure 1.12. The crystal size can be calculated also from the line broadening from the XRPD pattern using the Scherrer formula [89].

$$d(\text{\AA}) = \frac{k\lambda}{\beta \cos\theta} \quad (1.4)$$

where k is an empirical constant equal to 0.9, λ is the wavelength of the X-ray source, (Cu-K α radiation; 1.5405 $\text{\AA}$), β is the full width at half maximum of the diffraction peak in radians, and θ is the angular position of the peak.

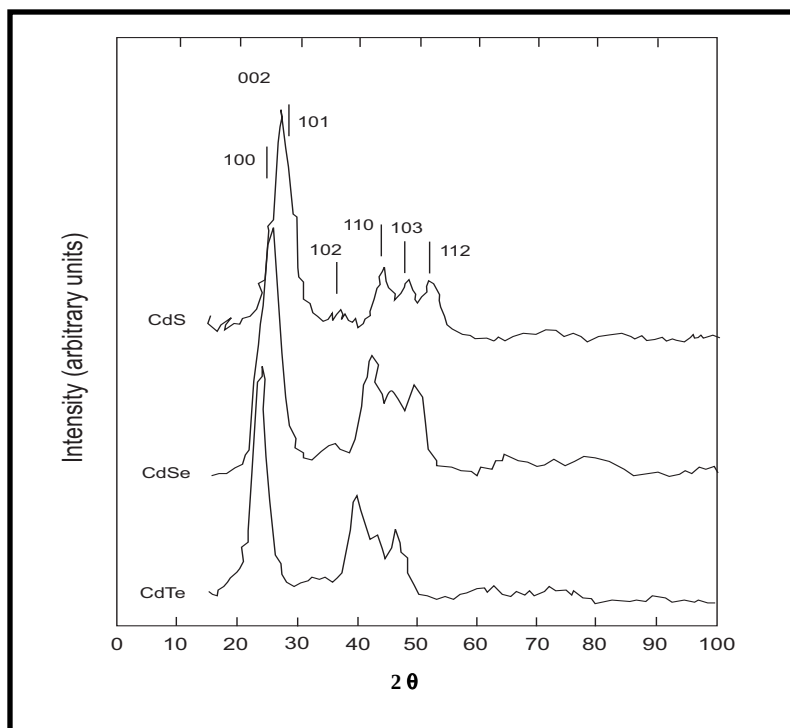


Figure 1.12: Typical powder X-ray diffraction spectra of CdS, CdSe and CdTe nanocrystals [17].

Other physicochemical techniques used to investigate the surface properties of coated nanoparticles are; atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FTIR), secondary ion mass spectra (SIMS), conductimetry, potentiometry, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and solid-state NMR [90]. These techniques are used to describe the nature and strength of the bonding between the nanoparticle surface and the capping and to understand the influence of the capping on the properties of the

nanoparticles. TEM and XRPD are employed in this work.

The interactions of QDs capped with various mercaptocarboxylic acid groups (thioglycolic acid, mercaptopropionic acid and L-cysteine) (**1a-c**) and MN capped with hydroxyl or 3-aminopropyltriethoxysilane cappings (**2a, 2b**) (Figure 1.13) with metallophthalocyanines are studied in this thesis.

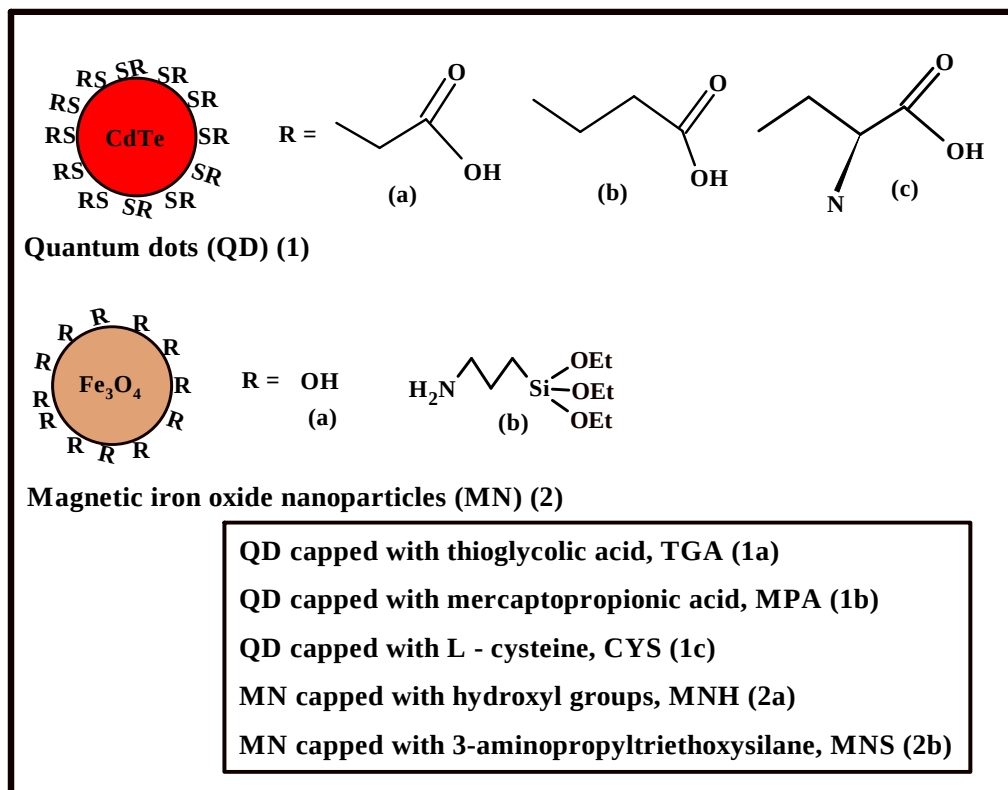


Figure 1.13: Structural representation of studied nanoparticles.

1.2 Metallophthalocyanines (MPcs)

Phthalocyanines (Pcs) are a versatile class of compounds that have extensive application in everyday life commercially, industrially and biomedically [91]. Pcs were first accidentally discovered but unrecognized in 1907, as a by-product during the synthesis of *o*-cyanobenzamide from phthalamide [92,93]. It was described then as an insoluble bluish

compound (later known as free-base Pc). In 1927, the copper complex was encountered but not correctly formulated by de Diesbach [94]. The structural identification by Linstead [95] followed from the accidental discovery of iron Pc in 1928 at the Scottish Dyes Ltd [96,97]. The structure elucidated was confirmed by X-ray crystallography in 1935 [98,99] with the chemical formula $C_{32}H_{18}N_8$ for the metal-free derivative, and the name 'phthalocyanine' was coined from its precursor phthalic acid derivative 'phthalo' and 'cyanine' from the Greek word for blue.

MPcs have a wide variety of applications stemming from their diverse chemical, structural, electronic and optical properties. Owing to their bright beautiful blue, green to violet colour, considerable chemical and photochemical stability and excellent fastness to light [96], Pcs are used worldwide as dyestuffs for jeans and other clothings, inks in ballpoint pens, paints for plastics or metal surfaces and for colouring contact lenses [100]. Their functionality in various processes that are visible light driven makes them applicable in photoredox reactions, photooxidation in solution [91,101], photochemical and photovoltaic cells [102].

Due to their narrow bandwidth, excellent thermal, chemical as well as photochemical stability and compatibility with semiconductor diode lasers, Pcs have been successfully applied in laser-optical recording media. They are particularly attractive for applications in long-term optical data storage, rewritable optical media (CD-RW) [103], photoconducting materials in laser printers and photocopiers [104], non-linear optics [105,106] Langmuir-Blodgett (LB) films [107,108], semi-conductor devices [107,109] and as electrochemical and chemical sensors [110,111].

MPcs have several potential technological applications, including energy conversion

[112], liquid crystal displays [113], gas sensing [103] and electrocatalysis in fuel cells [114]. MPcs are well known as catalysts for both homogeneous and heterogeneous reactions [115]. MPcs catalyse a number of environmentally toxic pollutants such as chlorophenols by being immobilised or supported onto resins or polymer matrixes [116]. They also find use in the petroleum industry as catalysts in sulphur compounds oxidation (known as the Merox process) [117]. The cobalt complex especially, is produced on a large scale for the catalytic oxidation of mercaptans in petroleum distillates.

Pcs have also attracted much attention in oncology as photosensitizers for malignant tumor treatment by PDT. PDT uses a combination of a photosensitizing drug (e.g. MPcs containing non-transition metal centres) and light in the presence of molecular oxygen to obtain a therapeutic effect that depends on selective cell injury. Lipophilic and water-soluble Pcs have been considered as candidates for PDT [118-121] since the drug will have to be injected into the blood stream and traverse lipid membranes. Commercially available Photosens[®], (mixed sulfonated aluminium phthalocyanine (AlPcS_{mix})) has been successfully used for diagnosis and clinical PDT of various cancers including small lung tumors in Russia [122].

1.2.1 Structure of phthalocyanines

Pcs are aromatic macrocyclic compounds which have a conjugated system of 18 π electrons and possess very high thermal and chemical stability with high extinction coefficients of the order of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$. They are highly symmetrical and contain four isoindole groups that are linked together by four nitrogen atoms resulting in a closed ring, hence high thermal stability [91]. The structure of the Pc ring is similar to the naturally occurring porphyrins (P) (**3**) Figure. 1.14, though, unlike porphyrins, Pcs do not occur in

nature and are not involved in biochemical processes; they are completely synthetic organic compounds. The substitution of nitrogen for a meso carbon bridge in **(3)** gives an azaporphyrin **(4)**, while the replacement of all four with nitrogens gives a tetraazaporphyrin (porphyrazine) **(5)**, Figure 1.14. Fusion of four benzene rings on the pyrrole β -positions of a **(3)** results in a tetrabenzoporphyrin **(6)**, while the combination of replacement of the four meso carbon bridges with nitrogen atoms and fusion of benzene rings on the pyrrole β -positions of **(3)** results in a Pc **(7)**, Figure 1.14 [91,93,109]. Infact, Pcs were formally known as tetrabenzo [5, 10, 15, 20] tetraazaporphyrins (TBTAP) [123].

The central cavity of the Pc dianion (Pc^{2-}) can accommodate a wide variety of metal ions (over 70 are known) by coordinate-covalent bonding between the metals and the nitrogen

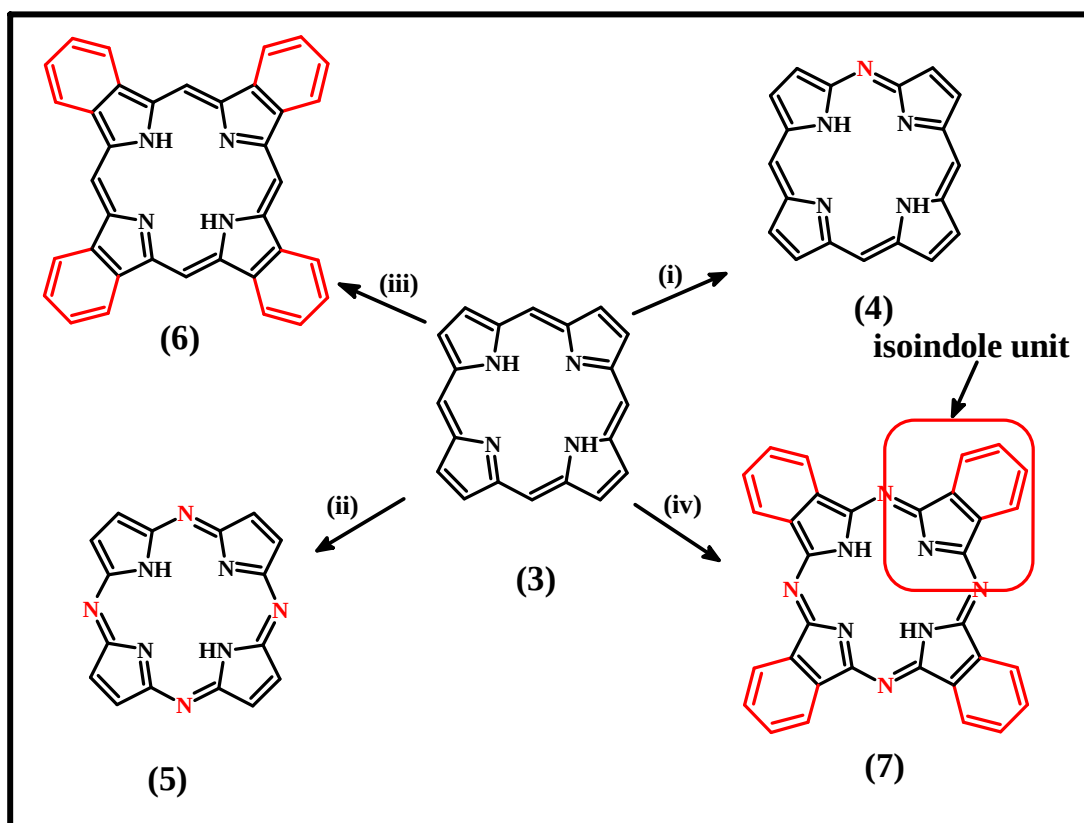


Figure 1.14: Molecular structures of porphyrin-like molecules.

atoms to form a metallophthalocyanine (MPc) (**8**), Figure 1.15. Today, literally thousands of different Pc derivatives exist with a variety of metals, axial ligands and ring substituents [91,109,124]. A free-base Pc (H_2Pc) (**7**), Figure 1.14 is formed in the absence of a metal ion.

H_2Pc (**7**), Figure 1.14 has a square planar geometry with D_{2h} symmetry, the insertion of a metal into the cavity of the ring without affecting the planarity of the complex, increases

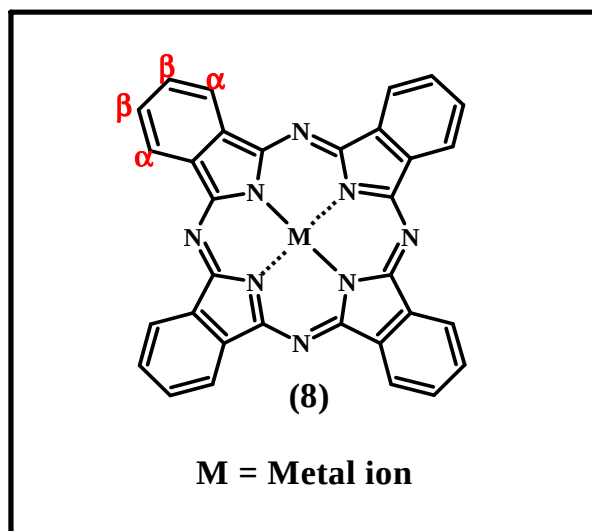


Figure 1.15: Molecular structure of metallophthalocyanines.

the symmetry to D_{4h} (MPc) with a simultaneous reduction in allowed electronic transitions of the molecule. However, because the diagonal distance of the two N atoms within the centre of the Pc ring is just 396 pm [125], some metal ions such as, Ge^{2+} , Sn^{2+} and Pb^{2+} do not perfectly fit into the Pc cavity due to their ionic size [126-128] hence, a decrease in symmetry to C_{4v} is observed, though, the presence of axial ligands like the chloride ions on SnPc and GePc as (Cl_2SnPc and Cl_2GePc) maintains their symmetry as D_{4h} . Zn^{2+} can also be slightly displaced 45 pm from the plane of the aromatic ring resulting in a domed shape [129,130].

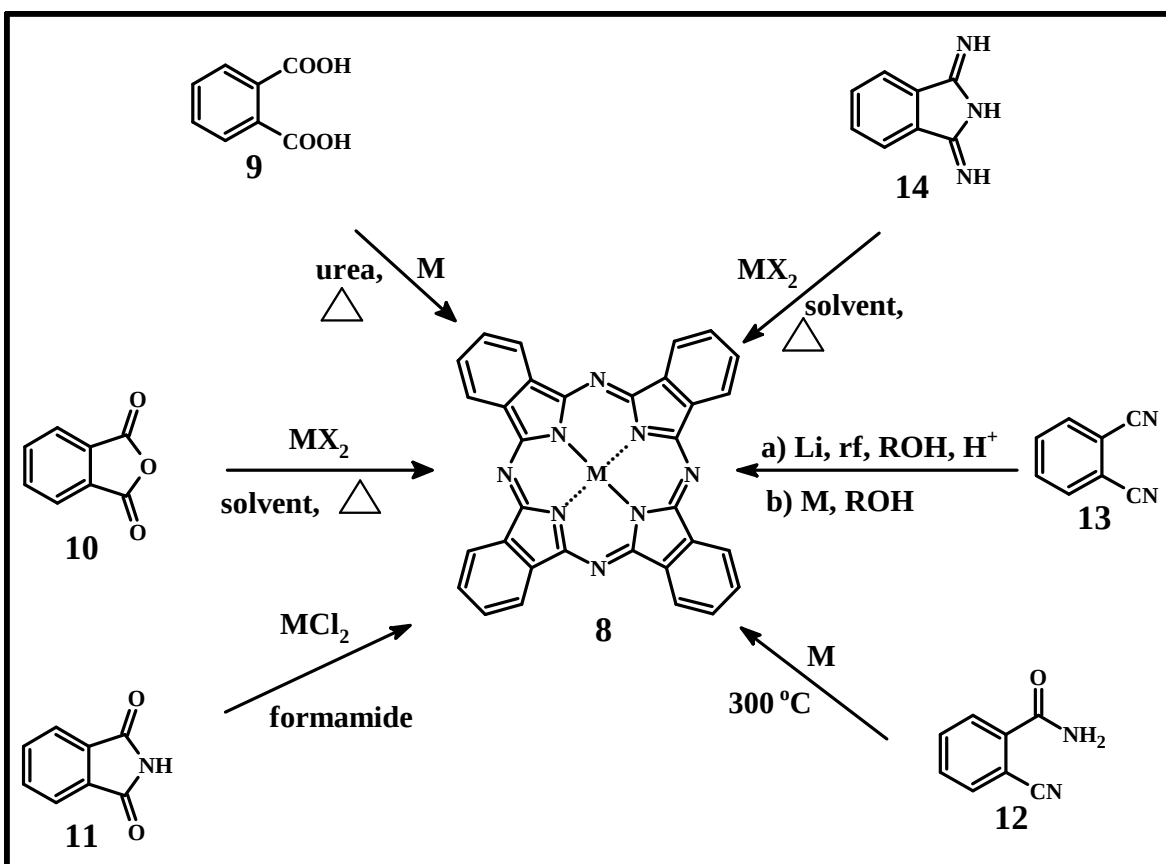
1.2.2 Syntheses of Phthalocyanines

Synthesis of Pcs can be achieved using different routes depending on the type of Pcs to be synthesized, (metal free or metallated, symmetrical or asymmetrical), nature of the substituents and the metal to be inserted into the macrocycle. Conditions such as, temperature, solvent, choice of base and catalyst can be varied accordingly.

1.2.2.1 Unsubstituted phthalocyanines

The strategy of synthesis of Pcs is to start from molecules which correspond to the four identical corners (isoindole units) of the Pc macrocycle Figure 1.14. Such molecules are derivatives of phthalic acid (**9**): for example, phthalic anhydride (**10**), phthalimide (**11**), o-cyanobenzamide (**12**), phthalonitrile (**13**) or diiminoisoindole (**14**) [131-133]. Common synthetic routes for the preparation of MPc complexes are shown in Scheme 1.2 [134]. Phthalic anhydride (**10**) is normally employed for large scale production of MPc complexes because the synthetic route is a relatively cheap one [109]. The choice of phthalonitrile (**13**), as a starting material affords an easy and clean process with high purity products [134,135] that are suitable for purposes of research.

Generally, phthalonitriles form Pcs under various conditions. Both metallated and metal free Pcs may be produced with ease. Synthesis of unsubstituted metal-free Pcs (H_2Pc (**7**)) using phthalonitrile (**13**) as precursor involves heating of **13** with a strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-en (DBN) or ammonia (NH_3) in alcohols (e.g. pentan-1-ol). Basic solvents such as 2-*N,N*-dimethylaminoethanol (DMAE) can also be employed [131]. Of particular interest and value is the method in which labile metals or metal salts such as lithium, sodium or magnesium alkoxides are used in primary alcohols for the cyclotetramerisation. The



Scheme 1.2: Synthesis of MPcs from typical starting materials.

metal ions are easily removed to yield H_2Pc by addition of acid [136,137].

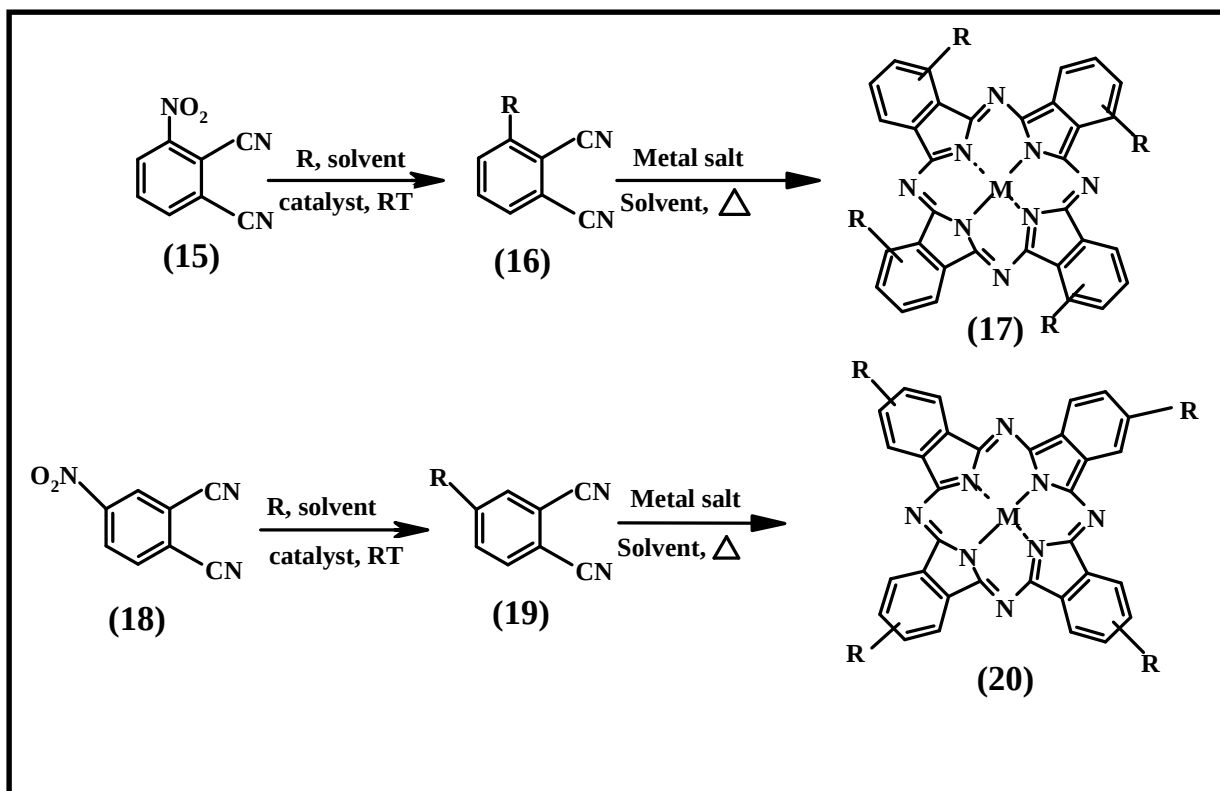
Another approach involves melting phthalonitrile with organic reducing agents such as hydroquinone, 1,2,3,6-tetrahydropyridine or 4,4'-dihydroxobiphenyl. These reducing agents enhance the formation of Pcs by donating the two protons and two electrons required for cyclotetramerisation of the phthalonitrile in the reaction [95,131,137]. Cerium (III) salt has also been employed as a promoting agent in alcohol in the formation of H_2Pc [138].

H_2Pc (**7**) can be metallated by refluxing in the presence of suitable metal salt, using appropriate solvents [139]. However, this is only suitable for metal ions with small radii that can fit into the cavity of the Pc ring.

1.2.2.2 Ring substituted phthalocyanines

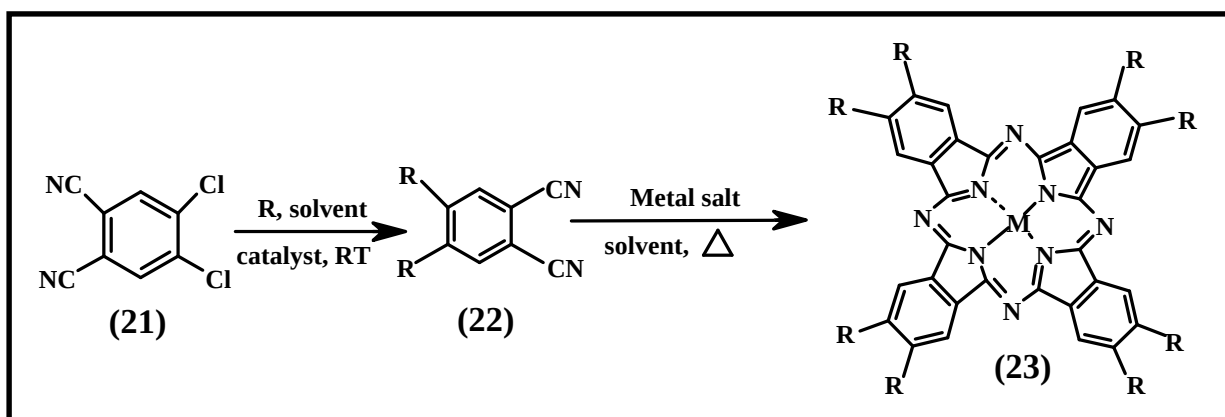
Introduction of substituents at some or all of the sixteen positions on the periphery, either the α (non-peripheral) or β (peripheral) positions on the Pc rings Figure 1.15 improves solubility and alters their basic properties since the electronic distribution of the Pc ring is affected [140-144].

A substituted Pc complex is obtained by substitution on a preformed Pc ring or by cyclotetramerisation of the appropriate substituted phthalonitrile [145,146]. With the use of phthalonitrile (13), monosubstitution can be afforded at the 3- or 4-position. If monosubstituted phthalonitriles are employed, tetrasubstituted PCs with constitutional isomers are obtained Scheme 1.3. The isomers have been documented to be 12.5 % (C_{4h}), 12.5 % (D_{2h}), 25.0% (C_{2v}) and 50.0 % (C_s) [147,148], through the use of specially



Scheme 1.3: Synthesis of tetrasubstituted MPcs from monosubstituted phthalonitrile both at the non-peripheral (17) and peripheral positions (20).

designed high performance liquid chromatography (HPLC) column separation. During the investigations in this thesis, particularly tedious and difficult task of separating the reaction mixture for individual isomers has been omitted, as an isomeric mixture seems not to be less suitable for photochemical and electrochemical applications than a single isomer. The octasubstituted Pcs are obtained from disubstituted phthalonitriles Scheme 1.4 and are known to be isomerically pure, making them easier to purify compared to the tetrasubstituted Pcs. Though the mixture of isomers obtained with the tetrasubstituted Pcs may be seen as a drawback, the presence of the isomers plus the unsymmetrical arrangement of the substituents at the periphery of the Pc have been found to enhance solubility compared to their corresponding octa-substituted derivatives [141,142,145].

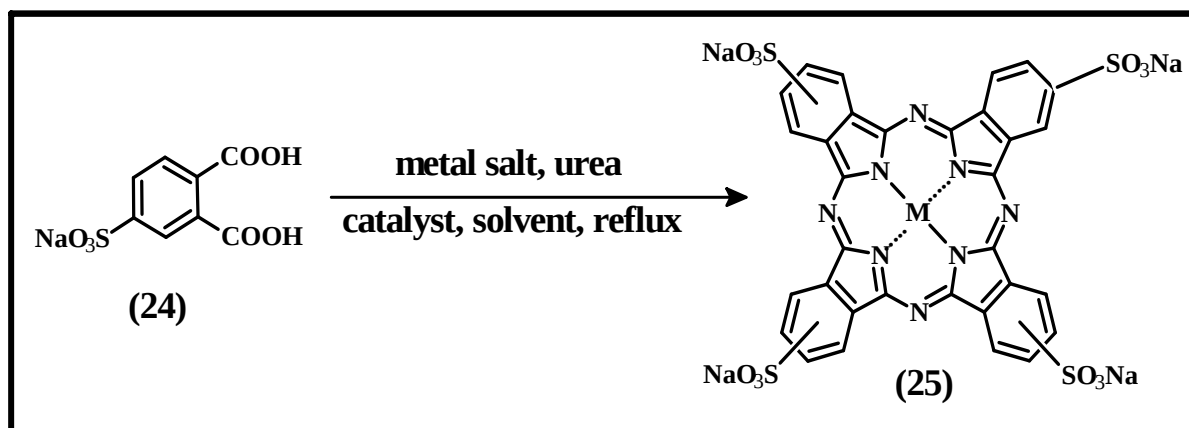


Scheme 1.4: Synthesis of octasubstituted MPcs from disubstituted phthalonitrile

1.2.2.3 Water-soluble phthalocyanines

The first water-soluble Pcs were those made by peripheral sulfonic acid substitution [149]. This development inducted Pcs into the family of ionic dyes. Introduction of substituents such as sulphonic [150,151], carboxylic [152,153] or phosphonic acid [154] at the periphery of the MPc ring enable the complexes to be water-soluble. Weber and

Busch [150] synthesized tetrasulfonated MPc complexes (MPcS₄) (**25**) by refluxing a mixture of monosodium salt of 4-sulphonic acid (**24**), urea and appropriate metal salt in nitrobenzene in the presence of ammonium molybdate as catalyst at a high temperature (about 180°C), Scheme 1.5.

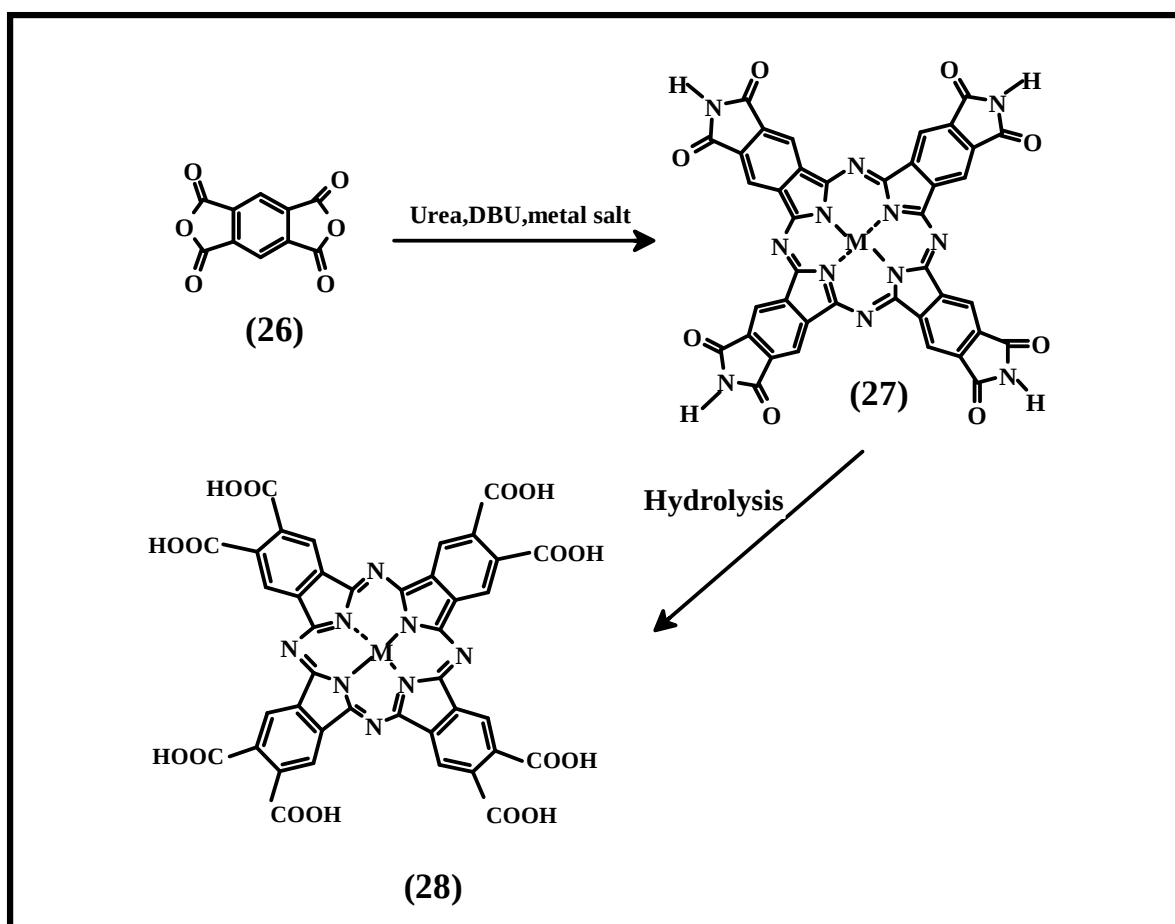


Scheme 1.5: Synthesis of tetrasulfonated MPc (MPcS₄) [150].

A mixture of sulfonated MPc complexes (MPcS_{mix}) which is also water-soluble can be obtained by direct sulphonation of preformed unsubstituted MPc with oleum [155] resulting in the formation of a complex mixture of mono-, di-, tri- and tetra- sulfonated MPc since the degree of sulphonation is uncontrollable during the preparation of the complexes. It has however been observed that the temperature, reaction time and the central ion play important roles in the control of sulfonation [156].

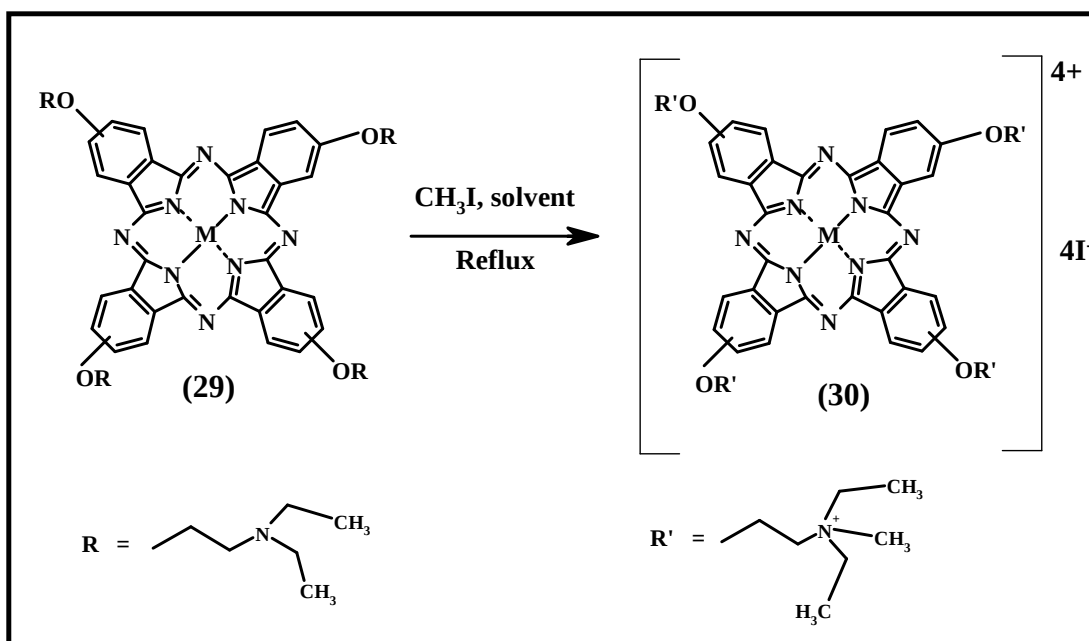
In the synthesis of water-soluble octacarboxymetallophthalocyanine (MOCPc) complexes (**28**), an intermediate product, octa-amido metallophthalocyanine (**27**) is first obtained using benzene-1,2,4,5-tetracarboxylic dianhydride (**26**) in the presence of urea with DBU as a catalyst [152,153], Scheme 1.6. The intermediate (**27**) is then easily converted by hydrolysis to the MOCPc complexes (**28**) by reacting it with aqueous sulphuric acid.

Water-soluble Pcs are also obtained through quaternization. It has been shown that the



Scheme 1.6: Synthesis of water-soluble octacarboxymetallophthalocyanine (MOCPc) [152,153].

benzene rings of the Pc can be replaced with pyridine and the pyridine nitrogen can be quaternized to obtain a tetracationic water-soluble tetrapyridinoporphyrazine [157,158]. The quaternized tetrapyridinoporphyrazines were found to be less aggregated [157,158] compared to some anionic MPcs. Quaternization of tertiary amines has provided a valuable method of preparing water-soluble positively charged Pcs [159-163], Scheme 1.7. MPcs substituted with aminoalkanethio groups (29) can be quaternized resulting in MPcs with quaternary ammonium cations (30) which are soluble in water. The quaternary ammonium cations are formed by complete alkylation of the amines through exhaustive methylation. Reagents such as diethyl sulphate (DES), dimethyl sulphate



Scheme 1.7: Quaternization of tertiary amine substituted phthalocyanines [161].

(DMS) and methyl iodide (CH_3I) are used in quaternization. CH_3I is an excellent substrate for $\text{S}_{\text{N}}2$ substitution reactions [164].

In this work, the physicochemistry and potential applications as photosensitizers; of anionic and cationic water-soluble tetra and octa substituted MPc complexes ($\text{M} = \text{Zn}$, Al , Si , Ge and Sn) alone or in the presence of QDs and/or MF, will be explored.

Aims of the thesis

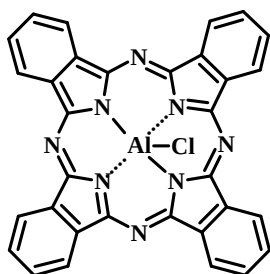
The MPc complexes studied in this work are shown in Figure 1.16. Water-soluble Pcs are still preferred as photosensitizers especially for PDT since they can be injected directly into the bloodstream against lipophilic Pcs which are associated with cutaneous toxicity. Anionic MPcs such as tetrasulfonated aluminium and zinc (AlPcS_4 (**34**) and ZnPcS_4 (**33**)) [165] as well as unsubstituted AlPc (**31**) and ZnPc (**32**) have shown excellent photosensitizing behaviour in literature but the physicochemistry of the tetrasulfonated group 14 (IV) metals such as Si and Ge have not been fully explored, hence,

tetrasulfonated, tetracarboxy and octacarboxy silicon and germanium MPcs (SiPcS₄ (**35**), GePcS₄ (**36**), SiTCPc (**39**), GeTCPc (**40**), SiOCPc (**43**) and GeOCPc (**44**) respectively) will be synthesized and their photophysicochemistry will be explored. ZnPc, AlPc and their derivatives (**33**, **34**, **33**, **34**, **37**, **38**, **41**, and **42**) are expected to show improved photophysical behaviour in the presence of nanoparticles. Aminoalkanethio-derivatised MPcs (**47-49**) are synthesized in this work due to the presence of the tertiary amine on the substituent that can be easily quaternized for water solubility and their physicochemical behaviour is explored since literature is sparse on the photophysical and photochemical characteristics of these complexes.

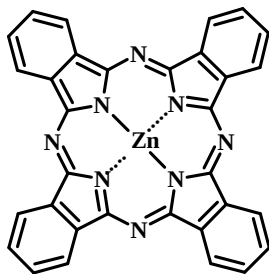
Very few SnPc derivatives are known, and some of these have shown interesting chemistry [166-168]. However, there is very little study on the photophysical and photochemical behaviour of SnPc complexes inspite of their interesting chemistry. Sn is a heavy atom and it is expected that it will have tremendous effect on the triplet state quantum yields of MPcs and subsequently improve their use as photosensitizers. Moreover, aryloxy groups have been shown to improve the photophysical and photochemical properties of MPcs, hence, phenoxy, tert-butyl phenoxy and benzyloxyphenoxy tetra-substituted Sn⁴⁺ MPc complexes (**45a-c** and **46a-c**) are synthesized and studied in this work for the elucidation of their photochemical and photophysical behaviour.

As earlier mentioned, the nature and position of substituents can influence the properties of MPcs. MPcs can therefore be tailored to consist of certain properties which are required for various applications with the possibility of combining an unlimited number and type of substituents with a great number of central metals. Hence, the MPcs used in

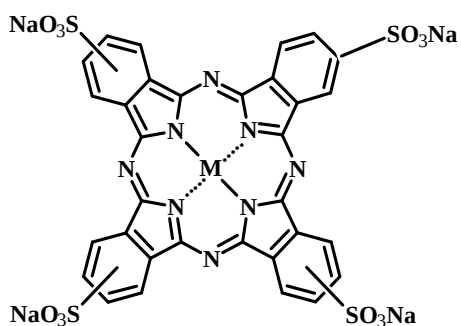
this thesis are investigated for their interesting photophysicochemical and photovoltaic properties which hitherto have not been explored.



(31)



(32)

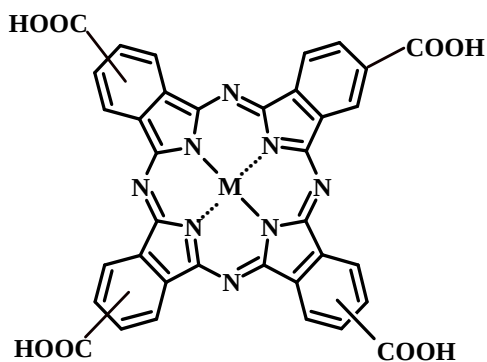


(33) ZnPcS_4 : $\text{M} = \text{Zn}$

(34) AlPcS_4 : $\text{M} = \text{Al}(\text{OH})$

(35) SiPcS_4 : $\text{M} = \text{Si}(\text{OH})_2$

(36) GePcS_4 : $\text{M} = \text{Ge}(\text{OH})_2$

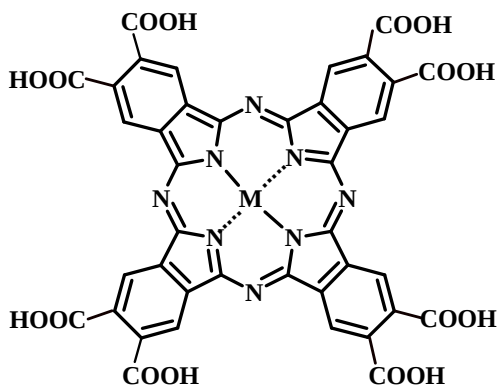


(37) ZnTCPc : $\text{M} = \text{Zn}$

(38) AlTCPc : $\text{M} = \text{Al}(\text{OH})$

(39) SiTCPc : $\text{M} = \text{Si}(\text{OH})_2$

(40) GeTCPc : $\text{M} = \text{Ge}(\text{OH})_2$



(41) ZnOCPc : $\text{M} = \text{Zn}$

(42) AlOCPc : $\text{M} = \text{Al}(\text{OH})$

(43) SiOCPc : $\text{M} = \text{Si}(\text{OH})_2$

(44) GeOCPc : $\text{M} = \text{Ge}(\text{OH})_2$

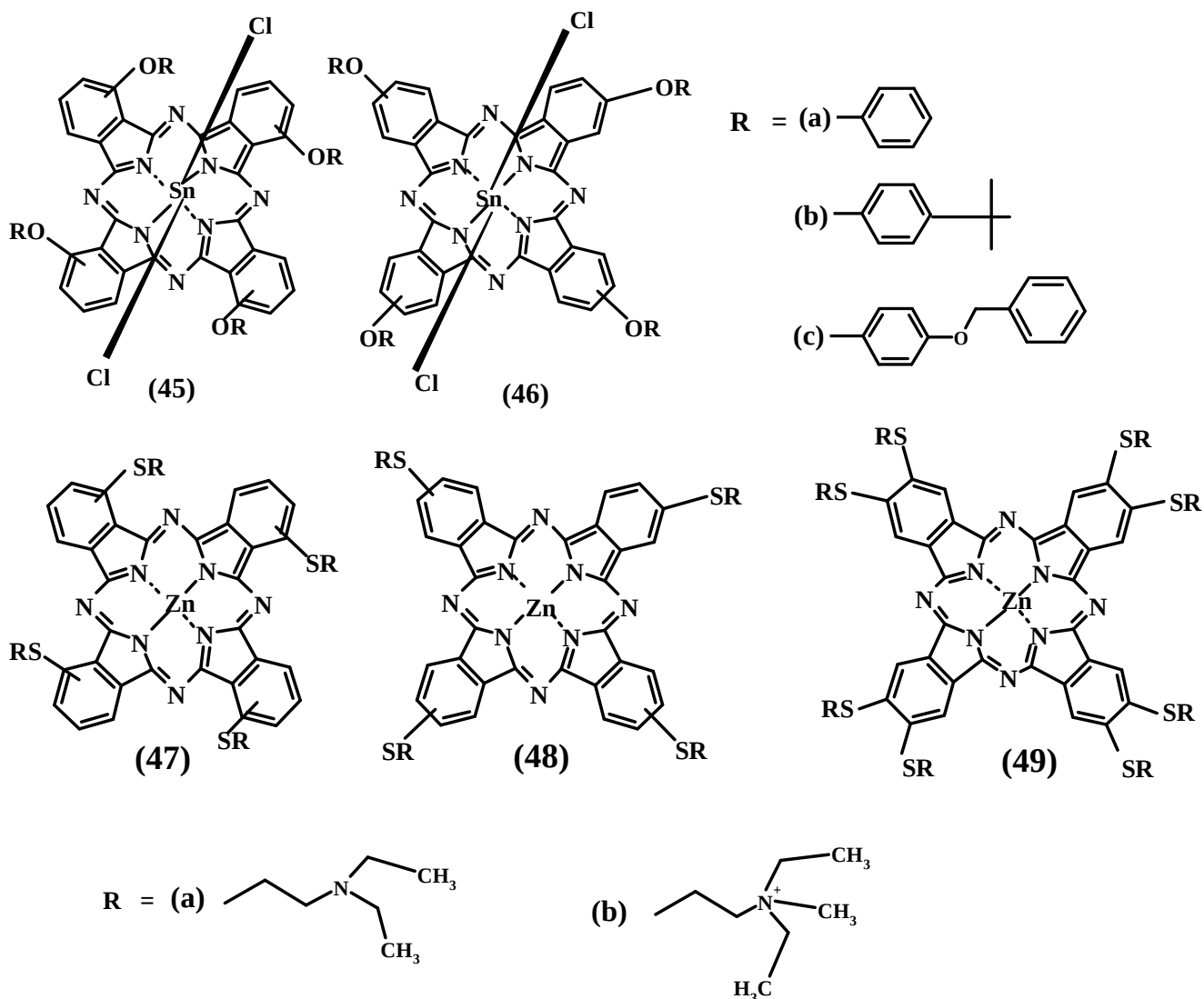


Figure 1.16: Structures of studied MPcs.

1.2.3 Electronic absorption spectra of phthalocyanines

A characteristic feature of the absorption spectra of MPcs is the presence of two very intensive bands; the Q band in the visible region with molar extinction coefficient greater than $10^5 \text{ M}^{-1}\text{cm}^{-1}$ accompanied by a series of vibrational bands Q_{vib} and a weaker B or Soret band in the UV region around 350 nm (Figure 1.17). A broad B band is observed due to the superimposition of the B_1 and B_2 bands [124,129, 169]. Additionally, bands such as N, L and C occurs at high-energy (below 300 nm) in the ground state electronic

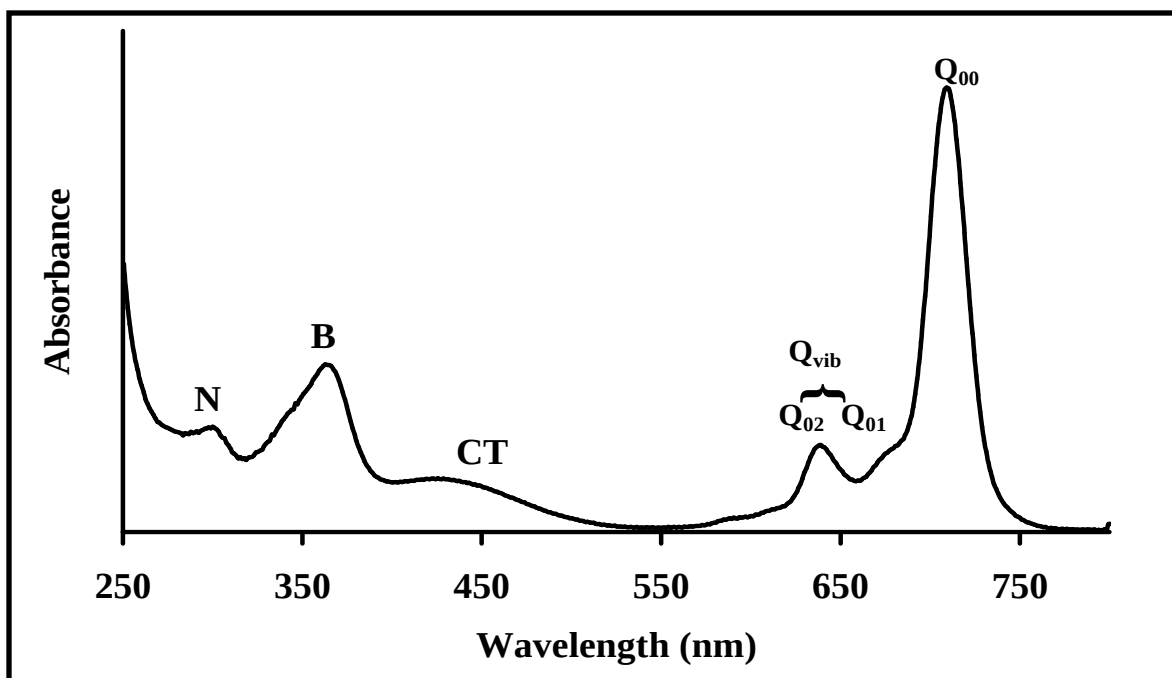


Figure 1.17: Ground state electronic absorption spectra of a typical metallophthalocyanine complex. CT= Charge transfer.

absorption spectra of some diamagnetic MPcs such as ZnPcs and MgPcs [129,170]. These are mostly observed in transparent solvents such as dichloromethane. The bands observed in Pcs are primarily due to π - π^* electronic transitions in the Pc ligand and their origins can be explained by Gouterman's four-orbital linear combination of atomic orbital model, Figure 1.18. The model considers the top two highest occupied molecular orbitals (HOMO) and the degenerate lowest unoccupied molecular orbital (LUMO) [125]. The Q band (Q_{00}) absorption is due to transitions from the HOMO, (a_{1u} symmetry (π)), to the LUMO (e_g symmetry (π^*)) while the transition from a_{2u} and b_{2u} to e_g results in the B band absorptions. The Q band is more intensified than the B band and ~350 nm apart from it due to the large energy gap between the a_{1u} and a_{2u} orbitals that gives no room for configurational interaction.

There are also possibilities of charge transfer transitions (CTTs) [124] which usually

appear as weak absorption bands between Q and B bands (400 - 500 nm region) or in the near infrared (NIR) when the central metal's d-orbital lie within the HOMO-LUMO gap of the Pc ring [125,171]. CTT can either be from ligand to metal; (ligand-to-metal charge

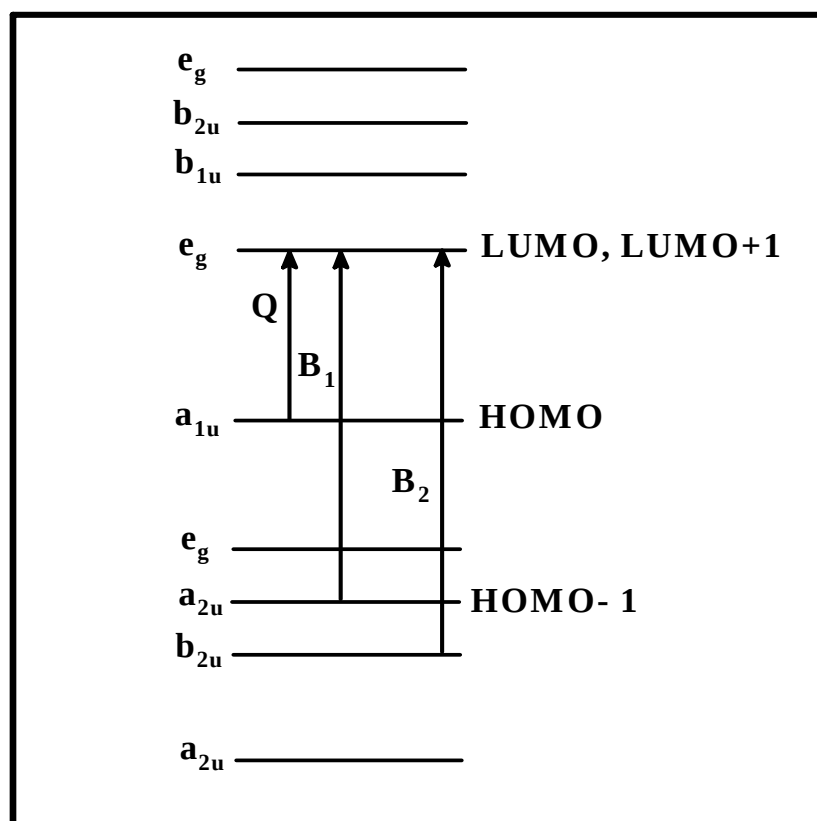


Figure 1.18: Electronic transitions in MPcs showing the origin of Q and B absorption bands [125].

transfer, LMCT) or from metal to ligand (metal-to-ligand charge transfer, MLCT).

For H_2Pc , the Q band splits into a doublet Figure 1.19 with one of the components found at slightly longer wavelength than is the case with MPcs. This splitting of the Q band arises from lower symmetry (D_{2h}) in comparison with metallophthalocyanine (D_{4h}). Consequently, the LUMO orbital loses degeneracy [172] due to the presence of the two core protons giving rise to Q_x and Q_y states which are of varying energy.

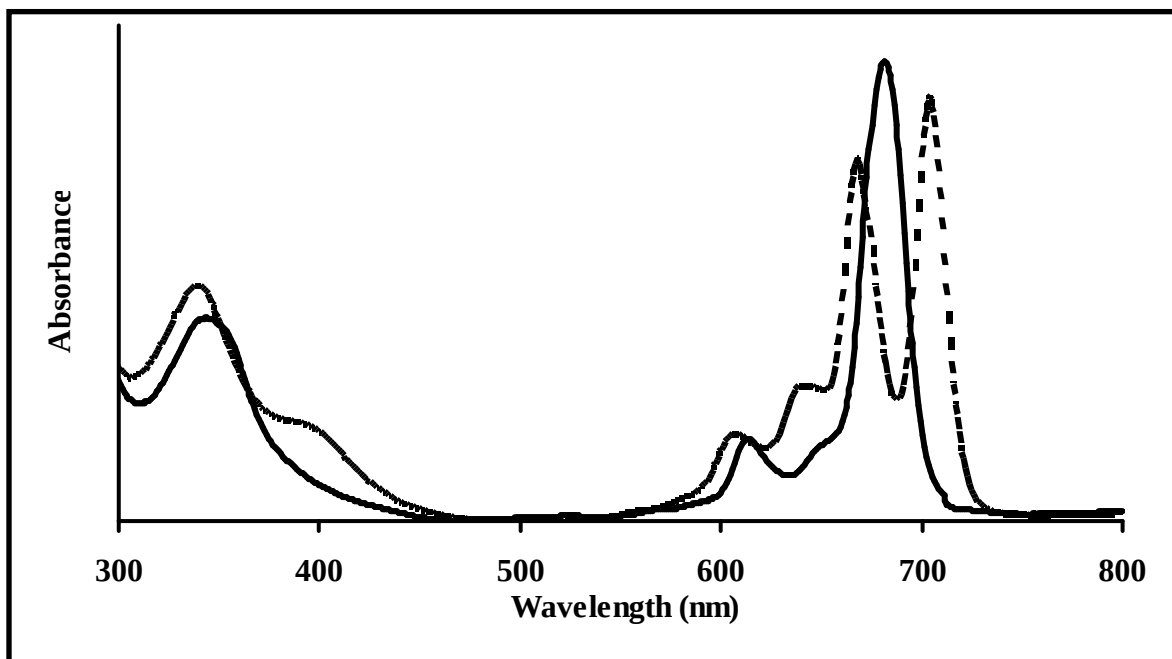


Figure 1.19: Ground state absorption spectra of metal-free (dashed line) and metallated (solid line) phthalocyanine.

Position, appearance and intensity of the bands depend on the type, number and position of peripheral substituents, metallation, solvent as well as aggregation of the molecules [173,174]. Non-peripheral substitution (α) results in a larger red shift compared to peripheral (β) substitution, Figure 1.15. It has been documented [175] that ring substitution at the α position with electron donating groups results in a red shift of the Q and B bands due to reduction in the HOMO-LUMO energy gap, while at the β position, a shift to shorter wavelength is experienced. The effect of electron-withdrawing groups was observed to be exactly the opposite with respect to the α and β positions. Conjugated and aromatic solvents have been shown to shift Q bands to longer wavelengths [176], acidic solvents like chloroform have been found to oxidize the Pc ring [169] thereby leading to decreased intensity of the Q band with appearance of a broad band around 500

nm while solvents with high refractive indices such as 1-chloronaphthalene results in red-shifting of the Q band [177].

1.2.3.1 Aggregation in MPcs

Aggregation of symmetrically substituted Pcs gives rise to pronounced spectral changes that extend from broadening to an observed splitting of the Q band or a blue or red shift of the Q band [178], indicating presence of additional electronic levels of the aggregates (Figure 1.20).

The exciton coupling theory [179,180] explains that, the result of the interaction of two adjacent D_{4h} MPcs is the appearance of four degenerate states. The four degenerate states arise from splitting of ^1E_u excited states. Transitions are formally allowed only to the upper pairs of states (^1E_u). Hence, a blue shift of the Q and B bands occur following dimerization. Transitions to the lower energy pairs of states (^1E_g) are symmetry forbidden Figure 1.20. A transition to the lower energy LUMO can still occur to a small extent even though it is forbidden, thus resulting in a broad absorption spectrum.

Aggregation in MPcs is well documented [181-196] especially that due to π - π interaction between the rings. Generally, most water-soluble Pcs have charged groups at their periphery and they can disaggregate better in aqueous solution in micelles formed from surfactants that are oppositely charged [165,197-202]. However non-ionic or neutral surfactants also have some effect on some Pcs.

All water-soluble Pcs prepared in this work have charged groups at their periphery, such as a sulfonate or quaternary amine, however, cremophore EL (CEL), Figure 1.21 which is a nonionic or neutral surfactant was used in disaggregation them. This is to ensure similarity/comparison in the effect of the surfactant on the photosensitizing properties of

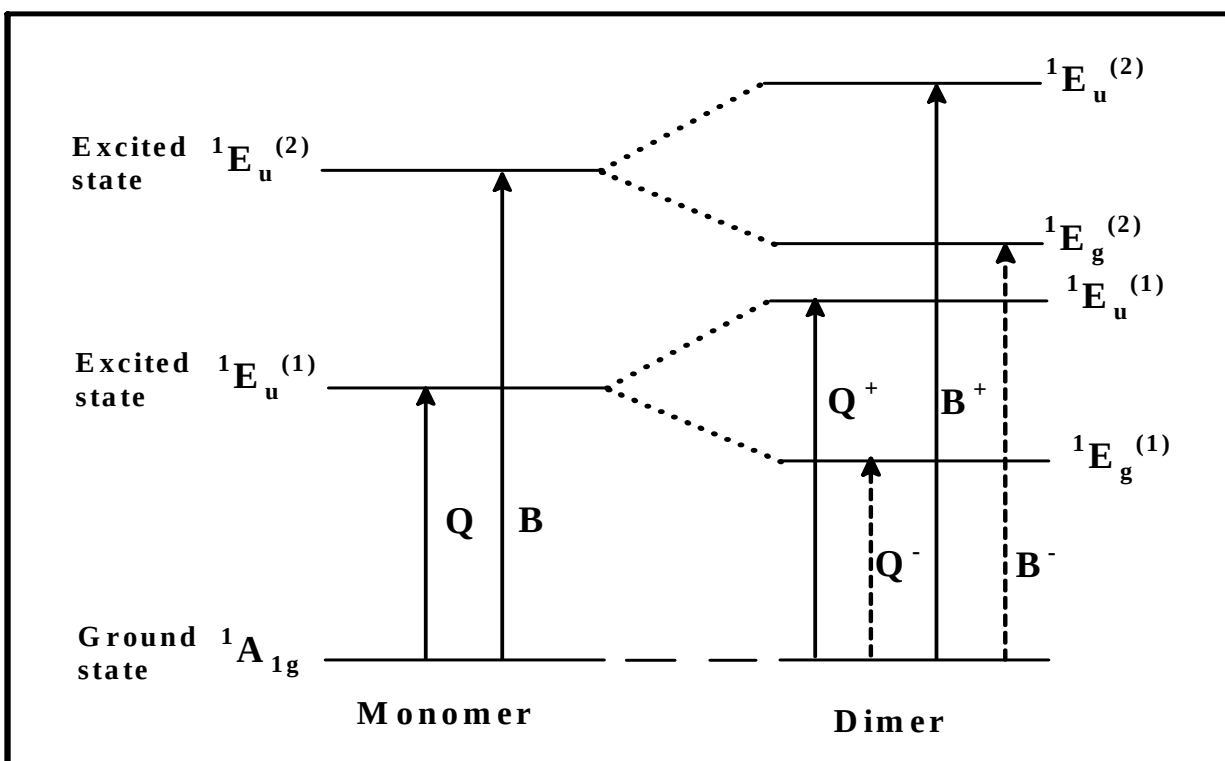


Figure 1.20: Interaction between two coplanar D_{4h} metallophthalocyanine rings showing the effect of aggregation on the LUMO of Pcs (full and dashed arrows indicate allowed and forbidden transitions, respectively) [180].

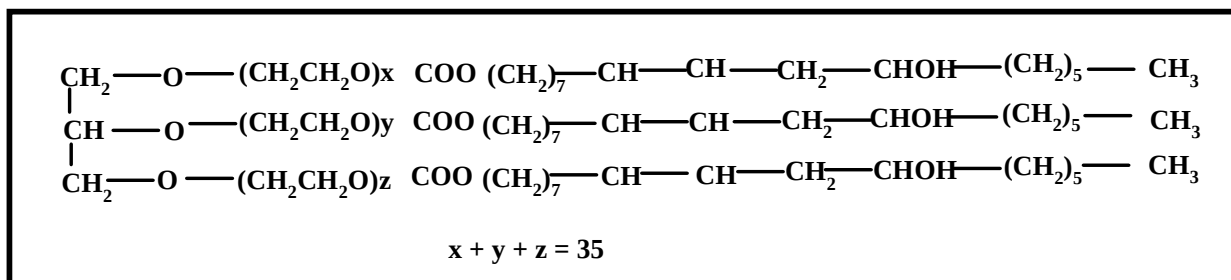


Figure 1.21: Structure of cremophore EL [203].

the Pcs. Apart from acting as a surfactant, CEL which is an excipient to drugs also acts as a drug vehicle [203-206]. Addition of water miscible organic solvents (methanol, ethanol, *N,N*-dimethylformamide (DMF), pyridine, dimethylsulfoxide (DMSO)) to aqueous solutions of aggregated Pcs also often has the effect of reducing aggregates formation.

The increase in the low energy component of the Q band of aggregated MPcs in the presence of surfactants may be used to assess the degree of aggregation in MPcs. In this study, CEL was used to estimate the degree of aggregation of the studied water-soluble complexes using equation 1.5 [207]:

$$\% \text{ Agg} = \frac{\text{Abs}_{(\text{CEL})} - \text{Abs}}{\text{Abs}_{(\text{CEL})}} \times 100 \quad (1.5)$$

where $\text{Abs}_{(\text{CEL})}$ and Abs are the absorbances at the Q band maxima in the presence and absence of the surfactant, CEL.

Photophysical and photochemical studies of water-soluble aggregated MPcs in the presence of CEL is not known, hence a study is warranted. In this work, the effects of aggregation and non-ionic surfactant, CEL on the photosensitizing abilities of some water-soluble MPcs is studied.

The dimerization constant (K_D) for the simple monomer-dimer equilibrium represented by $2M \leftrightarrow D$ of the aggregates can be determined, and it is defined by Equation 1.6:

$$K_D = \frac{[D]}{[M]^2} \quad (1.6)$$

where $[M]$ and $[D]$ are the molar concentration of the monomer and dimer, respectively.

Following the conservation of mass; the total concentration of MPc, C is given by Equation 1.7:

$$C = [M] + 2[D] \quad (1.7)$$

$[M]$ and $[D]$ are expressed as [208,209],

$$[M] = \frac{[-1 + \sqrt{(1 + 8K_D C)}]}{4K_D} \quad (1.8)$$

$$[D] = \frac{[1 + 4K_D C - \sqrt{(1 + 8K_D C)}]}{8K_D} \quad (1.9)$$

The absorbance of a solution containing both the monomer and dimer is given by Equation 1.10

$$\text{Abs} = (\epsilon_M[M] + \epsilon_D[D])l \quad (1.10)$$

where l is the optical path length.

Substitution of Equation 1.8 and 1.9 into Equation 1.10 followed by rearrangement leads to Equation 1.11:

$$\text{Abs} = \frac{[1 - \sqrt{(1 + 8K_D C)}][\epsilon_D/2 - \epsilon_M] + 2\epsilon_D K_D C}{4lK_D} \quad (1.11)$$

The value of ϵ_D and K_D can be determined by using non-linear least square fit procedure using MATLAB, OriginPro or other statistical software. In this work, K_D and ϵ_D of the aggregated MPcs studied are determined to be able to evaluate the monomer-dimer equilibrium. Table 1.1 shows variation in dimerization constants for some known MPcs [195,207,210-213].

Table 1.1: Variation in dimerization constants (K_D) of some MPcs in aqueous medium.

Complex	K_D (M^{-1})	Solvent	Temp. ($^{\circ}C$)	Reference
ZnPc(SO ₃ Na) ₄	2.50×10^6	H ₂ O	20	[210]
ZnPc(SO ₃ Na) ₄	4.70×10^5	H ₂ O	20	[211]
ZnPc(SO ₃ Na) ₄	1.00×10^6	H ₂ O	58	[212]
ZnPc(COOH) ₄	9.20×10^4	H ₂ O	20	[195]
AlPc(SO ₃ Na) ₄	1.00×10^6	H ₂ O/90% MeOH	20	[213]
SnPc(SO ₃ Na) ₄	2.70×10^4	H ₂ O	RT	[207]

1.2.3.2 Spectral studies of interaction of MPcs with QDs

A short review follows on the spectral studies of interactions of MPcs with QDs since interactions of water-soluble cationic MPcs with anionic CdTe QDs will be studied spectroscopically in this thesis.

UV/Vis spectroscopy or ground state electronic absorption is important in the characterization of the ground state interactions or charge transfer reactions within the ion pairs and it can easily help in detection of supramolecular assemblies. Complexation of the ions can be monitored by UV/Vis spectrophotometric titration and using the continuous variation method, otherwise known as the Job's method, the stoichiometry of the mixed complexes can be determined [214-216].

The assumption of the continuous variation method is that; the absorbance of a mixture of solutes that do not interact is equal to the sum of the absorbances of the solutes separately. The departures from additivity are therefore interpreted as the formation of a complex as the composition of the solution is varied. The extent of departure is recorded versus the composition of the mixture, and the composition at which the deviation from additivity is greatest determines the stoichiometry of the complex.

The measured absorptions for mixtures with various ratios of cationic MPcs and anionic QDs, at a given wavelength are used to calculate the function $F(x)$ in Equation 1.12a [214].

$$F(x) = d(x) - (\epsilon_{\text{QD}} - \epsilon_{\text{MPc}})x - \epsilon_{\text{MPc}} \quad (1.12a)$$

where x is the mole fraction of the CdTe QDs, $d(x)$ is the absorbance of a mixture at the selected wavelength divided by the sum of the concentrations of the solutes, ϵ_{QD} and ϵ_{MPc}

are the molar extinction coefficients of the CdTe QDs and MPcs respectively, ϵ_{QD} is estimated using the empirical fitting functions from literature in Equation 1.12b [217]

$$\epsilon_{\text{QD}} = 3450\Delta E(D)^{2.4} \quad (1.12b)$$

where ΔE is the transition energy corresponding to the first absorption peak of the QD in eV, D is the diameter or size of the QD. Deviation from additivity of the absorption of a mixture of x M of CdTe QDs and $(1-x)$ M (where M is the concentration) of MPc is thus represented by $F(x)$ in molar absorption units. Continuous variation plots, $F(x)$ versus x for titration of MPc with varying concentrations of CdTe QDs show the stoichiometry of the mixed complexes.

The measure of the strength of the interaction of the QDs with the MPcs (association constants) may be determined from the spectrophotometric titrations using Equation 1.13 [218].

$$\frac{A_0}{\Delta A} = \frac{A_0}{\Delta A_{\text{max}}} + \frac{A_0}{\Delta A_{\text{max}}} \frac{1}{K_a} \frac{1}{C_t} \quad (1.13)$$

where $\Delta A = A_0 - A$, A_0 and A are the absorbances of the respective MPc in the absence and presence of total CdTe QD concentration (C_t), respectively and ΔA_{max} is the maximum change in absorbance. The association constant K_a is obtained from the ratio of $A_0/\Delta A_{\text{max}}$ and the slope of the plot of $A_0/\Delta A$ versus $1/C_t$.

Aims of thesis

The few reports in literature have been on the interaction of organic soluble QDs with MPcs [219-226] via FRET mechanism. Maslov and co-workers reported on the interaction of QDs with porphyrazines [227] annexing the lone pair of electrons on the

nitrogen atoms of the porphyrazine to act as complexing agents to the atoms of the QDs. However, they worked in organic medium, thus limiting biological applications.

The interactions of ion pairs of cationic MPcs grafted with quaternary ammonium groups (2-diethylmethylaminoethylsulfanyl) and anionic thiol capped CdTe QDs are investigated spectroscopically in this study. Electrostatic interaction of anionic QDs and cationic MPcs is not known and since both have potential as photosensitizers and/or photocatalysts, and on combination, the wavelength spans through the electromagnetic spectrum, an exploration of their interaction is warranted as light harvesters.

1.3 Fluorescence studies

1.3.1 Fluorescence spectra

The concept of energy absorption, and consequently excitation, is clearly described by the Jablonski diagram [228] (Figure 1.22). This diagram visualizes photophysical processes that allow an electronically excited molecule to dissipate its energy by radiative (fluorescence (F), phosphorescence (P)) and non-radiative (vibrational relaxation (VR), internal conversion (IC), intersystem crossing (ISC)) deactivation phenomena [228]. The change of multiplicity in ISC is spin-forbidden. However, it may occur as a consequence of spin-orbit coupling (SOC) which occurs when electrons flip their spin. Paramagnetic compounds or atoms with high nuclear charge (heavy atoms) enhance SOC such that population of the lowest energy triplet state is enhanced.

Fluorescence properties of MPcs such as spectral shifts, fluorescence quantum yields and lifetimes are influenced by the presence and nature of the central metal, aggregation, nature of solvent, pH, halogenation, photo-induced electron transfer or electronic energy transfer and structural features such as double bond torsion and weak bonds [229,230]. It

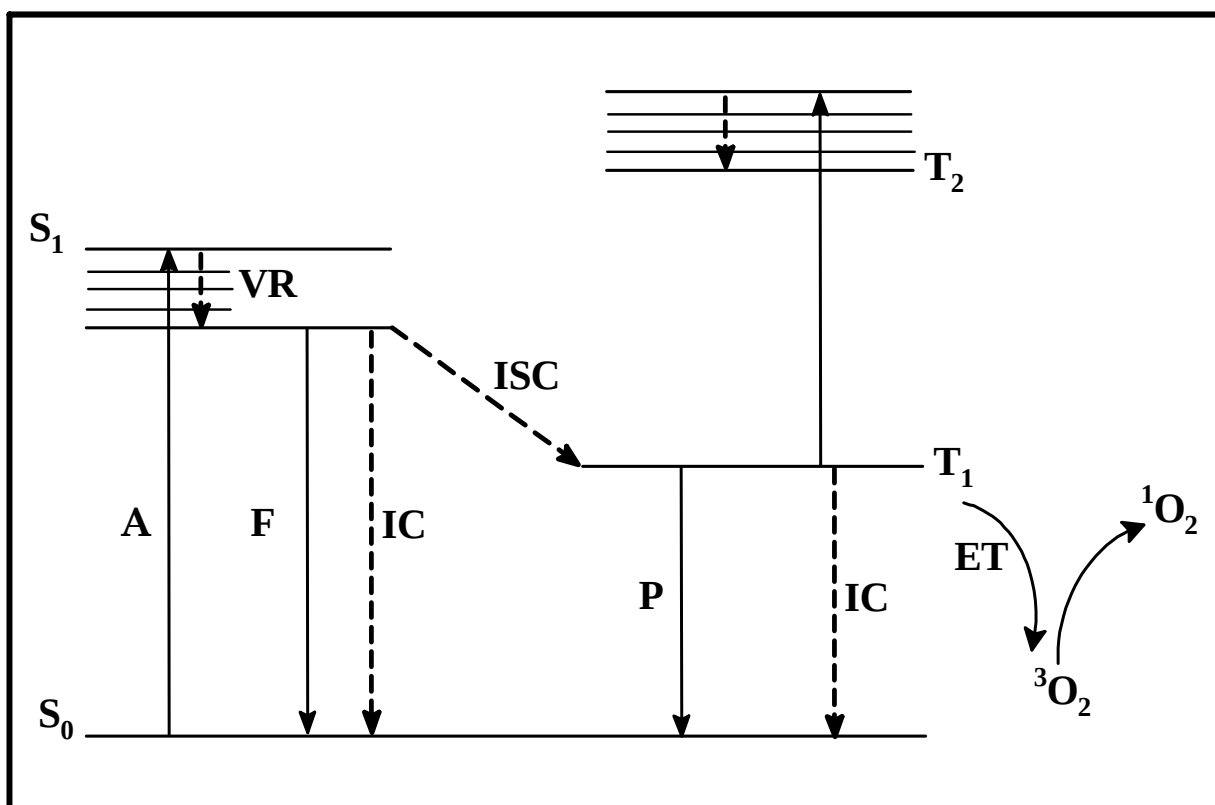


Figure 1.22: A simplified Jablonski diagram showing the transitions between the ground and excited electronic state. A = absorption, F = fluorescence, IC = internal conversion, VR = vibrational relaxation, ISC = intersystem crossing, P = phosphorescence, S_0 = singlet ground state, S_1 = singlet excited state and T_1 = triplet excited state. Radiative transitions are indicated with solid arrows, while non-radiative transitions are indicated with dashed arrows.

is believed that dimers in MPcs are non-fluorescent [166], therefore reducing the fluorescing ability of an aggregated Pc, though cooled solutions of aggregated MPcs have been shown to fluoresce [231].

The fluorescence emission spectrum of an MPc is red shifted and a mirror image of its absorption spectrum, Figure 1.23 with Stokes' shifts of less than 10 nm. The magnitude of the Stokes' shift in MPcs can be affected by the rigidity of the environment, solvent polarity or viscosity.

Fluorescence excitation spectrum of MPcs provides information about the absorption spectrum of the fluorescent molecules. It is obtained by scanning for fluorescence excitation at a fixed emission wavelength. Excitation spectra are comparable to their corresponding absorption spectra as said above and both are meant to be mirror images of the emission spectra. However, there are cases when lack of conformity between these

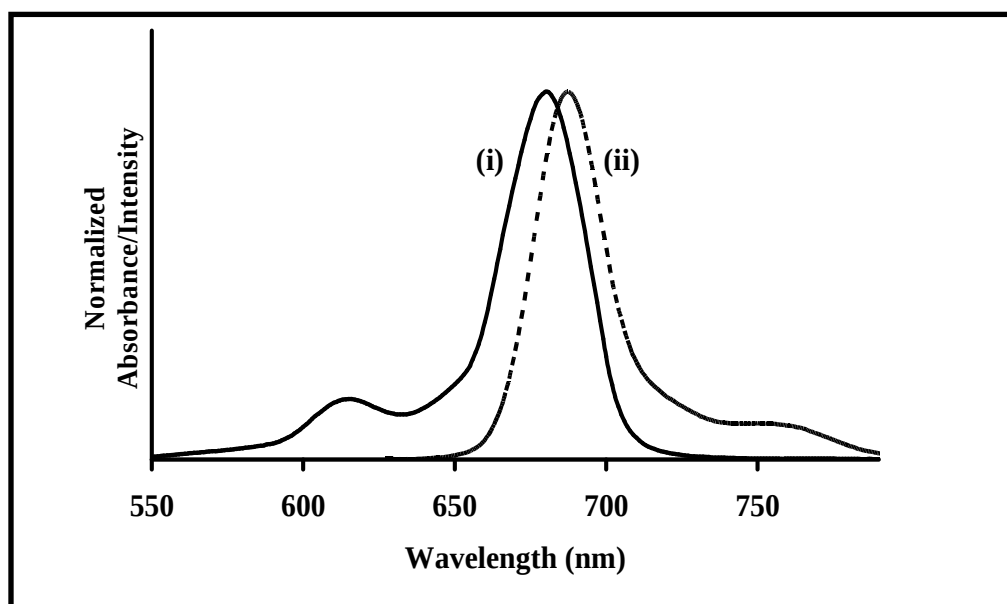


Figure 1.23: Normalized absorption (i) and emission (ii) spectra of a typical MPc.

spectra occurs Figure 1.24 e.g. where one component is fluorescent in a mixture, the excitation spectrum will be that of the fluorescing component although the absorption spectrum will contain bands for the fluorescing and non-fluorescing components. This is common with aggregated MPcs [166].

There could also be non-conformity to the mirror image rule due to change in geometry of the absorbing species after excitation prior to emission implying a difference in the nuclear configuration of the ground and excited states i.e. alteration of the electronic

energy levels [232]. Excited state reactions resulting in formation of charge transfer complexes also results in the breakdown of this rule.

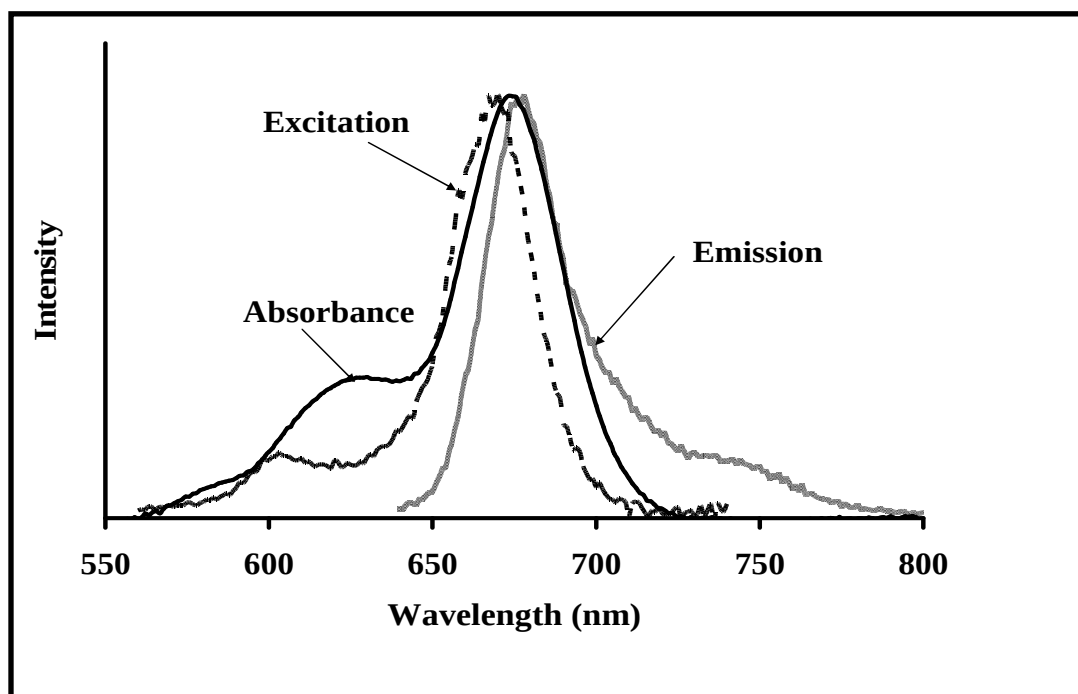


Figure 1.24: Normalized absorption, fluorescence excitation and emission spectra of a typical MPc with only one fluorescent component in a mixture [166].

1.3.2 Quantum yields and lifetimes

Fluorescence quantum yield (Φ_F) is a measure of the efficiency of an emission process.

It is defined as the number of photons emitted relative to the number of photons absorbed i.e. the fraction of the excited molecules that get deactivated by emitting a photon.

Practically, the Φ_F is determined by a comparative method using a standard reference [233]. The quantum yield of an unknown is then related to that of the standard by

Equation 1.14 Compounds that have known Φ_F in specific solvents such as ZnPc in

DMSO ($\Phi_F = 0.2$) [234] may be used as standards for the determination of the unknown.

$$\Phi_F = \Phi_{F(\text{std})} \frac{F \cdot A_{\text{std}} \cdot n^2}{F_{\text{std}} \cdot A \cdot n_{\text{std}}^2} \quad (1.14)$$

where F and F_{std} are the areas under the fluorescence emission curves of the sample and standard respectively. A and A_{std} are the respective absorbances of the sample and standard at the excitation wavelength while n and n_{std} are the refractive indices of the solvents used for the sample and standard, respectively.

Fluorescence intensity varies linearly with absorbed intensity but non-linearly with the concentration of the analyte. A linear dependence can however be assumed between the analyte concentration and the fluorescence intensity as long as the absorbance at the wavelength of excitation is ≤ 0.05 . This is necessary to avoid the inner filter effect [235] which results in self-quenching and decreased Φ_F values. Most typical MPcs have Φ_F values ranging from 0.10 – 0.70 [236].

The Φ_F values as shown in Table 1.2 demonstrate the influence of the environment of the fluorescing molecules on their fluorescence efficiency, with the central metal ion of the MPc having a great effect. In a particular solvent, Φ_F values are found to be larger for MPc complexes containing lighter atoms (e.g. Al and Si), and smaller for those MPc complexes containing heavier atoms (e.g. Ge, Zn and Sn); this can be attributed to the heavy atom effect, which results in intersystem crossing for the heavier atoms hence, less fluorescence [166]. MPcs with central metals that carry substituents sometimes also possess high fluorescence values due to their ability to prevent intermolecular interactions without any evidence of ligand-macrocycle quenching [237]. Loss of symmetry and protonation has been reported in the fluorescence behaviour of some zinc

Table 1.2: Photophysical parameters of some MPcs.

MPc	Solvent	Φ_F	Φ_T	τ_T (μ s)	Ref
AlPc(SO ₃ Na) ₄	H ₂ O	-	-	500	[166]
ZnPc(SO ₃ Na) ₄	H ₂ O	0.32	0.56	245	[166]
SnPc(SO ₃ Na) ₄	Methanol(aq)	0.11	0.80	30	[207]
AlPcS _{mix}	PBS 7.4	0.44	0.44	2.93	[166]
	DMSO	0.39	0.52	800	[166]
SiPcS _{mix}	PBS 7.4	0.34	0.45	2.90	[166]
	DMSO	0.29	0.58	430	[166]
GePcS _{mix}	PBS 7.4	0.30	0.67	2.76	[166]
	DMSO	0.21	0.79	760	[166]
SnPcS _{mix}	PBS 7.4	0.05	0.59	2.52	[166]
	DMSO	0.13	0.87	120	[166]
(Cl) ₂ GePc-(o-methyl-phenoxy) ₈	DMSO	0.31	0.50	168	[167]
(Cl) ₂ SnPc-(o-methyl-phenoxy) ₈	DMSO	0.06	0.45	32	[167]
(Cl) ₂ SnPc-(Hexyl) ₈	Toluene	0.16	0.30	20	[168]
(Cl) ₂ SnPc-(Decyl) ₈	Toluene	0.15	0.35	10	[168]
SiPc bis(1-pyreneacetate)	DCM	0.84	-	-	[237]

complexes [238]. Fluorescence behaviour of MPc complexes containing central metals which can bind one or two axial ligands (that can prevent aggregation through steric

hindrance on each side of the ring) such as in the case of Al (III), Si(IV), Ge(IV) and Sn(IV) derivatives is of great interest. Hence, the fluorescing abilities of MPCs with Al, Si, Ge and Sn as central metals will be studied in this work both in aqueous and non-aqueous media.

The lifetime of an excited state is the time taken to diminish the population of the molecules in that state to 1/e or ~ 37 % of its initial concentration. Fluorescence lifetimes can be determined in the wavelength or time domain by a pulsed laser able to pulse atpicosecond (ps) intervals using techniques such as the steady-state or time-correlated single-photon counting respectively [239,240].

The fluorescence lifetimes (τ_F) can be evaluated with Equation 1.15, using experimentally determined Φ_F values.

$$\Phi_F = \frac{\tau_F}{\tau_0} \quad (1.15)$$

The values of τ_0 (radiative lifetime) can be estimated by the Strickler-Berg derived equation, Equation 1.16, [241,242] using the absorbance and fluorescence emission spectra,

$$\frac{1}{\tau_0} = 2.88 \times 10^{-9} \cdot \eta^2 \frac{\int \frac{F(\lambda)}{\lambda^2} \cdot d(\lambda)}{\int F(\lambda) \cdot \lambda \cdot d(\lambda)} \int \frac{\epsilon(\lambda)}{\lambda} \cdot d(\lambda) \quad (1.16)$$

where $F(\lambda)$ and $\epsilon(\lambda)$ are the areas under the fluorescence and absorption spectra respectively.

Fluorescence lifetime can also be determined using the PhotochemCAD software package [243] which is based on the Strickler-Berg equation [241]. Predictions of fluorescence lifetimes of various MPC complexes have been obtained with the program

[167,244] using their absorbance and emission spectra. The equation however is only valid for molecules that do not interact with the solvent and that do not undergo geometric changes on excitation.

Fluorescence lifetimes for MPc complexes are of the order of few nanoseconds (< 10 ns) [167,244] and are strongly dependent on nature of the central metal ion, nature of substituents on the periphery of the Pc, the solvent and the presence of other species interacting with the molecule in the S_1 state.

1.3.3 Fluorescence quenching

Fluorescence quenching refers to any process which decreases the fluorescence intensity of a given sample. The decrease in fluorescence intensity is induced by a variety of molecular interactions such as excited state reactions, energy transfer, charge transfer, ground state complex-formation, molecular rearrangements and collisional quenching [245]. Other factors such as high concentration, turbidity, ionic strength, pH, solvent effects, aggregation and heavy atom effect can also result in decreased fluorescence intensity. The decrease in fluorescence intensity due to quenching occurs because there is a depopulation of the excited state without fluorescence emission. Fluorescence quenching in MPcs is quite interesting because MPcs are structurally similar to biologically important chlorophyll which acts as a sensitizer in photosynthesis.

Dynamic (collisional) quenching results from collisional encounters between the fluorophore in the excited state and the quencher without any photochemical reaction occurring. Energy or electron transfer takes place with a decrease in the lifetime and fluorescence emission intensity. The quencher diffuses to the fluorophore during the lifetime of the excited state and upon contact, the fluorophore returns to the ground state

without emission of a photon. In this type of quenching, the number of intermolecular collisions determines the extent of quenching, therefore, the reduction in fluorescence intensity is proportional to the quencher concentration, according to Stern and Volmer through Equation 1.17 [245].

$$\frac{F_0}{F} = 1 + K_{SV} [Q] \quad (1.17)$$

where F_0 and F are the fluorescence intensities of the complexes in the absence and presence of the quencher, respectively; $[Q]$ is the concentration of the quencher and K_{SV} is the Stern-Volmer (S-V) constant obtained from the slope of plot of F_0/F against $[Q]$. This plot is linear with an intercept of 1. K_{SV} is defined by Equation 1.18 as the product of the bimolecular quenching constant, k_Q and the fluorescence lifetime of the fluorophore, τ_F , in the absence of the quencher.

$$K_{SV} = k_Q \cdot \tau_F \quad (1.18)$$

An indication of the efficiency of quenching or the accessibility of the fluorophore to the quencher is given by k_Q with typical values near $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [246]. Smaller k_Q values may be a result of steric shielding of the fluorophore, while larger values may be due to some type of binding interaction.

The bimolecular rate constant for diffusion-controlled reactions (k_D) is related to the bimolecular quenching constant (k_Q) by Equation 1.19 [245]:

$$k_Q = f k_D \quad (1.19)$$

where f is the collision efficiency, k_D can be obtained from the Einstein-Smoluchowski relationship:

$$k_D = 4\pi N_A (D_f + D_q)(r_f + r_q) \quad (1.20)$$

where N_A is the Avogadro's number; D_f and D_q , the diffusion coefficients of the fluorophore and quencher respectively and r_f and r_q are the radii of fluorophore and quencher respectively.

The diffusion coefficient D is given by the Stokes' equation (Equation 1.21) [245].

$$D = \frac{kT}{6\pi\eta r} \quad (1.21)$$

where k is the Boltzman constant; T , the absolute temperature; η , the solvent's viscosity and r , the fluorophore (or quencher) radius.

k_Q values can be determined from Equation 1.19 using the calculated k_D value. f is often assumed to be unity for a diffusion controlled reaction.

A large number of reactions deviate from the S-V relationship resulting in non linear S-V plots. Such plots are an indication that the quenching mechanism is complicated and in many instances, it is accompanied by competing photochemical reactions. A positive deviation from the S-V relationship is recognized by an upward curvature (Figure 1.25) of the S-V plot observed when the extent of quenching is large. Positive deviations indicate a combination of dynamic and static quenching contribution usually influenced by charge effects in the quenching. Static quenching occurs as a result of the formation of a non-fluorescent complex between the fluorophore and quencher. The S-V relationship can be modified as in Equation 1.22 to accommodate for these deviations:

$$\frac{F_0}{F} = (1 + K_{sv}[Q])(1 + K_a[Q]) \quad (1.22)$$

The first term is the original S-V equation, Equation 1.17, which accounts for the dynamic quenching, the second term accounts for the upward curvature (static

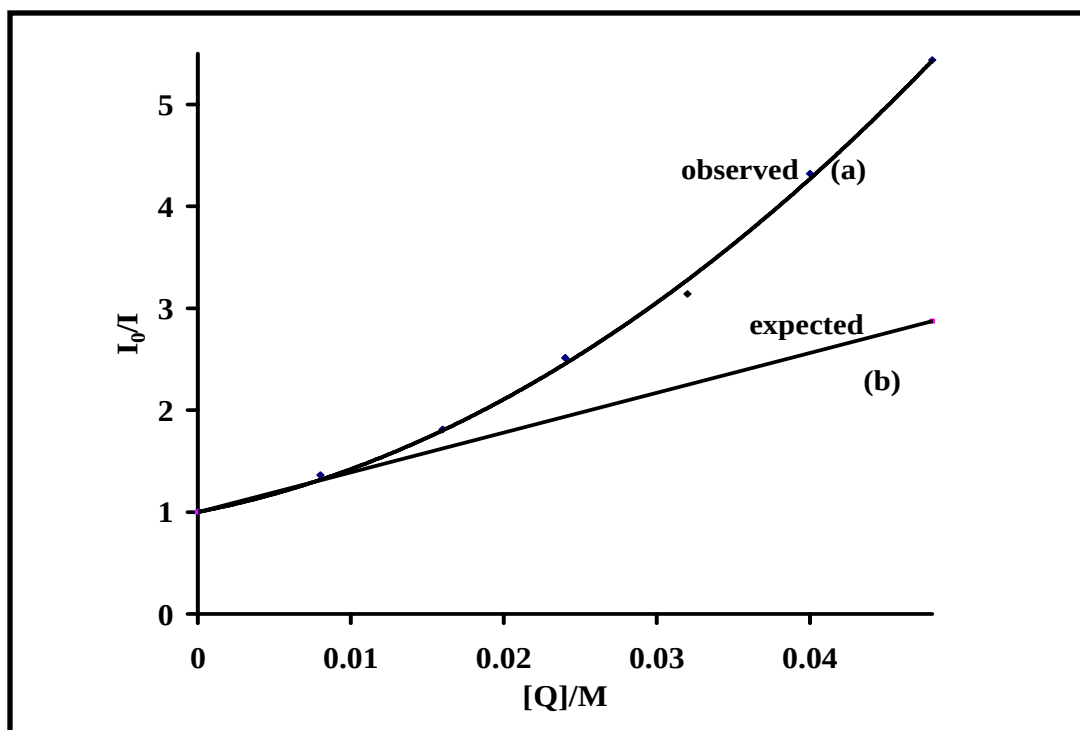


Figure 1.25: Typical positive deviation from Stern-Volmer plot (a) and expected Stern-Volmer plot (b) [245].

quenching). The quenching constant for the second term (K_a) is termed association (static) constant. To solve for K_a , apparent values of K_{SV} (K_{app}) are calculated using Equation 1.17. The calculated K_{app} values are plotted against $[Q]$ and extrapolated to $[Q] = 0$ [247] to obtain the dynamic quenching constant in this case at $[Q] = 0$. K_a is then determined by rearranging Equation 1.22 to give Equation 1.23

$$\frac{F_0}{F(1 + K_{SV})[Q]} = 1 + K_a [Q] \quad (1.23)$$

Using the value of K_{SV} obtained above, the plot of $\frac{F_0}{F(1 + K_{SV})[Q]}$ against $[Q]$ gives the static quenching constant, K_a .

There are situations in which positive deviation from S-V is observed with no evidence of complexation between the fluorophore and quencher. In this case, an apparent static

quenching is postulated. It is believed to be due to close proximity of the fluorophore and quencher at the instant of excitation which results in immediate quenching. The modified S-V equation for this is given by a rearranged Equation 1.23 to give Equation 1.24 [248]:

$$\frac{F_0}{F(1 + K_{sv}[Q])} = e^{K_s[Q]} \quad (1.24)$$

The apparent quenching constant (K_s) is estimated from the plot of $\ln \frac{F_0}{F(1 + K_{sv}[Q])}$ against $[Q]$.

The basic reaction between an MPc complex and BSA or QD is represented as in Equation 1.25, using BSA as an example:



The expression for the binding constant (K_b) in the above equation is given by Equation 1.26:

$$K_b = \frac{[BSA : (MPc)_n]}{[BSA][MPc]^n} \quad (1.26)$$

The number of binding sites on a BSA molecule can be estimated by rewriting Equation 1.26 as Equation 1.27:

$$K_b = \frac{[F_0 - F]}{[F - F_\infty][MPc]^n} \quad (1.27)$$

where F_0 is the fluorescence intensity of BSA in the absence of MPc; F , the fluorescence intensity of BSA in the presence of MPc; F_∞ , the fluorescence intensity of BSA saturated with MPc; and n , the number of binding sites on a BSA molecule.

Taking the logs of both sides of Equation 1.27 and rearranging gives Equation 1.28:

$$\log\left[\frac{(F_0 - F)}{(F - F_\infty)}\right] = \log K_b + n \log[\text{MPC}] \quad (1.28)$$

Plots of $\log\left[\frac{(F_0 - F)}{(F - F_\infty)}\right]$ versus $\log[\text{MPC}]$ should give a straight line with slope n and

intercept $\log K_b$.

Examples of quenchers used in this work include benzoquinone (BQ), bovine serum albumin (BSA), QDs and MPCs. QDs will be discussed later under FRET. Fluorescence quenching can occur without any fluorescence being observed from the quencher as is the case for BQ and BSA.

1.3.3.1 Benzoquinone (BQ) as a quencher

Photoredox reactions involving electron transfer such as in the photoexcited singlet state of chlorophyll are known between the MPC singlet excited state and quenchers such as BQ [249,250], hydroquinone (HQ) [166] and methyl viologen [215]. The fluorescence quenching of MPC complexes by BQ has been reported to obey S-V kinetics [250], which is consistent with diffusion-controlled bimolecular reactions or show positive deviations from S-V [249]. In rare cases, loss of symmetry due to protonation has been observed in the ground state absorption spectrum of some MPC complexes while the fluorescence of the protonated complex remains unquenched by BQ [251]. However, the thermodynamics of the quenching have not been explored. Fluorescence quenching of differently substituted MPCs using BQ will be explored in this thesis to study the intriguing mechanisms involved in the thermodynamics of the quenching. The use of fluorescence quenching for the determination of MPC fluorescence lifetimes which is sparse in literature, will also be reported.

1.3.3.2 Serum albumin fluorescence quenching

Prior to localization at tumor tissue, the photosensitizer is transported by the blood and interacts with serum proteins. The serum proteins, albumin and low-density lipoprotein (LDL) have been identified as important natural drug carriers [252]. Pharmacokinetic investigations have led to the general agreement that a photosensitizer binds to both albumin and lipoproteins with the hydrophilic ones binding preferentially to albumin and are localized in the vascular stroma while their hydrophobic counterparts bind to lipoproteins [206,253].

Serum albumins are the major binding protein for most drugs. They represent 52-60% of the total plasma protein with a typical concentration of 5g/100 mL. As the major soluble protein constituent of the circulatory system, they play an important role in the transport of many exogenous and endogenous ligands, binding covalently or reversibly to these ligands and increasing the passive tumor selectivity of the drug by enhanced permeation and retention effect [254]. Therefore for many drugs, binding to serum albumin is an important determinant of their distribution and fate in the body [255].

Bovine serum albumin, the serum albumin of a ruminant mammal, has been widely used [256,257] and found to be medically important, having unusual binding properties [257].

It is well suited for the investigation of binding of albumin to porphyrin-like drugs because it has been extensively characterized [257,258].

Interaction between BSA and MPcs

Spectroscopic methods provide a means of studying the interaction between MPcs and BSA since the intrinsic fluorescence of the tryptophan residues of proteins is usually quenched upon binding to tetrapyrrolic compounds [259]. This allows the determination

of quenching constants (K_{SV}^{BSA} and k_q) using Equations 1.17 to 1.24 as well as binding constants, K_b and binding stoichiometry, n between the MPcs and BSA. Some examples of n and K_b values for BSA binding are given in Table 1.3. The table also gives data for quenching constants of BSA fluorescence by MPcs.

The interaction of some MPc complexes with BSA has been reported [206,258,259] however; there is still room for literature expansion in this area. Sulfonated MPcs (MPcS_{mix}) (containing a mixture of differently sulfonated MPc derivatives) when in the non-aggregated form showed a decrease in Φ_F in the presence of BSA [259] and an increase in Φ_F when aggregated. The binding constants K_b , for the binding of some MPcS_{mix} to BSA was found to be of the order of $1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$ [259] as shown in Table 1.3.

Table 1.3: Quenching and binding data for some water-soluble MPc complexes with BSA in PBS 7.4, (values are from Ref 259 unless otherwise stated).

Complex	$K_{SV}^{BSA} (M^{-1})$	$k_q (M^{-1}s^{-1})$	$K_b (dm^3 \text{ mol}^{-1})$	n
AlPcS _{mix}	11.45×10^4	11.40×10^{12}	17.21×10^6	1.4
SiPcS _{mix}	6.90×10^4	6.90×10^{12}	1.29×10^6	1.3
GePcS _{mix}	4.54×10^4	4.54×10^{12}	0.81×10^6	1.1
ZnPcS _{mix}	$7.36 (6.72) \times 10^4$	$7.36 (6.72) \times 10^{12}$	$0.10 (0.34) \times 10^6$	1.0
SnPcS _{mix}	$1.98 (3.19) \times 10^4$	$1.98 (3.19) \times 10^{12}$	$0.08 (0.21) \times 10^6$	1.0
SnPc(SO ₃ Na) ₄	8.00×10^7	8.00×10^{15}	1.40×10^6	0.8 [207]

K_{SV}^{BSA} = Stern-Volmer quenching constant of BSA, k_q = bimolecular quenching constant, K_b = binding constant.

AlPc carboxylate was used as fluorescent probe in its interaction with BSA [260]. However, the interaction of isomerically pure water-soluble MPc complexes with BSA is yet to be fully explored; there is no account of their triplet state properties in the presence of BSA. Again, interaction of tetrasulfonated Si and Ge MPcs with BSA has not been studied. This work gives an in-depth account of interaction of BSA with various anionic and cationic MPc derivatives. The photophysicochemical consequences of the binding are also studied.

Interaction of BSA and QDs

Studies were also done on the quenching of BSA fluorescence by QDs since, studying the interaction of CdTe QDs with BSA in aqueous medium, will give a representative model of the effect of QDs on cells in *in vivo* studies. The interaction of cadmium sulphide (CdS) QDs with BSA has been studied in reverse micelles [261] due to the insolubility of CdS QDs in aqueous medium. As stated above, for cell applications, water solubility is necessary. Chemically reduced BSA has also been employed to modify the surface of QDs [262,263] and has been reported to improve their chemical stability and photoluminescence [263]. This improvement could lead to an increase in applications of the QDs [264]. Having a crosslinker between BSA and CdTe QDs can also give an understanding of the capabilities of biomolecules–QDs coupling techniques. Bifunctional reagents like glutaraldehyde has been widely used in crosslinking of biomaterials, however, a negative effect on their biocompatibility can hardly be avoided [265]. Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) [264,266] has been found to be comparable to glutaraldehyde as a crosslinker. The effect of BSA on QDs without prior chemical reduction of the former in aqueous medium is spectroscopically explored

in this thesis with a choice of EDC as a coupling agent for the coordination of CdTe QDs (through carboxylic acid groups) to the amino group of BSA. The interaction of water-soluble CdTe QDs with BSA and the effect of QDs on BSA fluorescence is explored in this thesis.

1.3.4 Förster Resonance Energy Transfer (FRET)

FRET is a photophysical process through which an electronically excited fluorescent donor molecule transfers its excitation energy to an acceptor molecule (as depicted in Figure 1.26) [245,267,268] non-radiatively such that the excited state lifetime of the donor decreases and the acceptor is raised to a higher energy state. The acceptor may or

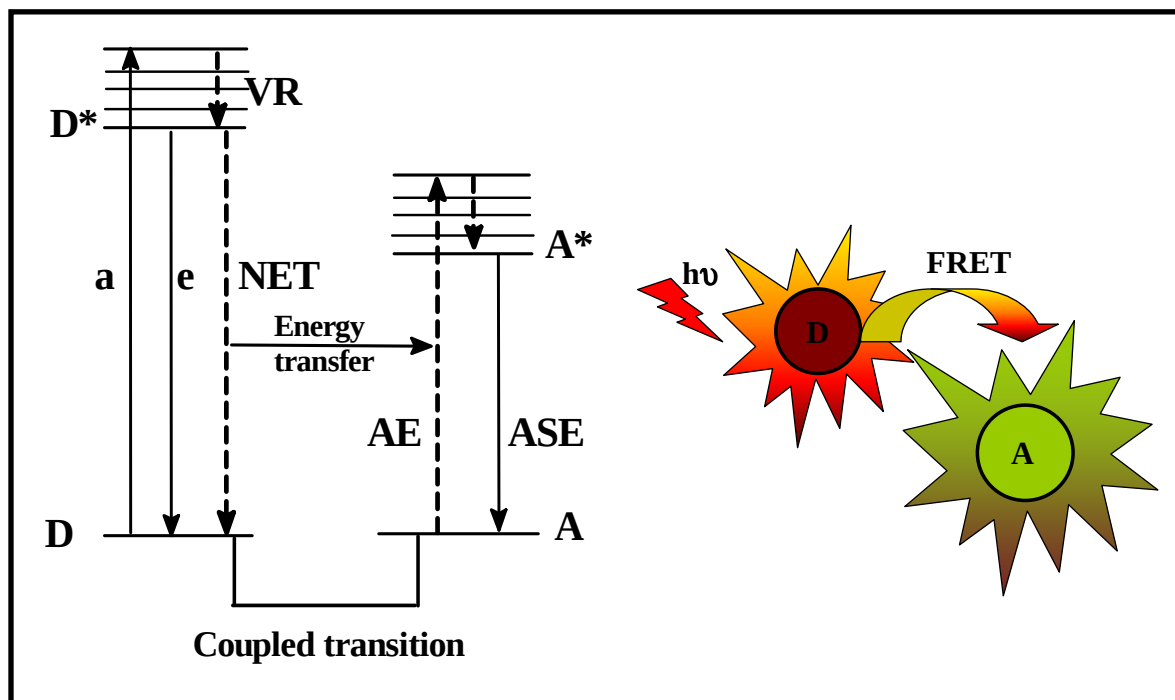


Figure 1.26: Förster resonance energy transfer Jablonski diagram illustrating coupled transitions between donor emission and acceptor absorbance in FRET. D = donor, A = acceptor, a = absorption, e = emission, VR = vibrational relaxation, NET = non-radiative donor energy transfer, AE = non-radiative acceptor excitation and ASE = acceptor sensitized emission [268]. Pictorial representation of FRET.

may not be fluorescent and the donor and acceptor fluorophores may be separated or attached. Initially, the acronym FRET referred specifically to situations where the donor and acceptor pairs were both fluorophores but various experiments have shown the same fundamental principles obeyed, even when there is no fluorescence. Therefore, the acronym FRET has been suggested to apply to both the specific (fluorescence) and general (Förster) resonance energy transfers [269]. FRET requires fluorescence emission spectrum of the donor molecule to overlap with the absorption spectrum of the acceptor and the two to be within the minimal spatial range for the donor to transfer its excitation energy through space to the acceptor. It is also dependent on the relative orientation of the donor and acceptor transition dipoles and the quantum yield of the donor [245,270]. The lifetime of the excited donor plays important role, as the probability of energy transfer is proportional to this lifetime. The Förster treatment is semi-classical and employs the point-dipole approximation.

Practically, there is a consequential quenching in the donor photoemission and a sensitized acceptor's fluorescence is observed when FRET has occurred. FRET efficiency (Eff) is determined experimentally from the fluorescence quantum yields of the donor in the absence and presence of the acceptor and it is defined by Equation 1.29 [245, 270]

$$Eff = 1 - \frac{\Phi_{F(DA)}}{\Phi_{F(D)}} \quad (1.29)$$

There is an inverse 6th order law dependence of Eff on the center-to-center separation distance between donor and acceptor (r) due to the dipole-dipole coupling mechanism; hence Eff is related to r (Å) by Equation 1.30 [245,267]:

$$Eff = \frac{R_0^6}{R_0^6 + r^6} \quad (1.30)$$

where R_0 (The Förster distance, Å) is the critical distance between the donor and the acceptor molecules for which efficiency of energy transfer is 50%, and depends on the quantum yield of the donor, extinction coefficient of the acceptor and all other factors governing FRET as mentioned above [245,267].

R_0 is expressed by Equation 1.31:

$$R_0^6 = 8.8 \times 10^{23} \kappa^2 n^{-4} \Phi_{F(QD)} J \quad (1.31)$$

where κ^2 is the dipole orientation factor; n , the refractive index of the medium; Φ_F , the fluorescence quantum yield of the donor in the absence of the acceptor; and J is the Förster overlap integral calculated as (Equation 1.32):

$$J = \int f_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (1.32)$$

where f_D is the normalized emission spectrum of the donor; and ϵ_A the molar extinction coefficient of the acceptor. Förster distances are normally reported for an assumed value of κ^2 i.e. 2/3; such assumption is often made for donor-acceptor pairs in a liquid medium, which are considered to be isotropically oriented during their fluorescence lifetimes since the extent of energy transfer can also be influenced by the presence of donor to acceptor diffusion during the donor lifetime. FRET parameters are computed using the PhotochemCAD programme software [243].

Studies on the ability of QDs to transfer energy to organic dye photosensitizers have recently attracted attention [219-227,271-273]. Interaction of some negatively charged MPcs and QD in a mixture of solvents was recently reported by our group [274]. Apart from Burda's group and a few others [219-227], literature is sparse on the study of energy

transfer from QDs to MPcs. It has been observed by Maslov's group that the interaction of metal-free tetrapyrrolineporphyrine (TPPA) (structurally similar to MPcs) with CdSe QDs led to the quenching of the QD fluorescence emission and sensitized emission of the TPPA in chloroform with an estimated efficiency of 0.925 on the assumption that they were within a distance of 25 Å [227]. Burda and co-workers have observed energy transfer from CdSe QD to MPc [219,220]. They also discovered that in some cases energy transfer can take place through a non Förster type energy transfer mechanism due to the involvement of surface states in the energy transfer process [223,225]. Recently, a two-photon based energy transfer from QDs to MPc was observed [221,222]. However, the work was done in organic medium, thus limiting biological applications. Though Selke's group worked in aqueous medium, their emphasis was on porphyrins [226]. To our knowledge, no study on energy transfer from QDs to MPcs in aqueous medium has been reported. In this thesis, fluorescence quenching of CdTe QDs capped with carboxylic acid thiol by MPcs in aqueous medium is investigated. Indirect activation of various substituted MPcs by photoluminescent CdTe QDs capped with mercaptocarboxylic acid through energy transfer in aqueous medium will be explored. Determination of the efficiency of energy transfer is also reported.

1.4 Triplet state absorption

Population of the triplet state with excited MPc molecules is of importance in visible light driven processes such as PDT, since these excited molecules transfer their energy to ground state oxygen to produce singlet oxygen which is essential in these processes.

A technique that is used to generate and study molecules at the triplet excited state is known as laser flash photolysis which gives information about the $T_1 \rightarrow T_n$ absorption (triplet-triplet absorption (TTA)) and the lifetime of the excited species [268]. A plot of the change in absorbance before and after a laser pulse (ΔA) results in a triplet decay curve, Figure 1.27.

A plot of $\ln A$ ($\ln$ of change in absorbance obtained from the flash photolysis experiment) vs. time gives k as the slope, the reciprocal of which gives the triplet lifetime ($\tau_T = 1/k$).

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

The differential absorption spectrum of an MPC Figure 1.28 consists of the bleaching of the Q band and the triplet-triplet absorption of MPCs. It gives clear indication of the condition of the transient species after excitation.

The triplet quantum yield (Φ_T) is based on the maximum absorption of the triplet state generated during laser flash photolysis experiment. The triplet state absorption of MPCs is

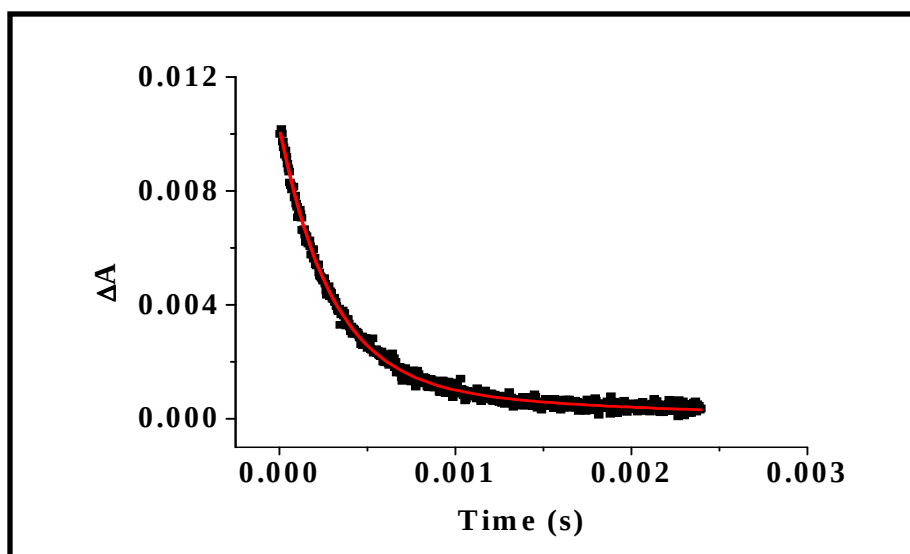


Figure 1.27: Typical triplet decay curve of MPCs following laser flash photolysis.

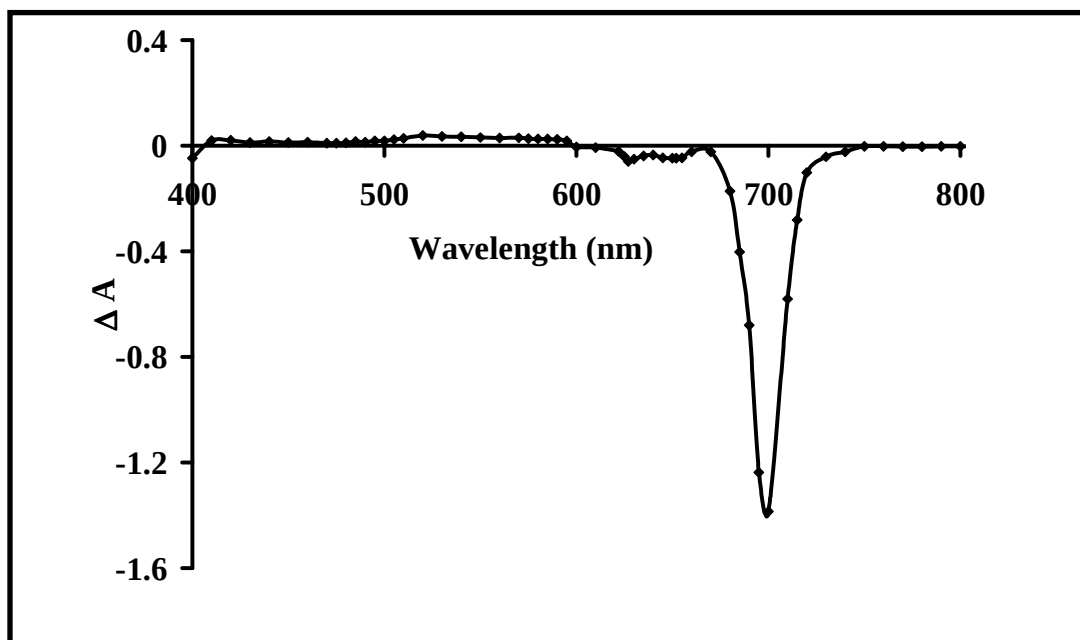


Figure 1.28: Typical differential absorption spectrum of MPCs following laser flash photolysis.

at ~ 500 nm, a region which is far away from their ground state absorption (Q band ~ 700 nm). This creates an ease in measuring the triplet absorption since there is no overlap.

The Φ_T which is the probability of a sensitizer to convert absorbed quanta of light to the T_1 state, can be determined using reference to a standard with known Φ_T using Equation

1.33

$$\Phi_T = \Phi_T^{\text{Std}} \frac{\Delta A_T^{\text{Sample}} \cdot \epsilon_T^{\text{Std}}}{\Delta A_T^{\text{Std}} \cdot \epsilon_T^{\text{Sample}}} \quad (1.33)$$

where $\Delta A_T^{\text{Sample}}$ and ΔA_T^{Std} are the changes in the triplet state absorbances of the sample and standard respectively, $\epsilon_T^{\text{Sample}}$ and ϵ_T^{Std} are the triplet state molar extinction coefficients of the sample and standard respectively.

ϵ_T is normally determined by the singlet depletion method using Equation 1.34

$$\varepsilon_T = \frac{(\Delta A)_T \cdot \varepsilon_S}{(\Delta A)_S} \quad (1.34)$$

where ε_S (molar extinction coefficient of the ground singlet state) is determined by the Beer-Lambert law.

Triplet state yield and fluorescence are two complementary photophysical processes. It is expected that high triplet state quantum yield (Φ_T) values be accompanied by low yields of fluorescence, Φ_F . MPcs with high Φ_T (> 0.40) long triplet lifetime, τ_T ($> 1\mu s$) and considerable Φ_F enough for visualization are efficient as photosensitizers. Φ_T and Φ_F values are affected by the nature of the central metal ion e.g. MPcs with heavy metal ions or paramagnetic metal ions enhancing the triplet state yield. Those with diamagnetic metals or metals with closed shells such as Zn or Al are also known to have high Φ_T values and long triplet lifetimes (Table 1.2). Introduction of heavy atoms on the periphery of the Pc also result in high Φ_T values. However, structural distortion associated with heavy atom substitution may promote T_1 to S_0 transition reducing the efficiency of energy transfer to ground state oxygen. Molecular rigidity, solvent type and aggregation are other factors that affect Φ_T and Φ_F values. Solvents containing heavy atoms like chlorine such as chloroform or carbon tetrachloride promote intersystem crossing of MPcs resulting in high triplet state yield and weak fluorescence. The exciton coupling theory predicts low Φ_F values for aggregated MPcs due to their non-fluorescent dimers. High Φ_T values are however predicted for MPc dimers, though with reduced photosensitizing ability due to vibronic coupling which rapidly deactivates the triplet excited state [275].

The typical lifetime in a T_1 state of an MPc is long; between the micro (μ s) and millisecond (ms) since the radiative or non radiative decay of the T_1 to the S_0 state is spin forbidden. This allows for substantial sensitization, chemical reaction or quenching at the T_1 state. As a result, phosphorescence of MPcs is not readily observed in solution at room temperature except in rigid glass [129]. From the above, it is clear that the rate of triplet formation is faster than the rate of triplet decay.

Gaining a deep understanding of the photophysics and photochemistry of MPcs is essential for realizing the numerous opportunities now available ranging from solar energy conversion to cancer treatment. Most prior studies of phthalocyanines have focused on the macrocycles that were available at the time. The new macrocycles now in hand present an opportunity to probe the photophysics and photochemistry of MPcs ranging from the monomeric state to the formation of diverse structured assemblies. The spectroscopic studies reported herein extend the large number of studies known in the literature [166,167,232,234,238,249, 275-278]. Some unexpected results of low triplet quantum yields have been reported for tin MPc complexes [168]. The photophysics and photochemistry of complexes containing a mixture of differently sulfonated derivatives (MPcS_{mix}) [166,249] have been reported as an average for the whole mixture. In this work, we investigate the photophysics and photochemistry of tetrasulfonated MPcs (MPcS₄) that contains only one specie (tetrasulfonated). Though, work on ZnPcS₄ is well documented [165,234], the photophysical properties of the silicon and germanium complexes are not known. Various water-soluble MPcs substituted with carboxylic, quaternary ammonium or aminoalkanethio groups (Figure 1.16) are also investigated. An in-depth study on the effect of central metal, substituents, solvents and aggregation on the

photophysical and photochemical properties of these MPc derivatives is reported. SnPcs substituted with aryloxy groups are also studied. Some work has been reported on the interaction of QDs and photosensitizers [219-227], but till date no triplet state quantum yield has been reported. To our knowledge, there is no report on the photophysics of MPcs disaggregated with the surfactant; cremophore EL, nor on the Φ_T of MPcs in the presence or absence of QDs.

Apart from Tedesco's group and a few others [279-286], literature is sparse on the study of the combination of magnetic iron oxide nanoparticles with photosensitizers. High Φ_T was observed for ZnPc in combination with magnetic fluid [279] reinforcing the idea of excellent photodynamic activity. Zinc phthalocyanine/magnetic fluid (ZnPc/MF) complex in liposomal medium has been observed to present lower dark toxicity compared to the ZnPc/MF complex in Hank's buffer [280]. However, biocompatibility of such work is important. Hence, the photophysics and photochemistry of various water-soluble MPcs on combination with nanoparticles such as QDs and magnetite and in the presence of surfactants is explored. The prospects of the relevance of these MPc derivatives in combination with nanoparticles for enhancement of the effectiveness of PDT are examined.

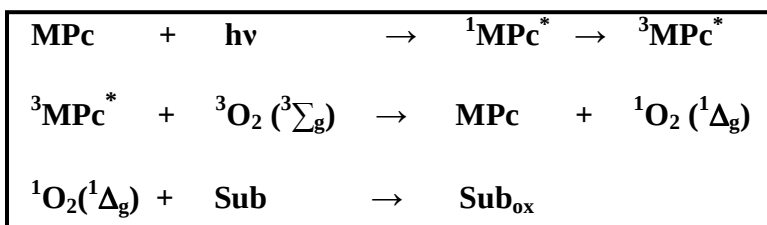
1.5 Singlet oxygen generation and photodegradation in MPcs

1.5.1 Singlet oxygen

The excited triplet state species ($^3\text{MPc}^*$) can impart their excitation energy to molecular oxygen, $^3\text{O}_2$ or O_2 ($^3\Sigma_g$), thus yielding the essential excited singlet oxygen $^1\text{O}_2$ ($^1\Delta_g$) by the process called photosensitization Scheme 1.8. The catalytic nature of these sensitizers is

appreciated when it is realised that following the transfer of the photosensitizer's energy to molecular oxygen, the former returns to its electronic ground state and provided that sufficient oxygen is available, singlet oxygen is produced several times from the same concentration of the sensitizer. With time, singlet oxygen may react with and degrade the sensitizer.

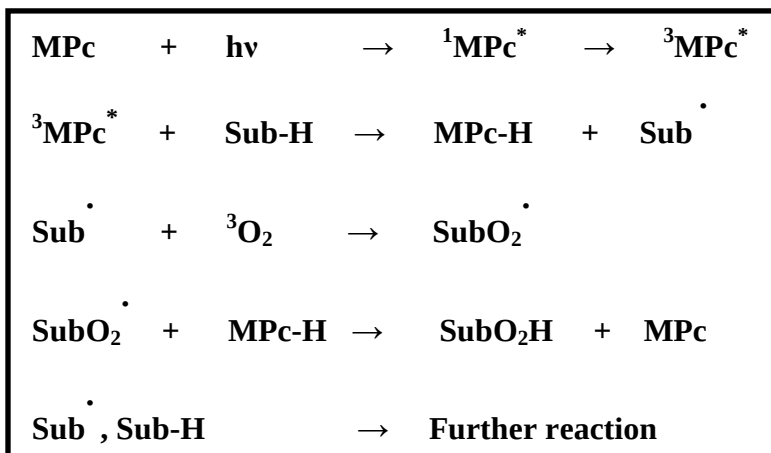
Singlet oxygen, $^1\text{O}_2$ is the oxidative species in photo-induced oxidative processes e.g. it is the chief cytotoxic species that causes tumor necrosis in PDT. The capability of MPcs to generate singlet oxygen is due to the fact that their triplet energy 1.1 - 1.3 eV ($\sim 110 - 126 \text{ kJ mol}^{-1}$) is more than the required energy 0.98 eV ($\sim 94 \text{ kJ mol}^{-1}$) to allow for efficient energy transfer to ground state oxygen [165,287] to form $^1\text{O}_2$ ($^1\Delta_g$) through Type II mechanism Scheme 1.8 [165]. Type II mechanism is especially prevalent in oxygen-rich or air saturated environments where the oxygen concentration is in the range of 10^{-2} to 10^{-3} M . Photosensitization can also occur via the Type I and Type III mechanisms.



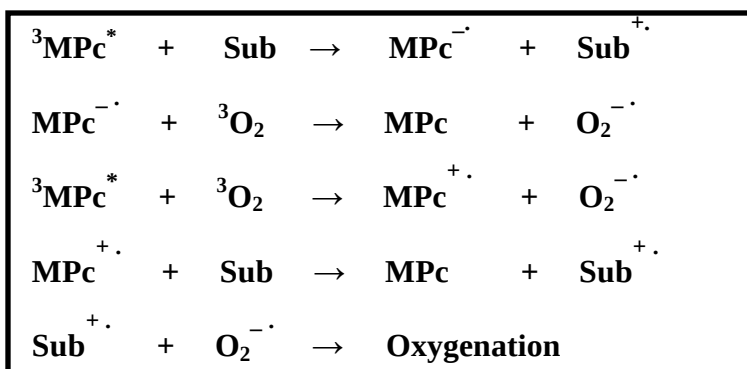
Scheme 1.8: Type II photoreaction mechanism in a metallophthalocyanine photosensitizer.

In these pathways, $^3\text{MPc}^*$, interacts directly with a molecule of substrate that is in close proximity or molecular oxygen by electron transfer. Type I mechanism involves hydrogen atom abstraction, which initiates free radical autoxidative process Scheme 1.9 [288]. Alternatively, in the Type III pathway, Scheme 1.10 electron transfer from

substrate to excited sensitizer may occur, in which case the oxygenation products result from the coupling of the substrate cation radical with superoxide anion radical. Only ground state molecular oxygen ($^3\text{O}_2$) is involved [288] irrespective of whether the mechanism of oxygenation is a photoinitiated autooxidation or an electron transfer photo-oxidation. Both pathways can be termed Type I since radicals are formed in either case. They usually take place in oxygen poor environments and depend on substrate concentration. Hence, several tests have been developed to distinguish between singlet oxygen and radical mechanisms e.g. 1,4-diazabicyclo-octane (DABCO), sodium azide,



Scheme 1.9: Type I photoreaction mechanism in a metallophthalocyanine photosensitizer.



Scheme 1.10: Type III photoreaction mechanism in a metallophthalocyanine photosensitizer.

1,3-diphenylisobenzofuran (DPBF) and tetrasodium α,α -(anthracene-9,10-diyl) dimethylmalonate (ADMA) can be used to either quench or trap singlet oxygen produced through Type II mechanism. On the other hand, free-radical inhibitors such as 2,6-di-*t*-butylphenol will inhibit radical mediated processes. The rates of singlet oxygenation are insensitive to reaction temperature due to their low activation energies but this is not the case with free radical autooxidations.

It is generally believed that the route via singlet oxygen (Type II mechanism) is the dominant process in PDT and most photo-oxidation processes. Singlet oxygen, $^1\text{O}_2$ can be detected from its fluorescence at 1270 nm or through use of $^1\text{O}_2$ scavengers. Frequently employed $^1\text{O}_2$ quenchers include DPBF, ADMA, DABCO, sodium azide, ascorbic acid, and tryptophan. In this method, 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 thus serves as a monitor for $^1\text{O}_2$. The depletion of $^1\text{O}_2$ in the mixture in the presence of the quencher (e.g. DPBF) can be via several competing pathways as depicted in Scheme 1.11.

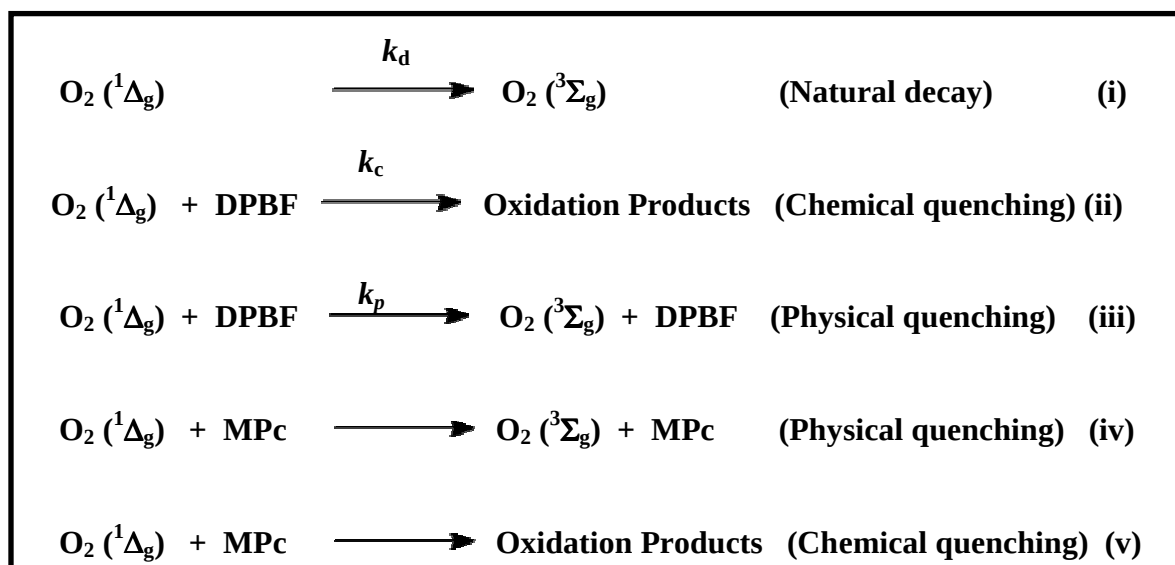
The quenchers employed in this work, ADMA and DPBF act exclusively as chemical quenchers [289,290] and thus reaction (iii) is ignored. Additionally, $^1\text{O}_2$ yield is independent of the photosensitizer (MPc) concentration therefore reaction (iv) is ignored. Also, reaction (v) is ignored since the rate of reaction of $^1\text{O}_2$ with the photosensitizer is negligible compared to that with quencher, DPBF. Thus the rate of decay of singlet oxygen depends on reactions (i) and (ii).

Singlet oxygen quantum yields (Φ_Δ) are normally calculated using Equation 1.35

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \cdot \frac{R I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} I_{\text{abs}}} \quad (1.35)$$

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard, R and R^{Std} are the DPBF (or singlet oxygen quenchers) photobleaching rates in the presence of the respective complexes under investigation and the standard respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the complexes and the standard, respectively.

Efficient generation of $^1\text{O}_2$ from MPc complexes (Table 1.4) can be affected by the nature of the central metal. Closed shell metals such as Al^{3+} , Zn^{2+} , Ge^{4+} or Si^{4+} manifest long lifetimes in the excited state, so there is the possibility of high yields of $^1\text{O}_2$ as shown in Table 1.4. Also, the presence of heavy atoms promotes ISC so the probability of $^1\text{O}_2$ formation is high due to increased SOC in the molecule. Photochemical properties of various substituted zinc MPcs in different solvents is known [234,291], but silicon and germanium complexes are yet to be fully explored. An in-depth photochemical study of these complexes in aqueous medium will be carried out in this thesis.



Scheme 1.11: Processes involved in the decay of singlet oxygen in solution in the presence of sensitizer (MPc) and a quencher, DPBF. k_d , k_c and k_p are the rate constants for the first order natural decay, chemical and physical quenching by DPBF respectively.

Table 1.4: Photochemical parameters of some MPcs.

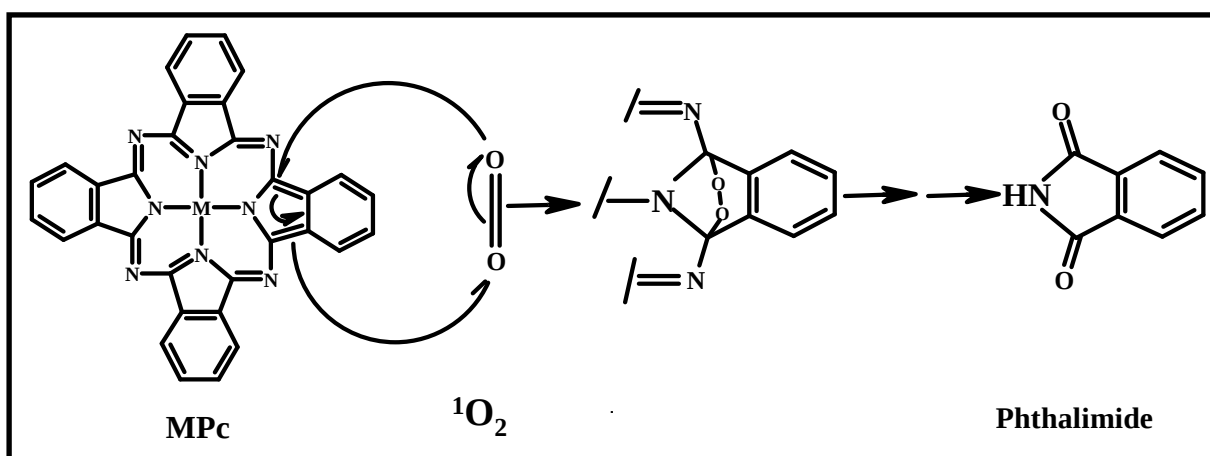
MPc	Solvent	Φ_{Δ}	$\Phi_P (10^{-5})$	Ref
AlPcS _{mix}	PBS 7.4	0.42	0.40	[166]
SiPcS _{mix}	PBS 7.4	0.49	0.71	[166]
GePcS _{mix}	PBS 7.4	0.68	0.45	[166]
SnPcS _{mix}	PBS 7.4	0.42	1.59	[166]
(Cl) ₂ GePc4,5-(o-methyl-phenoxy) ₈	DMSO	0.24	-	[167]
(Cl) ₂ SnPc4,5-(o-methyl-phenoxy) ₈	DMSO	0.34	-	[167]
ZnPc 3-(BenzloxyPhenoxy) ₄	DMSO	0.76	0.50	[251]
ZnPc 4-(BenzloxyPhenoxy) ₄	DMSO	0.52	0.33	[251]
SnPc(SO ₃ Na) ₄	Methanol (aq)	-	0.11	[207]
ZnPc(SO ₃ Na) ₄	DMSO	0.46	4.03	[234]
ZnPc(SO ₃ Na) ₄	H ₂ O, Triton-X	0.3	-	[291]
AlPc(SO ₃ Na) ₄	H ₂ O	0.22	-	[290]

1.5.2 Photodegradation

Photodegradation is a process of degradation of the photosensitizer molecule oxidatively with time by light-mediated processes into lower molecular weight fragments [292]. Photodegradation generally depends on the structure of the molecule, concentration, solvent and light intensity. It is believed that photodegradation is a ¹O₂ mediated process [293,294] since ¹O₂ can react with macrocyclic metal complexes. With tetra-azaporphyrin derivatives, a Diels-Alder [4 + 2] cycloaddition occurs with ¹O₂ [294]. Phthalimide was found to be the photo-oxidation product following degradation of MPcs [293] Scheme 1.12. There are some speculations that free radicals may also play a role in photodegradation [295].

Photodegradation of the sensitizers are normally carried out to determine the stability of the MPc towards photo-irradiation. The sensitizer will be ineffective in the treatment of tumors if photodegradation occurs too quickly and alternatively if the rate of photodegradation is more controlled, the sensitizer concentration may be reduced in the body and thus reduce the damage to healthy tissue [296].

The presence of electron-withdrawing substituents on the MPc ring tends to stabilize the ring thereby resulting in difficulty of oxidation of the MPc ring and hence slow photodegradation process [277,297]. Electron-donating substituents however accelerate the photodegradation process [297]. Photodegradation rates are different in various media [298]. Photodegradation is faster in chlorinated solvents such as chloroform (CHCl_3) and dichloromethane (DCM) because radicals formed from C-Cl bond cleavage aid in the photodecomposition. It is known that singlet oxygen has a longer lifetime in deuterated solvents, hence increasing its probability of reacting with the MPc ring such that the rate of photodegradation is enhanced [277,297]. Rates of photodegradation are found to decrease in the presence of some $^1\text{O}_2$ scavengers like DABCO and in argon saturated



Scheme 1.12: [4+2] cycloaddition reaction of MPc with singlet oxygen.

solutions [277,297]. Low rates of photodegradation are observed in aqueous solutions probably due to aggregation rates [299]. Aggregates tend to phototransform into monomers in some cases [300].

The number of molecules degraded per photon of light which is the quantum yield of photodegradation Φ_p or measure of stability of the macrocycle can be determined from Equation 1.36.

$$\Phi_p = \frac{(C_0 - C_t)VN_A}{S.t.I_{abs}} \quad (1.36)$$

where C_t and C_0 are the MPc complexes concentration in mol dm^{-3} (M) after and prior to irradiation, respectively. V is the reaction volume, S is the irradiation area of the cell, t the irradiation time, N_A is the Avogadro's number and I_{abs} the overlap integral of the irradiation light source intensity and the absorption of the MPc in the region of the interference filter transmittance [301].

First order kinetics apply to only the initial degradation process (first 15%) [294]. Therefore C_0 and C_t should be taken at 0% and about 10% bleaching, respectively for accurate results.

An intended aim of this thesis was to study the ability of the various water-soluble phthalocyanines to generate $^1\text{O}_2$ in solution as well as to study the photodegradation behaviour of these compounds. Sn(IV)Pc and Sn(II)Pc complexes have been reported in the literature [167,302-304], and show ease of photoreduction in the presence of light [167,304] rather than the more common photodegradation shown by most MPc complexes, yet little is known about the singlet oxygen generating behaviour of SnPc complexes. Hence, it is explored in this work in addition to photodegradation behaviour.

1.6 Summary of Aims of Thesis

The aims of this thesis are summarized as follows:

1. Synthesis, and detailed photophysical (triplet quantum yields and lifetimes, fluorescence quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) studies of anionic (sulfonated and carboxy phthalocyanine complexes of aluminium, zinc, silicon and germanium), cationic (quaternary zinc MPc complexes), α and β aryloxy-derivatised tetra substituted Sn^{4+} , and aminoalkanethio-derivatised MPc complexes (Figure 1.16) and photoelectrochemical studies on some selected complexes.
2. Spectroscopic, photophysical and photochemical studies of synthesized water-soluble phthalocyanines in the presence of
 - a. magnetic iron oxide nanoparticles (MN)
 - b. semiconductor CdTe QDs and
 - c. photophysical behaviour of linked MN, QD and MPc conjugates.
3. Spectroscopic and photophysicochemical studies of synthesized water-soluble phthalocyanines in the presence of a surfactant (cremophore EL).
4. Quenching of
 - a. QD fluorescence by MPc or bovine serum albumin through FRET and
 - b. MPc fluorescence by benzoquinone or BSA

The MPc complexes studied (Figure 1.16) are:

Unsubstituted zinc and chloroaluminium phthalocyanine (**ClAlPc (31) ZnPc (32)**)

Tetrasulfonated metallophthalocyanines: (**ZnPcS₄ (33), AlPcS₄ (34), SiPcS₄ (35), GePcS₄ (36)**)

Tetracarboxy metallophthalocyanines: (**ZnTCPc (37)**, **AlTCPc (38)**, **SiTCPc (39)**, **GeTCPc (40)**)

Octacarboxy metallophthalocyanines: (**ZnOCPc (41)**, **AlOCPc (42)**, **SiOCPc (43)**, **GeOCPc (44)**)

Peripherally and non-peripherally tetra substituted Sn(IV)Pc complexes substituted with phenoxy, tert-butylphenoxy or 4-(benzyloxy)phenoxy groups (**45a-c** and **46a-c**)

Peripherally and non-peripherally tetra and peripherally octa substituted ZnPc complexes substituted with 2-diethylaminoethylsulfanyl or 2-diethylmethylamino ethylsulfanyl groups (**47a**, **47b**, **48a**, **48b**, **49a** and **49c**)

The nanoparticles studied (Figure 1.13) are:

Mercaptocarboxylic acid capped CdTe QDs capped with thioglycolic acid, mercaptopropionic acid or L-cysteine (**1 a-c**)

Magnetic iron oxide nanoparticles covered with hydroxyl groups or 3-aminopropyl triethoxysilane (**2a** and **2b**).

CHAPTER 2

EXPERIMENTAL

2.1 Materials

Methanol, ethanol, dichloromethane (DCM), tetrahydrofuran (THF), toluene, chloroform (CHCl_3), dimethylsulfoxide (DMSO), dimethyl formamide (DMF), ammonium molybdate, ammonium chloride, sodium hydroxide, potassium bromide, potassium hydroxide, potassium carbonate, sodium carbonate, sodium dihydrogen phosphate, sodium hydrogenphosphate, sodium chloride, sodium borohydride, zinc acetate, zinc chloride, potassium nitrate, potassium chloride, sulfuric acid (98 %), nitric acid (55 %) and hydrochloric acid (32 %) were purchased from SAARCHEM. Deuterated chloroform (CDCl_3), deuterated DMSO ($\text{DMSO}-d_6$), 4-sulfophthalic acid, 1,4-benzoquinone (BQ), trimellitic acid anhydride, benzene-1,2,4,5-tetracarboxylic dianhydride, 4,5-dichlorophthalic acid, 4-tert-butylphenol, 4-benzyloxyphenol, phenol, 3-diphenylisobenzofuran (DPBF), anthracene-9, 10-bis-methylmalonate (ADMA), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) 1-pentanol, iodo-methane, iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, triethylamine, ferric nitrate, cadmium chloride, tellurium powder (200 mesh), thioglycolic acid, 3-mercaptopropionic acid, L-cysteine, thionyl chloride, ammonia (25 % or 32 %), formamide, acetic anhydride, acetonitrile, cremophore EL (CEL), urea, aluminium chloride, silicon tetrachloride, germanium tetrachloride, eosin-Y, tetrabutylammonium iodide (TBAI), iodine, 3-aminopropyltriethoxysilane, 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC) and tin (II) chloride were purchased from Sigma–Aldrich. Bovine serum albumin (BSA) and ethylene carbonate were obtained from Fluka. Chromatography was performed on silica gel 60 (0.04–0.063 mm) from Merck or neutral alumina from Aldrich. All solvents were dried as described by Perrin and Armarego [305] before use. All other reagents were of analytical grade and

were used as received from the suppliers. Ultra pure water, from a Milli-Q water purification system (Millipore Corp, Bedford, MA, USA) was used for all aqueous solutions. Phosphate-buffered (PBS) solution (0.01 M, pH 7.4) was prepared using appropriate amounts of Na_2HPO_4 , KH_2PO_4 and chloride salts, dissolved in ultra pure water.

2.2 Instrumentation/ Equipment

1. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer.
2. Infra-red (IR) spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR spectrometer.
3. Ground state electronic absorption spectra were recorded on a Cary 500 UV-Vis/NIR spectrophotometer.
4. Elemental Analyses were performed using Elementar Vario Microcube ELIII.
5. Mass spectra were recorded with Finnigan MAT LCQ ESI-MS.
6. Transmission electron microscope (TEM) pictures were obtained using a JEOL JEM 1210 transmission electron microscope at 100 kV accelerating voltage.
7. X-ray powder diffraction patterns were recorded on a Phillips PW1050 goniometer equipped with a proportional counter, using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter). Data were collected in the range from $2\theta = 5^\circ$ to 60° , scanning at 1° min^{-1} with a filter time-constant of 1 s. Samples were placed on a glass slide, on a thin layer of petroleum grease where necessary, and a paper spacer was placed between the slide and the goniometer head to compensate for the thickness of the grease layer. The X-ray diffraction data were treated using

the freely-available Fityk curve fitting software. Baseline correction was performed on each diffraction pattern by subtracting a spline fitted to the curved background, the control points having been selected manually by inspection. Pearson7-type curves were fitted to the raw data, having been found to provide the best fit, and the full-width at half-maximum values used in this study were obtained from the fitted curves.

8. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrophotometer using a 1cm pathlength cuvette at room temperature.
9. Triplet absorption and decay kinetics were recorded on a laser-flash photolysis system (schematically shown in Figure 2.1). The excitation pulses were produced by a Nd:YAG laser (Quanta-Ray providing 400 mJ, 90 ns pulses of laser light at 10 Hz) pumping a tunable dye laser (Lambda Physik FL 3002, Pyridin 1 dye in methanol). The single pulse energy ranged from 2-7 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was

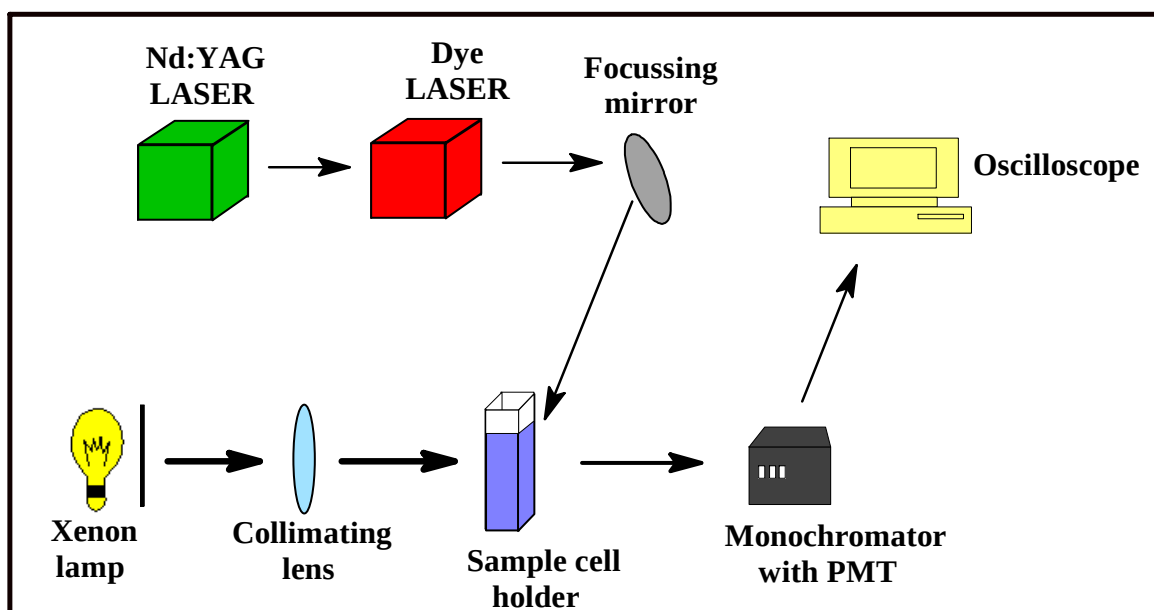


Figure 2.1: Schematic diagram of a laser flash photolysis set-up.

used as a detector. Signals were recorded with a two-channel, digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses.

10. Photo-irradiations for singlet oxygen and photodegradation quantum yields 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 or 700 nm, depending on the wavelength of maximum absorbance of the phthalocyanine with a band width of 40 nm) was additionally placed in the light path before the sample as shown in Figure 2.2.
11. Light intensity was measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter.
12. Electrodeposited eosin-Y / ZnO hybrid thin films were prepared at the Justus-

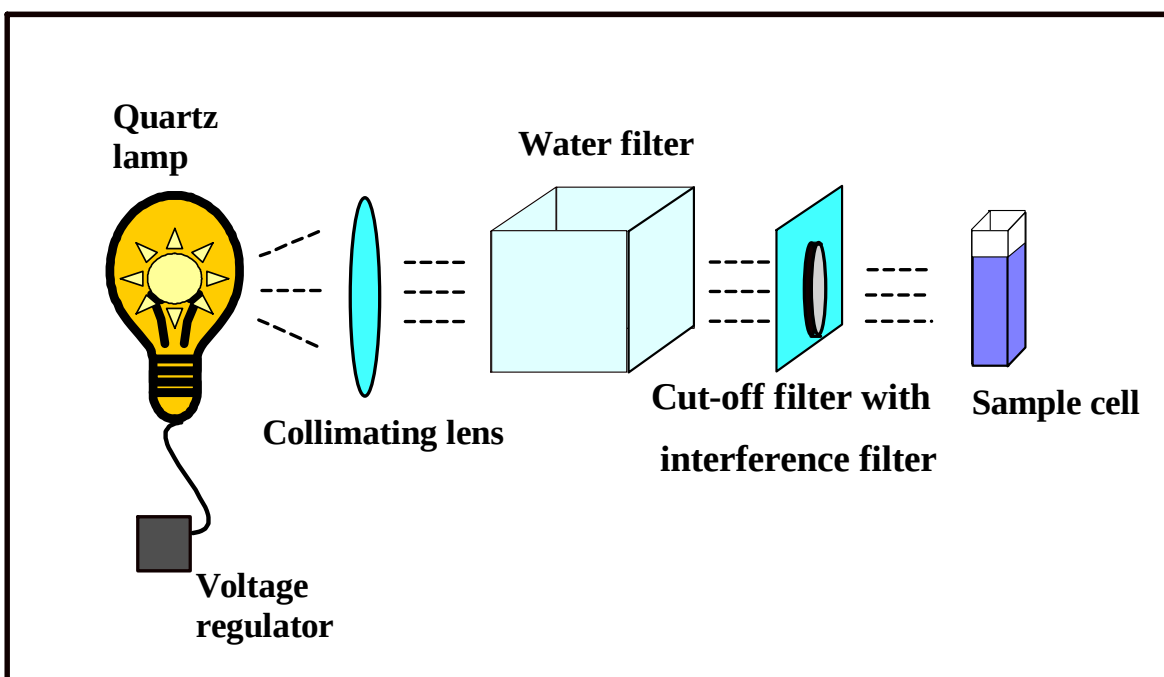


Figure 2.2: Schematic diagram of a photochemical set-up.

- Liebig University, Giessen Germany using a rotating disk electrode (Radiometer CTV101, controller), in solutions containing eosin-Y (EY), ZnCl_2 and dissolved oxygen.
13. Photoelectrochemical data were performed at the Justus-Liebig University, Giessen Germany using a conventional three-electrode arrangement in a 5 mL glass cell with the deposited thin film as a window of the cell illuminated from the glass/ fluorine-doped tin oxide (FTO) side and used as the working electrode, a Pt counter electrode and a Ag/AgNO_3 reference electrode with acetonitrile as internal solvent. 0.5 M TBAI and 0.05M I_2 in a 1: 4 by volume mixture of acetonitrile with ethylene carbonate was used as electrolyte.
 14. Scanning electron microscope (SEM) pictures were either obtained from Justus-Liebig University Giessen Germany or using a JEOL JSM 840 scanning electron microscope at 5KV accelerating voltage.
 15. Raman data was obtained using a Bruker Vertex 70-Ram II spectrometer equipped with a Nd:YAG laser that emit at 1064 nm and a liquid nitrogen cooled germanium detector.

2.3 Methods

2.3.1 Absorption and fluorescence studies

The interaction between MPcs and CdTe QDs was studied spectrophotometrically, by gradual addition of aliquots of (5 μL) of [1×10^{-6} M] solution of CdTe QDs to 5 mL of 10^{-5} M solution of the MPc complexes. Measurements were performed in a 1cm quartz cell at room temperature. Methanol: water (60:40) solvent mixture was employed. In this mixture MPc derivatives are monomeric while aggregated in water alone.

The solutions of the MPcs and QDs investigated as well as the standards were prepared such that the absorbance of each at the wavelength of excitation is ~ 0.05 for fluorescence studies. The excitation bandwidth was kept small since excitation is assumed to be monochromatic. Emission spectra were recorded and the areas under the curves were measured. Corrections for refractive indices were done where different solvents for MPc and standard were used. Fluorescence quantum yields were calculated using Equation 1.14, with unsubstituted ZnPc in DMSO ($\Phi_F = 0.20$ [234] or Rhodamine 6G in ethanol ($\Phi_F = 0.94$ [245,306]) as standards.

2.3.2 Fluorescence quenching

Quenching of MPcs fluorescence by BQ or QDs; BSA fluorescence by MPcs or QDs and QDs fluorescence by MPcs were carried out.

2.3.2.3 Quenching of the fluorescence of MPcs by BQ or QDs

BQ as fluorescence quencher

Experiments of the quenching of MPcs fluorescence by BQ were carried out by addition of increasing concentrations of the quencher, BQ, i.e, 0 to 0.0014 M to a fixed concentration of MPc complex (1.0×10^{-6} M). MPc fluorescence spectra were recorded in the absence and presence of the various BQ concentrations on exciting at the MPc excitation wavelength and the changes in fluorescence intensity with quencher concentration analysed by the Stern-Volmer (S-V) equation, Equation 1.17. The ratios F_0/F at each quencher concentration were plotted against BQ concentrations, [BQ].

QD as fluorescence quencher

This was carried out by the addition of increasing concentrations (0 to 4×10^{-7} M) of the respective CdTe QD solution to a fixed concentration of MPc ($\sim 1.0 \times 10^{-5}$ M). The steady decrease in the emission intensity of the MPcs were recorded at each CdTe QD concentration and related to CdTe QDs concentration by the Stern-Volmer's plot.

2.3.2.2 Quenching of the fluorescence of BSA by QD or MPcs

An aqueous solution of BSA (fixed concentration 3.0×10^{-6} M) was titrated with increasing concentrations (0 to 9.7×10^{-7} M) of the respective QD solution or (0 to 1.10×10^{-5} M) of the respective MPc solution. BSA was excited at 280 nm and fluorescence spectra recorded between 290 nm and 500 nm. The steady decrease in the fluorescence of BSA was noted and related to QDs or MPcs' concentration by the Stern-Volmer's plot (Equation 1.17) and used in the determination of binding constant and number of binding sites according to Equation 1.28.

2.3.2.3 Quenching of the fluorescence of QD by MPcs

Fluorescence quenching of QDs by some MPcs was also studied at room temperature by titrating an aqueous solution of QDs (fixed concentration of 10^{-6} M) with varying concentrations (0 to 6.18×10^{-6} M) of the respective MPc solution (as the quencher). Excitation was at 400 nm and fluorescence recorded between 400 and 700 nm in the absence and presence of the quencher. The quenching resulted in FRET.

2.3.3 Triplet quantum yields and lifetimes

Triplet quantum yields (Φ_T) and lifetimes were determined by recording the triplet

absorption and decay kinetics from the laser flash photolysis system shown in Figure. 2.1. The investigated MPc solution (absorbance ~ 1.5) was placed in a 1 cm pathlength spectrophotometric cell, bubbled with argon for 20 mins and irradiated at the Q-band maximum with laser light from a Nd:YAG laser. Φ_T values were determined by the comparative triplet absorption method, Equation 1.33 with unsubstituted ZnPc in DMSO ($\Phi_T = 0.65$ [307]) or ZnPcS₄ in H₂O ($\Phi_T = 0.56$ [308]) employed as standard. Triplet lifetimes were obtained by exponential fitting of the kinetic curves using OriginPro 7.5 software.

2.3.4 Singlet oxygen and photodegradation quantum yields

Determination of quantum yields of singlet oxygen (Φ_Δ) and photodegradation (Φ_p) were carried out using a home-made photochemical set-up shown in Figure 2.2 [277, 300] and Equations 1.35 for Φ_Δ and 1.36 for Φ_p respectively. Air-saturated solution of the respective MPcs (2.0 mL) with the respective singlet oxygen quencher (DPBF or ADMA) for singlet oxygen (absorbance of MPc ~ 0.2 at the irradiation wavelength in the final solution) or without quencher for photodegradation, (absorbance of MPc ~ 1.0) were placed in a 1 cm pathlength spectrophotometric quartz cell that is fitted with a tight-fitting stopper and then photolysed at the Q-band region using a 300 W General electric quartz lamp as described above. The solutions were prepared in the dark. The wavelength of the interference filter was chosen such that it was close to the Q band absorption of the MPc.

The steady reduction in the Q band absorption intensity with irradiation time was recorded and used for the calculation of Φ_p according to Equation 1.36.

For singlet oxygen quantum yields (Φ_{Δ}), DPBF or ADMA were employed as quenchers in organic and aqueous media respectively. Φ_{Δ} values were determined by monitoring the absorbance decay of the quencher at 416 nm for DPBF or 380 nm for ADMA with time and used for the calculation of Φ_{Δ} according to Equation 1.35. The concentration of DPBF was kept at $\sim 3 \times 10^{-5}$ M while that of ADMA was $\sim 6 \times 10^{-5}$ M to avoid chain reactions. The initial quencher concentrations (corresponding to an absorbance of ~ 1.0) were kept the same for both the standard and the MPcs. $\text{ZnPcS}_{\text{mix}}$, ($\Phi_{\Delta}^{\text{Std}} = 0.45$ in aqueous solution [309] and ZnPc ($\Phi_{\Delta}^{\text{Std}} = 0.67$ in DMSO [310]) were employed as standards.

In some experiments, singlet oxygen was generated from MPcs in the presence of QDs, obtained by excitation of QDs using a 532 nm laser light (240 mW) with beam diameter of 5 mm in a spectrophotometric quartz cell using Eosin Y ($\Phi_{\Delta}^{\text{Std}} = 0.6$ in water as reference [311]) and data were treated as above.

2.3.5 Photoelectrochemical measurements

The photoelectrochemical behaviour of the MOCPC complexes was studied as follows. EosinY-ZnO were electrochemically deposited using a three electrode single compartment cell containing 120 mL of 0.1M KCl solution with a saturated calomel electrode (SCE) as reference electrode, a Zn rod (Riedel de Haën) as counter electrode and $2.5 \times 2.5 \text{ cm}^2$ pieces of fluorine-doped tin oxide (FTO) on glass (Asahi Glass) as working electrode under potentiostatic control at -1.0 V vs. SCE for 25 min at 70°C . The FTO was mounted to a rotating electrode through a designed attachment and set to 500 rpm.

For the desorption of EY, an EosinY-ZnO film is dipped into KOH aqueous solution (pH 10.5) for 24 hours to dissolve the structure directing agent (SDA) from the surface of ZnO. Thereafter, the ZnO thin film is dried in an oven at 150 °C in air for 1 hour to remove water and activate the ZnO surface. The film is put into an MPC solution (1mM) preheated to 80°C, the solution is kept at this temperature for 1 hour and the MPC is adsorbed onto the surface of the ZnO. The re-adsorbed film is rinsed with distilled water, blown dry with air and stored in the dark.

2.4 Synthesis

2.4.1 Synthesis of Quantum dots (1a-c) (Scheme 3.1) [40]

The preparation of thiol capped QD was performed via a modified method adopted from literature [40]. $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (2.35 mmol) was dissolved in 125 mL of water and 5.7 mmol of the respective mercaptocarboxylic acid (thioglycolic acid (TGA) for TGA capped QDs (**1a**), 3-mercaptopropionic acid (MPA) for MPA capped QDs (**1b**) or L-cysteine (CYS) for CYS capped QDs (**1c**)) was added under stirring. The solution was adjusted to pH 12 by addition of 1 M NaOH solution dropwisely. Nitrogen gas was bubbled through the solution for about 1 hour. The aqueous solution was reacted with H_2Te gas. H_2Te gas was generated by the reaction of NaBH_4 with Te powder in the presence of 0.5 M H_2SO_4 under a flow of nitrogen gas. The molar ratio of $\text{Cd}^{2+}:\text{Te}^{2-}:\text{Thiol}$ was 1:0.5:2.4 (Te as powder). A change of colour was observed at this stage. The solution was then refluxed under air at 100°C for different times to control the size of the CdTe QDs. Different sizes are formed at different reaction times, the solution was continuously sampled to record the emission spectra of the quantum dots until the desired wavelength (hence size) was attained. On cooling, the respective QDs were precipitated out from solution using

excess ethanol; the solutions were then centrifuged to harvest the QDs and dried in vacuo to give QD complexes (**1a-c**): (i) TGA capped CdTe with emission peaks at 587 nm TGA1 (3.2 nm) **1a(i)** and at 632 nm TGA2 (3.7 nm) **1a(ii)**, (ii) MPA capped CdTe with emission peaks at 550 nm MPA1 (2.3 nm) **1b(i)** and at 649 nm MPA2 (3.6 nm) **1b(ii)** and (iii) CYS capped CdTe with emission peaks at 567 nm CYS1 (3.0 nm) **1c(i)**, 626 nm CYS2 (3.5 nm) **1c(ii)** and at 632 nm CYS3 (3.6 nm) **1c(iii)**. The sizes were determined by using the polynomial function in Equation 2.1[217].

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84) \quad (2.1)$$

TGA1 (1a(i)): IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3328 cm^{-1} (O-H), 2873 cm^{-1} (C-H), 1530 cm^{-1} (C=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 550 (5.10).

TGA2 (1a(ii)): IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3330 cm^{-1} (O-H), 2882 cm^{-1} (C-H), 1530 cm^{-1} (C=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 600 (5.20).

MPA1 (1b(i)): IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3468-3100 cm^{-1} (O-H), 2960 cm^{-1} (C-H), 1580 cm^{-1} (C=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 500 (4.81).

MPA2 (1b(ii)): IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3468-3100 cm^{-1} (O-H), 2960 cm^{-1} (C-H), 1580 cm^{-1} (C=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 595 (5.19).

CYS1 (1c(i)): IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3118 cm^{-1} (N-H), 1589 cm^{-1} (C=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 530 (5.05).

CYS2 (1c(ii)): IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3118 cm^{-1} (N-H), 1590 cm^{-1} (C=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 578 (5.17).

CYS3 (1c(iii)): IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3121 cm^{-1} (N-H), 1496 cm^{-1} (C=O) 1397 cm^{-1} (δNH_3^+). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 580 (5.18)

Conjugation of CdTe QDs to BSA.

Mercaptocarboxylic acid capped CdTe QDs were linked to BSA using EDC as a crosslinker in aqueous medium (PBS pH 7.4). CdTe QDs (3×10^{-7} M) and 1.04×10^{-5} M EDC were reacted together for 5 mins at room temperature to allow for activation of the carboxylic end of the QDs, then; 3×10^{-6} M BSA was added into the reaction mixture and incubated for 2 hours. Under the same conditions, a mixture of the CdTe QDs solution and BSA without EDC was made as a control experiment.

2.4.2 Synthesis of magnetic iron oxide nanoparticles (MN) (2a,2b)**Scheme 3.2 [281,312,313]****MN with surface hydroxyl groups, MNH (2a) Figure 1.13, Scheme 3.2 [281,312]**

Synthesis of magnetic fluid based on spinel ferrites was obtained by co-precipitation of Fe^{2+} and Fe^{3+} ions in alkaline medium as reported before with slight modification [281,312]. Under a blanket of nitrogen, a mixture of 6 mL concentrated nitric acid, 250 mL of aqueous solution of FeCl_2 (0.005 M) and 250 mL of aqueous solution of FeCl_3 (0.010 M) was heated to 95°C , under vigorous stirring (2700 rpm). An aqueous solution of sodium hydroxide (120 mL, 1 M) was quickly added to the stirring solution until pH 12 was reached to precipitate out the product. The product was magnetically separated from the supernatant and washed in aqueous solution until pH 7 was obtained. Thereafter the product was left overnight under an inert condition on a magnet to effect the magnetic ordering of the Fe ions. Further passivation was carried out by the enrichment of the Fe^{3+} with 10 mL of hot ferric nitrate $\text{Fe}_3(\text{NO}_3)$ (5.05 g, 0.5 M) under stirring for 3 minutes.

The particles were dispersed in an alkaline medium/water and adjusted to 5 wt % to form magnetic fluid (MF) for further use.

MN coated with 3-aminopropyl triethoxysilane, MNS (2b) Figure 1.13, (Scheme 3.2) [313]

Synthesis and purification was as described for complex **2a**, except after precipitation and washing of the product, **2a** was heated in a water bath with 10% aqueous solution of 3-aminopropyl triethoxysilane (APES) (40 mL) and glycerol for 3 hours. The APES solution used was adjusted to pH 4 and maintained at this pH with glacial acetic acid for the 3 hours of the experiment. The product was magnetically separated and thoroughly washed with distilled water to give MNS, **2b**.

MNH (2a): IR [(KBr) $\nu_{\max}$ / cm^{-1}]: 3402 (O-H), 635, 585, 423 (Fe-O).

MNS (2b): IR [(KBr) $\nu_{\max}$ / cm^{-1}]: 3450 (O-H), 3142 (N-H), 2882 (C-H), 1599 (δ NH₂). 1138, 1045, 986, (Si-O-Si/Si-OH), 635, 583 (Fe-O).

Mixed MNH (2a) and MPcs

MNH (30 mg) was combined with 5 mg (in 10 mL of PBS 7.4) of each of the MPc complex under vigorous stirring at 2700 rpm for 4 hrs to give a uniform mixture of MNH and MPc, thereafter photophysical and photochemical studies were carried out.

2.4.3 Synthesis of unsubstituted MPcs [314,315] and metallotetrasulfophthalocyanines, MPcS₄ [150,151] (Scheme 3.3)

The synthesis of chloroaluminum (III) phthalocyanine, ClAlPc (**31**) [314] and zinc (II) phthalocyanine, ZnPc (**32**) [315] are well documented and the complexes can be

purchased from suppliers.

ClAlPc (31) Yield: 66 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 1612, 1589, 1514, 1420, 1311, 1293, 1167, 1112, 1090, 961, 899, 885, 868, 804, 788, 770, 751, 723, 687, 612, 578, and 512.

UV/Vis (DMSO): $\lambda_{\max}$ nm (log ϵ) 351 (4.06), 645 (3.32), 679 (5.39).

ZnPc (32) Yield: 71%. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 1605, 1490, 1462, 1441, 1349, 1334, 1279, 1211, 1145, 961, 845, 809, 751 and 728. UV/Vis (DMSO): $\lambda_{\max}$ nm (log ϵ) 342 (4.02), 640 (3.58), 672 (5.38).

Zinc (ZnPcS₄) (**33**), aluminium (AlPcS₄) (**34**), silicon (SiPcS₄) (**35**) and germanium (GePcS₄) (**36**) tetrasulfophthalocyanine complexes were synthesized and purified using literature methods with some slight modifications [150,151]. Briefly, monosodium salt of 4-sulfophthalic acid (4.32 g, 16 mmol), ammonium chloride (0.47 g, 9.0 mmol), urea (5.8 g, 97 mmol), ammonium molybdate (0.34 g, 0.03 mmol) and the metal salt (4.8 mmol) (ZnCl₂ for zinc (II) tetrasulfophthalocyanine (**33**), AlCl₃ for aluminium (III) tetrasulfophthalocyanine (**34**), SiCl₄ for silicon (IV) tetrasulfophthalocyanine (**35**) and GeCl₄ for germanium (IV) tetrasulfophthalocyanine (**36**)) were thoroughly grinded together until a homogeneous mixture was formed. The mixture was added slowly to heated (180°C) nitrobenzene (10 cm³) (for zinc and aluminium complexes, but for silicon and germanium complexes, no solvent was employed) in a three-necked round-bottomed flask fitted with a thermometer and a condenser under stirring over a period of 1 hour at 180-200°C. Thereafter the mixture was heated for 6 hours at 200°C. The crude product was obtained as a dark solid cake. The product was washed with methanol and in cases where solvent was employed in preparation, the product was Soxhlet extracted with methanol for 24 hours to remove traces of nitrobenzene left. The final product was oven dried at 120°C

for 24 hours. The resulting product was dissolved in 150 cm³ of 1.0 M HCl saturated with NaCl and heated to boiling. The mixture was cooled to room temperature, filtered, dissolved in 0.1M NaOH (70 cm³) and then heated to 80°C. The solid impurities were separated by centrifugation, NaCl (27.0 g) was added to the filtrate and heated at 80°C with stirring until the evolution of ammonia gas was complete (this was monitored using litmus paper). The crystallized product was separated by centrifugation and this last process was repeated twice. The product was then washed with 80% ethanol until it was chloride-free (detected by testing with 1.0 M AgNO₃). Finally, the product was refluxed in 20 cm³ ethanol for 4 hours. Thereafter, cooled, filtered and dried in oven at 120°C overnight.

ZnPcS₄ (33): Yield: 45%. IR [(KBr) $\nu_{\max}$ / cm⁻¹]: 1644 (C=C), 1037 (S=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 351 (4.54), 638 (5.05), 676 (4.92).

AlPcS₄ (34): Yield: 42%. IR [(KBr) $\nu_{\max}$ / cm⁻¹]: 3462 (O-H), 1642 (C=C), 1035 (S=O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 348 (4.92), 648 (4.90), 680 (5.23).

SiPcS₄ (35): Yield: 32%. IR [(KBr) $\nu_{\max}$ / cm⁻¹]: 3500 (O-H), 1644 (C=C), 1037(S=O), 834 (Si-O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 348 (4.89), 636 (4.97), 679 (4.96).

GePcS₄ (36): Yield: 40%. IR [(KBr) $\nu_{\max}$ / cm⁻¹]: 3533 (O-H), 1650 (C=C), 1043 (S=O) 649 (Ge-O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 345 (4.79), 646 (4.88), 680 (4.83).

2.4.4 Synthesis of metallocarboxyphthalocyanines Schemes 3.4 and 3.5

2.4.4.1 Tetracarboxymetallophthalocyanines (MTCPC) [316,317] Scheme 3.4

Zinc (ZnTCPC) (**37**), aluminium (AlTCPC) (**38**), silicon (SiTCPC) (**39**) and germanium

(GeTCPc) (**40**) tetracarboxyphthalocyanine complexes were synthesized and purified according to literature methods [316,317] as follows: finely grinded mixture of trimellitic acid anhydride (**50**) (4.8 g, 25 mmol), urea (15 g, 250 mmol), ammonium chloride (0.27 g, 0.5 mmol), ammonium molybdate (0.6 g, 0.5 mmol) and metal salt (15 mmol) (ZnCl_2 for zinc(II) tetracarboxyphthalocyanine, (ZnTCPc) (**37**) AlCl_3 for aluminium (III) tetracarboxy phthalocyanine (AlTCPc) (**38**), SiCl_4 silicon (IV) tetracarboxy phthalocyanine (SiTCPc) (**39**) and GeCl_4 for germanium (IV) tetracarboxyphthalocyanine (GeTCPc) (**40**)) was added to nitrobenzene (40 mL) (for silicon and germanium complexes, no solvent was employed) and was heated under reflux at 185°C for 4 hrs. The dark coloured solid was filtered off and washed with methanol and in cases where solvent was employed in preparation, complexes were Soxhlet extracted overnight with methanol to remove any nitrobenzene left and dried overnight at 100°C to yield the tetraamide complex. The solid was then boiled with 275 mL of 1 M HCl saturated with NaCl. The residue was collected by filtration and washed with boiling water. An aliquot of the salt was dissolved in warm 1 M NaOH solution and filtered by suction. The tetracarboxy complex was precipitated from the sodium salt solution by addition of 1 M HCl. The complex was filtered and washed several times with boiling water until no more chloride was detected. The product (**37-40**) was further Soxhlet extracted with absolute ethanol and dried in vacuo.

ZnTCPc (37): Yield: 44 %. IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3397 (O-H), 1702 (C=O), 1344, 1281, 1250 (C-O). UV/Vis (DMSO): λ_{max} nm (log ϵ) 354 (4.62), 619 (4.58), 690 (5.00).

AlTCPc (38): Yield: 36 %. IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3350 (O-H), 1700 (C=O), 1331, 1227 1191 (C-O). UV/Vis (DMSO): λ_{max} nm (log ϵ) 360 (4.58), 625(4.54), 689 (5.21).

SiTCPC (39): Yield: 36 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3350 (O-H), 1702 (C=O), 1313, 1289, 1237 (C-O). UV/Vis (DMSO): $\lambda_{\max}$ nm (log ϵ) 368 (4.62), 614 (4.33), 681 (4.61).

GeTCPC (40): Yield: 28 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3402 (O-H), 1710 (C=O), 1484, 1399, 1255 (C-O). UV/Vis (DMSO): $\lambda_{\max}$ nm (log ϵ) 367 (4.58), 615 (4.11), 689 (4.99).

2.4.4.2 Octacarboxymetallophthalocyanines (MOCPC) [152,153] Scheme 3.5

Zinc (ZnOCPC) (**41**), aluminium (AlOCPC) (**42**), silicon (SiOCPC) (**43**) and (GeOCPC) (**44**) octacarboxyphthalocyanine complexes were synthesized and purified according to literature methods [152,153]. A mixture of benzene-1,2,4,5-tetracarboxylic dianhydride (**26**) (3.75 g, 17.25 mmol), urea (19.5 g, 330 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.1 g, 0.7 mmol) and metal salt (23.5 mmol) (zinc acetate for zinc(II) octacarboxyphthalocyanine, (ZnOCPC, **41**) AlCl_3 for aluminium (III) octacarboxyphthalocyanine (AlOCPC, **42**), SiCl_4 for silicon (IV) octacarboxyphthalocyanine (SiOCPC, **43**) and GeCl_4 for germanium(IV) octacarboxyphthalocyanine (GeOCPC, **44**) was placed in 100 mL two-necked flask fitted with a reflux condenser and a thermometer and heated at 250°C under reflux for about 20 minutes, resulting into formation of a fused product. The fused product was sequentially washed with water, acetone and 6 M HCl and dried. 3 g of the tetraamide product (**27**) formed was hydrolysed by refluxing with 20% H_2SO_4 (3.0 cm^3) for 3 days. The product was sequentially washed with 200 cm^3 portions of 5% H_2SO_4 , 100 cm^3 portions of water and acetone and air dried. It was further purified using column chromatography on an alumina column using 2% aqueous NaOH as eluent and reprecipitated each time with 20 % HCl. The pure products (**41**, **42**, **43** or **44**) were filtered and then dried at 120°C overnight.

ZnOCPc (41): Yield: 11 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3421 (O-H), 1702 (C=O), 1394, 1284, 1247, 1184 (C-O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 351 (4.89), 620 (4.55), 693 (5.25).

AlOCPc (42): Yield: 15 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3418 (O-H), 1701 (C=O), 1378, 1305, 1249, 1191 (C-O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 356 (4.90), 617 (4.57), 689 (5.26).

SiOCPc (43): Yield: 12 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3419 (O-H), 1708 (C=O), 1393, 1299, 1284, 1191 (C-O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 349 (4.70), 620 (4.57), 691 (5.10).

GeOCPc (44): Yield: 11 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3421 (O-H), 1710 (C=O), 1384, 1318, 1277, 1192 (C-O). UV/Vis (PBS pH 7.4): $\lambda_{\max}$ nm (log ϵ) 349 (4.79), 624 (4.52), 697 (5.15).

2.4.5 Synthesis of substituted phthalonitriles (Schemes 3.6 and 3.7) [318-320].

3 - Phenoxyphthalonitrile (51a): A mixture of phenol (3.50 g, 37 mmol) and 3-nitrophthalonitrile (**15**) (4.50 g, 26 mmol) was dissolved in dry DMSO (60 mL) under nitrogen. Anhydrous K_2CO_3 (7.19 g, 51 mmol) was added to the suspension and this was stirred at room temperature. Further K_2CO_3 (0.33 g, 2.4 mmol) was added portion-wise after 4 hrs and 24 hrs of stirring. The reaction was then left for further 24 hrs to ensure complete reaction. The crude product was precipitated out of the reaction by pouring it into ice water. It was filtered, washed with water and recrystallized from methanol/water (1:1) to yield a brownish yellow product. Yield: 79 %. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 2235

(C≡N), 1245 (C-O-C). ¹H-NMR (DMSO-d₆): δ, ppm 7.80-7.84 (2H, m, Ar-H), 7.46-7.53 (2H, t, Ar-H), 7.21-7.35 (4H, m, Ar-H).

3 - (4 -Tert-Butylphenoxy) phthalonitrile (51b): Synthesis and purification was as described for complex **51a**, using 4-tert-butylphenol (5.90 g, 39 mmol) and (**15**) (4.50 g, 26 mmol) to yield a brownish yellow product. Yield: (88 %). IR [(KBr) ν_{max}/cm⁻¹]: 2962 (t-Bu), 2230 (s) (C≡N), 1240 (C-O-C). ¹H-NMR (DMSO-d₆): δ, ppm 7.78-7.84 (2H, m, Ar-H), 7.50 (2H, d, Ar-H), 7.21-7.26 (1H, m, Ar-H), 7.14 (2H, d, Ar-H), 1.30 (9H, m, t-Bu).

3-[4-(Benzyloxy)phenoxy]phthalonitrile (51c): Synthesis and purification of **51c** was as described for compound **51a**, using 4-(benzyloxy)phenol (7.81 g, 39 mmol) and (**15**) (4.50 g, 26 mmol) to yield a brownish product. Yield: 91 %. IR [(KBr) ν_{max}/cm⁻¹]: 2241 (C≡N), 1260 (C-O-C). ¹H-NMR (DMSO-d₆): δ, ppm 7.53 (1H, s, Ar-H), 7.47-7.32 (6H, m, Ar-H), 7.05 (5H, m, Ar-H), 5.10 (2H, s, CH₂).

4 - Phenoxyphthalonitrile (52a): Synthesis and purification was as described for complex **51a**, using phenol (3.50 g, 37 mmol) and 4-nitrophthalonitrile (**18**) (4.50 g, 26 mmol) to yield a brownish yellow product. Yield: 82 %. IR [(KBr) ν_{max}/cm⁻¹]: 2230 (C≡N), 1235 (C-O-C). ¹H-NMR (DMSO-d₆): δ, ppm 7.73 (1H, d, Ar-H), 7.44 (2H, t, Ar-H), 7.22-7.34 (3H, m, Ar-H), 7.06 (2H, d, Ar-H).

4 - (4 - Tert-Butylphenoxy) phthalonitrile (52b): Synthesis and purification was as described for complex **51a**, using 4-tert-butylphenol (5.90 g, 39 mmol) and (**18**) (4.50 g, 26 mmol) to yield a brownish yellow product. Yield: 70 %. IR [(KBr) ν_{max}/cm⁻¹]: 2962

(t-Bu), 2233 (C≡N), 1246 (C-O-C). ¹H-NMR (DMSO-d₆): δ, ppm 7.35 (1H, d, Ar-H), 7.21 (2H, d, Ar-H), 7.15 (2H, d, Ar-H), 7.00 (2H, d, Ar-H), 1.30 (9H, m, t- Bu).

4-[4-(Benzyloxy)phenoxy]phthalonitrile (52c): Synthesis and purification was as described for compound **51a**, using 4-(benzyloxy)phenol (7.81 g, 39 mmol) and (**18**) (4.50 g, 26 mmol) to yield a brownish product. Yield: 84 %. IR [(KBr) ν_{max}/cm⁻¹]: 2235 (C≡N), 1251 (C-O-C). ¹H-NMR (DMSO-d₆): δ, ppm 7.52 (1H, d, Ar-H), 7.45-7.32 (5H, m, Ar-H), 7.21 (2H, m, Ar-H), 7.00 (4H, m, Ar-H), 5.10 (2H, s, CH₂).

3-Diethylaminoethylsulfanyl phthalonitrile (53a) Scheme 3.7: A mixture of 2-diethylaminoethanethiol hydrochloride (0.25 g, 1.5 mmol) and (**15**) (0.36 g, 2.07 mmol) was stirred in 20 mL anhydrous DMF under a blanket of N₂ for 10 minutes. Then, finely ground anhydrous K₂CO₃ (2.1 g, 16 mmol) was added in portions over 2 hours with efficient stirring. The reaction mixture was stirred at room temperature for 48 hrs under nitrogen. The solution was poured into ice water. The precipitate was filtered off, washed with water until the filtrate was neutral and dried in vacuo. The product was further purified by column chromatography with neutral alumina (eluent: CHCl₃: MeOH, 7:1) to yield a pinkish product. Yield: 90%. IR [(KBr) ν_{max}/cm⁻¹]: 2237(C≡N), 735 (C-S-C). ¹H NMR (CDCl₃) δ , ppm 7.61 (1H, d, Ar-H), 7.47 (1H, t, Ar-H), 7.20 (1H, s, Ar-H), 3.08 (2H, t, SCH₂), 2.72 (2H, t, NCH₂), 2.57 (4H, m, CH₂C), 1.07 (6H, m, CH₃).

4-Diethylaminoethylsulfanyl phthalonitrile (54a) Scheme 3.7: Synthesis and purification was as described for compound **53a** using 2-diethylaminoethanethiol hydrochloride (0.25 g, 1.5 mmol) and (**18**) (0.36 g, 2.07 mmol) to yield a brownish yellow product. Yield: 80%. IR [(KBr) ν_{max}/cm⁻¹]: 2239 (C≡N), 740 (C-S-C). ¹H NMR

(CDCl₃) δ , ppm 7.57 (1H, d, Ar-H), 7.46 (1H, dd, Ar-H), 7.20 (1H, s, Ar-H), 3.02 (2H, t, SCH₂), 2.72 (2H, dd, NCH₂), 2.53 (4H, m, CH₂C), 0.97 (6H, dd, CH₃).

1,2-Bis-(diethylaminoethylsulfanyl)-4,5-dicyanobenzene (55a) Scheme 3.7: Synthesis and purification was as described for compound **53a** except using 2-diethylaminoethanethiol hydrochloride (3g, 17.67 mmol), 4,5-dichlorophthalonitrile (**21**) (1.16g, 5.88 mmol), 50 mL anhydrous DMF and finely ground anhydrous K₂CO₃ (9.75 g, 70.68 mmol) to yield a brownish yellow product. Yield: 72%. IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 2238 (C $\equiv$ N), 739 (C-S-C). ¹H NMR (CDCl₃) δ , ppm 7.52 (2H, s, Ar-H), 3.10 (4H, t, SCH₂), 2.78 (4H, dd, NCH₂), 2.59 (8H, m, CH₂C), 1.03 (12H, m, CH₃).

2.4.6 Synthesis Aryloxy tetra-substituted phthalocyanines (Scheme 3.6)

2.4.6.1 Metal-free aryloxy tetra substituted phthalocyanines (56a-c and 57a-c)

Scheme 3.6 [297]

The synthesis of metal-free aryloxy substituted phthalocyanines was carried out using established procedures [297]. Briefly, the respective phthalonitrile derivatives, (**51a-c**, or **52a-c**) (0.1 mmol) were refluxed in pentan-1-ol (5 mL) in the presence of 0.1 mmol DBU for 14 hours under nitrogen. After cooling, the dark blue product was precipitated out with methanol, filtered and washed with methanol. The crude product was dissolved in dichloromethane (CH₂Cl₂), filtered and concentrated. The product was purified by passing it through a silica gel column, using CH₂Cl₂ as an eluent, giving metal-free tetraphenoxy (**56a** and **57a**), tetra-tert-butylphenoxy (**56b** and **57b**) and tetra-4-benzyloxyphenoxy (**56c** and **57c**) phthalocyanines which gave satisfactory spectroscopic characterization and were immediately used for SnPc synthesis.

Tin (IV) phthalocyaninato complexes (45a-c, 46a-c), Scheme 3.6.

A mixture of tin (II) chloride (1 mmol) and (56a-c, 57a-c) (1 mmol) was refluxed in pentan-1-ol (5 mL) for 1 hour under nitrogen. The mixture was cooled and methanol was added to precipitate the product. The dark green product was filtered and washed with methanol. It was isolated using a silica gel column, with CH₂Cl₂: MeOH (30:1) as the eluent, giving metallated tetraphenoxy (45a and 46a), tetra-tert-butylphenoxy (45b and 46b) and tetrabenzoyloxyphenoxy (45c and 46c) phthalocyaninato tin (IV) complexes.

1,(4)-(Tetraphenoxyphthalocyaninato) tin (IV) (45a). Yield: 30%. UV-vis (DMSO): $\lambda_{\max}$ (nm) (log ϵ) 339 (4.78), 652 (4.47), 733 (5.03). IR [(KBr) $\nu_{\max}$ (cm⁻¹)]: 3038 (Ar-CH), 2996 (C-H), 1580 (C=C), 1250 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 8.95–9.37 (4H, m, Pc-H), 8.04–8.25 (4H, m, Pc-H), 7.65–7.79 (4H, m, Pc-H), 7.16–7.46 (20H, m, phenyl-H). Calcd for C₅₆H₃₂Cl₂SnN₈O₄: C 62.83, H 3.01, N 10.47; Found: C 62.92, H 3.25, N 9.18.

1,(4)-(Tetra-tert-butylphenoxyphthalocyaninato) tin (IV) (45b). Yield: 37%. UV-vis (DMSO): $\lambda_{\max}$ (nm) (log ϵ) 343 (4.71), 657 (4.41), 737 (5.01). IR [(KBr) $\nu_{\max}$ (cm⁻¹)]: 2964 (C-H), 1582 (C=C), 1255 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 9.24–9.38 (4H, m, Pc-H), 8.89–9.08 (4H, m, Pc-H), 8.01–8.25 (4H, m, Pc-H), 7.55–7.80 (16H, m, phenyl-H), 1.29–1.46 (36H, m, t-Bu). Calcd for C₇₂H₆₄Cl₂SnN₈O₈: C 66.78, H 4.98, N 8.65; Found: C 67.37, H 5.23, N 8.26.

1,(4)-(Tetra [4-(benzyloxy)phenoxy]phthalocyaninato) tin (IV) (45c). Yield: 32%. UV-vis (DMSO): $\lambda_{\max}$ (nm) (log ϵ) 331 (4.85), 659 (4.51), 740 (5.18). IR [(KBr) ν

$\lambda_{\max}(\text{cm}^{-1})$]: 3032 (Ar-CH), 2936 (C-H), 1585 (C=C), 1231 (C-O-C). ^1H NMR (CDCl_3): δ , ppm 9.29-9.37 (4H, m, Pc-H), 9.05-9.13 (4H, m, Pc-H), 8.08-8.21 (4H, m, Pc-H), 7.44-7.53 (20H, m, phenyl-H) 7.06-7.26 (16H, m, phenyl-H) 5.21 (8H, m, CH_2). Calcd for $\text{C}_{84}\text{H}_{56}\text{Cl}_2\text{SnN}_8\text{O}_8$: C 67.49, H 3.78, N 7.50; Found: C 67.98, H 4.01, N 7.65.

2,(3)-(Tetraphenoxyphthalocyaninato) tin (IV) (46a). Yield: 52%. UV-vis (DMSO): $\lambda_{\max}$ (nm) (log ϵ) 356 (4.80), 639 (4.39), 709 (5.03). IR [(KBr) $\nu_{\max}$ (cm^{-1})]: 3020 (Ar-CH), 2920 (C-H), 1590 (C=C), 1231 (C-O-C). ^1H NMR (CDCl_3): δ , ppm 8.78-9.22 (4H, m, Pc-H), 8.19-8.38 (4H, m, Pc-H), 7.44-7.57 (4H, m, Pc-H), 7.14-7.32 (20H, m, phenyl-H). Calcd for $\text{C}_{56}\text{H}_{32}\text{Cl}_2\text{SnN}_8\text{O}_4$: C 62.83, H 3.01, N 10.47; Found: C 62.42, H 3.64, N 9.55.

2,(3)-(Tetra-tert-butylphenoxyphthalocyaninato) tin (IV) (46b). Yield: 48%. UV-vis (DMSO): $\lambda_{\max}$ (nm) (log ϵ) 349 (4.82), 637 (4.42), 711 (5.10). IR [(KBr) $\nu_{\max}$ (cm^{-1})]: 3014 (Ar-CH), 2962 (C-H), 1602 (C=C), 1234 (C-O-C). ^1H NMR (CDCl_3): δ , ppm 9.06-9.26 (4H, m, Pc-H), 8.80-8.98 (4H, m, Pc-H), 8.51-8.67 (4H, m, Pc-H), 7.48-7.69 (16H, m, phenyl-H), 1.39 (36H, s, t-Bu). Calcd for $\text{C}_{72}\text{H}_{64}\text{Cl}_2\text{SnN}_8\text{O}_8$: C 66.78, H 4.98, N 8.65; Found: C 66.70, H 5.81, N 8.51.

2,(3)-(Tetra [4-(benzyloxy)phenoxy]phthalocyaninato) tin (IV) (46c). Yield: 44%. UV-vis (DMSO): $\lambda_{\max}$ (nm) (log ϵ) 353 (4.90), 419 (4.42), 667 (4.72), 715 (5.07). IR [(KBr) $\nu_{\max}$ (cm^{-1})]: 3033 (Ar-CH), 2934 (C-H), 1611 (C=C), 1223 (C-O-C). ^1H NMR (CDCl_3): δ , ppm 8.78-9.22 (4H, m, Pc-H), 7.70-8.11 (4H, m, Pc-H), 7.36-7.58 (24H, m, Pc-H), 6.73-7.08 (16H, m, phenyl-H) 5.19 (8H, m, CH_2). Calcd for $\text{C}_{84}\text{H}_{56}\text{Cl}_2\text{SnN}_8\text{O}_8$: C 67.49, H 3.78, N 7.50; Found: C 68.80, H 3.88, N 7.31.

2.4.7 Synthesis of aminoalkanethio-substituted phthalocyanines (Scheme 3.8)

1(4)-Tetra (2-diethylaminoethylsulfanyl) phthalocyaninato zinc (II) (47a, Scheme 3.8) [160].

A mixture of 3-diethylaminoethylsulfanyl phthalonitrile (**53a**) (0.26 g, 1 mmol), 2-(dimethylaminoethanol) (1 mL) and anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.064g, 0.35 mmol) was refluxed under N_2 for 18h. After cooling to room temperature, MeOH: H_2O (1:1) was added to precipitate the product. The dark green product was filtered off and washed with water. It was isolated on a neutral alumina column with THF:MeOH (30:1) as eluent. Yield: 42%. UV-vis (DMSO): λ_{max} nm (log ϵ) 339 (4.78), 643 (4.57), 717 (5.30). IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3015 (Ar-CH), 2968-2797 (C-H), 1591 (C=C), 737 (C-S-C). ^1H NMR (DMSO- d_6) δ , ppm 8.99 (8H, m, Ar-H), 8.05 (4H, m, Ar-H), 3.14 (8H, m, SCH_2), 2.77 (8H, br, NCH_2), 2.59 (16H, m, CH_2C), 1.21 (24H, m, CH_3). LRAPCI-MS m/z : Calc. for $\text{C}_{56}\text{H}_{68}\text{N}_{12}\text{S}_4\text{Zn}$: 1102.85; found $[\text{M} + 2\text{H}]^{2+}$ 1104.4. Calc. for $\text{C}_{56}\text{H}_{68}\text{N}_{12}\text{S}_4\text{Zn}$: C 60.99, H 6.21, N 15.24; Found: C 59.72, H 6.65, N 15.25.

2(3) -Tetra (2-diethylaminoethylsulfanyl) phthalocyaninato zinc (II) (48a, Scheme 3.8).

Synthesis and purification was as outlined for **47a** except **54a** (0.26 g, 1 mmol) was employed instead of **53a** in the presence of 2-(dimethylaminoethanol) (1 mL) and anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.064g, 0.35 mmol). Yield: 45%. UV-vis (DMSO): λ_{max} nm (log ϵ) 363 (4.83), 627 (4.46), 694 (5.19). IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3007 (Ar-CH), 2967-2803 (C-H), 1600 (C=C), 743 (C-S-C). ^1H NMR (DMSO- d_6) δ , ppm 8.78 (4H, t, Ar-H),

8.02 (4H, m, Ar-H), 7.87 (4H, s, Ar-H), 3.37 (8H, br, SCH₂), 3.05 (8H, br, NCH₂), 2.76 (16H, quin, CH₂C), 1.16 (24H, t, CH₃). LRAPCI-MS *m/z*: Calc. for C₅₆H₆₈N₁₂S₄Zn: 1102.85; found [M + 3H]³⁺ 1106.1. Calcd for C₅₆H₆₈N₁₂S₄Zn: C 60.99, H 6.21, N 15.24; Found: C 60.88, H 6.31, N 14.22.

Octa (2-diethylaminoethylsulfanyl) phthalocyaninato zinc (II) (49a, Scheme 3.8).

Synthesis and purification was as outlined for **47a** except 1,2-bis-(diethylaminoethylsulfanyl)-4,5-dicyanobenzene, **55a** (0.5g, 1.28 mmol), was employed instead of **53a** in the presence of 2-(dimethylaminoethanol) (1.8 mL) and anhydrous Zn(CH₃COO)₂ (0.059g, 0.32 mmol). Yield: 19%. UV-vis (DMSO): λ_{max} nm (log ε) 370 (4.81), 639 (4.49), 709 (5.13). IR [(KBr) ν_{max}/cm⁻¹]: 2966-2666 (C-H), 1592 (C=C), 668 (C-S-C). ¹H NMR (DMSO-d₆) δ, ppm 9.19 (8H, s, Ar-H), 3.72 (16H, br, SCH₂), 3.15 (16H, br, NCH₂), 2.65 (32H, br, CH₂), 1.10 (48H, t, CH₃). Calcd for C₈₀H₁₂₀N₁₆S₈Zn: C 59.06, H 7.38, N 13.78; Found: C 58.95, H 7.19, N 13.49.

1(4)-Tetra (2-diethylmethylaninoethylsulfanyl) phthalocyaninato zinc (II) tetra iodide (47b, Scheme 3.8).

Compound **47a** (0.03g, 0.027 mmol) was dissolved in CHCl₃ (5 mL), and methyl iodide (0.15 g, 1.059 mmol) was added to this solution. The mixture was refluxed for 3 hours. After cooling to room temperature, the green precipitate was filtered off, washed with CHCl₃ and dried. Yield: 87%. UV-vis (DMSO): λ_{max} nm (log ε) 336 (4.81), 636 (4.66), 707 (5.41). IR [(KBr) ν_{max}/cm⁻¹]: 2927 (C-H), 1589-1565 (C=C). ¹H NMR (DMSO- d₆) δ, ppm 9.36 (4H, quin, Ar-H), 8.35 (8H, m, Ar-H), 4.09 (8H, br, SCH₂), 3.98 (8H, br, NCH₂), 3.65 (16H, m, CH₂C), 3.28 (12H, d, CH₃), 1.4 (24H, m, CCH₃). LRAPCI-MS

m/z : Calc. for $C_{60}H_{80}N_{12}S_4I_4Zn$: 1670.63; found $[M - I + 2H]^{2+}$ 1546. Calcd for $C_{60}H_{80}N_{12}S_4I_4Zn$: C 43.14, H 4.83, N 10.06; Found: C43.96, H 4.89, N 9.67.

2(3) Tetra-((2-diethylmethylaminoethylsulfanyl)-phthalocyaninato zinc (II) tetra iodide (48b, Scheme 3.8).

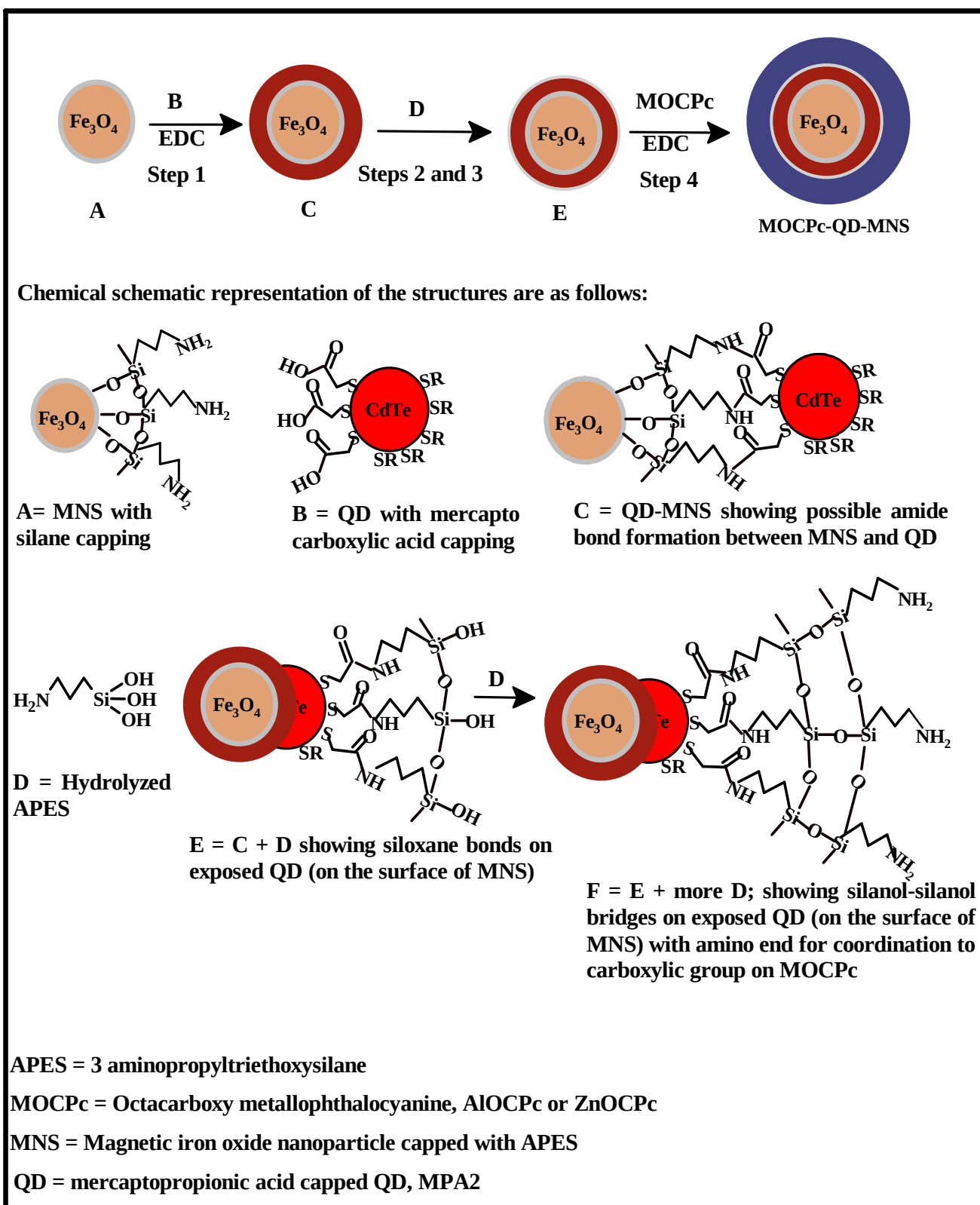
Synthesis and purification was as outlined for **47b** except **48a** (0.03g, 0.027 mmol) was employed instead of **47a** in the presence of $CHCl_3$ (5 mL) and methyl iodide (0.15 g, 1.059 mmol). Yield: 95%. UV-vis (DMSO): λ_{max} nm (log ϵ) 368 (4.85), 621 (4.54), 691 (5.34). IR [(KBr) ν_{max}/cm^{-1}]: 2974 (C-H), 1599 (C=C), 743 (C-S-C). ^1H NMR (DMSO- d_6) δ , ppm 9.48 (8H, m, Ar-H), 8.38 (4H, quin, Ar-H), 3.95 (8 H, br, SCH_2), 3.74 (8H, br, NCH_2), 3.56 (16H, t, CH_2C), 3.15 (12H, d, CH_3), 1.33 (24H, m, CCH_3). LRAPCI-MS m/z : Calc. for $C_{60}H_{80}N_{12}S_4I_4Zn$: 1670.63; found $[M - I + 2H]^{2+}$ 1546. Calcd for $C_{60}H_{80}N_{12}S_4I_4Zn$: C 43.14, H 4.83, N 10.06; Found: C44.60, H 4.86, N 9.75.

Octa-(2-diethylmethylaminoethylsulfanyl)-phthalocyaninato zinc (II) octaiodide (49b, Scheme 3.8).

Synthesis and purification was as outlined for **47b** except **49a** (0.036 g, 0.023 mmol) was employed instead of **47a** in the presence of $CHCl_3$ (5 mL) and methyl iodide (0.15 g, 1.059 mmol). Yield: 89%. UV-vis (DMSO): λ_{max} nm (log ϵ) 367 (4.98), 633 (4.63), 707 (5.37). IR [(KBr) ν_{max}/cm^{-1}]: 2974 (C-H), 1592 (C=C), 696 (C-S-C). ^1H NMR (DMSO- d_6) δ , ppm 9.26 (8H, s, Ar-H), 4.05 (16H, t, SCH_2), 3.78 (16H, t, NCH_2), 3.60 (32H, quin, CH_2C) 3.21 (24H, s, CH_3) 1.35 (48H, t, C CH_3). Calcd for $C_{88}H_{144}N_{16}S_8I_8Zn$: C 38.24, H 5.21, N 8.11; Found: C 38.13, H 5.12, N 8.01.

2.4.8 MOCPcs-QD-MNS (3-in-one photosensitizer conjugate) (Scheme 2.1 or 5.1) [35,313]

The preparation of MOCPc-QD-MNS was performed via modified literature methods [35,313]. EDC (0.1g, 0.52 mmol) was added to a 5 mL solution of QDs (0.1g in 2 mL), represented as compound **B** in Scheme 2.1 and stirred vigorously for 30 mins to allow for activation of the carboxylic end of the QDs so that they can be susceptible to attack by the amino groups of 3-aminopropyl triethoxysilane (APES) capped magnetic nanoparticles (MNS, compound **A** in Scheme 2.1) to result in an amide bond between QDs and MNS. To the crude product was added APES capped magnetic nanoparticles (MNS, **A**, 0.1 g diluted with doubly distilled water (5 mL)) under mechanical stirring for 12 h. The preformed particles were washed to remove excess reactants by centrifugation and re-dispersed in aqueous solution at 0.25 wt % to afford linked QD-MNS (compound **C** in Scheme 2.1, Step 1) sample solution. Now the QDs are surrounding MNS but may still have exposed carboxylic groups. Thereafter, 2 mL of 10% aqueous hydrolysed 3-aminopropyl triethoxysilane in glycerol (the ethoxysilane groups ($\text{Si-OCH}_2\text{CH}_3$) hydrolyze into silanol groups (Si-OH)), was added to 2 mL of the re-dispersed QD-MNS solution in the presence of EDC and stirred in a water bath (60°C) for 3 hours, to allow the coordination of the exposed carboxylic groups on the QDs with the amino group of the hydrolysed APES and expose the silanol groups, compound **E** in Scheme 2.1, Step 2. Then, fresh hydrolysed APES (compound **D** in Scheme 2.1, Step 3) was incorporated to tailor the nanocrystal surface functionality, this forms silanol-silanol bridges with the exposed silanol groups (Si-OH) on the QDs and exposes the NH_2 groups (compound **F** in Scheme 2.1) for functionalization.



Scheme 2.1: Schematic representation of synthesis of MOCPC-QD-MNS

*Activated MOCPC (2 mL, 3×10^{-5} M) was thereafter added under stirring. The mixture was left to stir for another 12 h. The product was precipitated with ethanol and thoroughly washed to remove excess reactants by sonication and centrifugation. It was re-dispersed in aqueous solution at 0.25 wt % to afford MOCPC-QD-MNS (ZnOCPC-QD-MNS or AlOCPC-QD-MNS) solution, Step 3, Scheme 2.1.

*Activated MOCPC was obtained by stirring an aqueous solution of MOCPC compound **41 or 42** (0.6 mmol) in the presence of NHS (0.115g, 1.00 mmol) and EDC (0.23g, 1.20 mmol) under nitrogen atmosphere for 3 hours.

ZnOCPC-QD-MNS: IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3550-3321 (O-H), 3154 (N-H), 2968, 2932 cm^{-1} , 2892 (C-H), 2009 (C=N), 1702 (C=O), 1601, 1394, (C=C), 1116, 988 (Si-O-Si/Si-OH), 601 (Fe-O). [Raman $\nu_{\max}/\text{cm}^{-1}$]: 601, 688, 716, 1399, 1452, 1471, 1429, 1512, 1612.

AlOCPC-QD-MNS: IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3470-3250 (O-H), 3142 (N-H), 2963 cm^{-1} 2894 (C-H), 2001 (C=N), 1701 (C=O), 1580 1378, 1305 (C=C), 1138, 1047, 989, (Si-O-Si/Si-OH), 635, 592 (Fe-O). [Raman $\nu_{\max}/\text{cm}^{-1}$]: 574, 601, 663, 1309, 1352, 1371, 1429, 1512, 1604.

CHAPTERS

3-6

RESULTS AND DISCUSSION

PUBLICATIONS

Publications in peer-reviewed journals that resulted from the results presented in this thesis are listed below. These articles are not referenced in this thesis:

1. Photophysical and photochemical studies of zinc and aluminium phthalocyanines in the presence of magnetic fluid, **Mopelola Idowu** and Tebello Nyokong, *J. Photochem. Photobiol. A: Chem.*, **188** (2007) 200.
2. Excited state dynamics of zinc and aluminium Phthalocyanine carboxylates, **Mopelola Idowu**, Abimbola Ogunsipe and Tebello Nyokong, *Spectrochim. Acta Part A*, **68** (2007), 995.
3. Photoinduced energy transfer between water soluble CdTe quantum dots and aluminium tetrasulfonated phthalocyanine, **Mopelola Idowu**, Ji-Yao Chen and Tebello Nyokong, *New J. Chem.*, **32** (2008) 290.
4. Photophysical and photochemical properties of tetrasulfonated silicon and germanium phthalocyanines in aqueous and non-aqueous media, **Mopelola Idowu** and Tebello Nyokong, *J. Photochem. Photobiol. A: Chem.*, **197** (2008) 273.
5. Interaction of water soluble thiol capped CdTe quantum dots and bovine serum albumin (BSA), **Mopelola Idowu**, Emmanuel Lamprecht and Tebello Nyokong, *J. Photochem. Photobiol. A: Chem.*, **198** (2008) 7.
6. Generation of singlet oxygen via the composites of water-soluble thiol-capped CdTe quantum dots-sulfonated aluminium phthalocyanine, Jiong Ma, Ji-Yao

- Chen, **Mopelola Idowu** and Tebello Nyokong, *J. Phys. Chem. B*, **112** (2008) 4465.
7. Synthesis, photophysics and photochemistry of tin (IV) Phthalocyanine derivatives, **Mopelola Idowu** and Tebello Nyokong, *J. Photochem. Photobiol. A: Chem.*, **199** (2008) 282.
 8. Photosensitizing properties of octacarboxy metallophthalocyanines in aqueous medium and their interaction with bovine serum albumin, **Mopelola Idowu** and Tebello Nyokong, *J. Photochem. Photobiol. A: Chem.*, **200** (2008) 396.
 9. Interaction of water soluble CdTe quantum dots with octacarboxy metallophthalocyanines: A photophysical and photochemical study, **Mopelola Idowu** and Tebello Nyokong, *J. Lumin.*, **129** (2009) 356.
 10. Synthesis, photophysical and photochemical studies of water soluble cationic zinc phthalocyanine derivatives, **Mopelola Idowu** and Tebello Nyokong, *Polyhedron*, **28** (2009) 416.
 11. Study of the photophysical behaviour of tetrasulfonated metallophthalocyanines in the presence of CdTe quantum dots, **Mopelola Idowu** and Tebello Nyokong, *Polyhedron*, **28** (2009) 891.
 12. Photophysical and fluorescence quenching studies of tetra- and octa-octacarboxy substituted silicon and germanium phthalocyanines, **Mopelola Idowu** and Tebello Nyokong, *J. Photochem. Photobiol. A: Chem.*, (IN PRESS).
 13. Photoelectrochemical characterization of electrodeposited ZnO thin films sensitized by octacarboxy metallophthalocyanine derivatives, **Mopelola Idowu**

Thomas Loewenstein, Andrew Hastall, Tebello Nyokong and Derck Schlettwein,
J. Porphyrins Phthalocyanines, (ACCEPTED WITH REVISION).

14. Spectroscopic behaviour of cationic metallophthalocyanines in the presence of anionic quantum dots, **Mopelola Idowu** and Tebello Nyokong, *Polyhedron*, (SUBMITTED).

CHAPTER 3

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION

This chapter deals with the synthesis and spectroscopic characterization of nanoparticles and metallophthalocyanines used in this work. Tables 3.1-3.3 give a compiled list of the nanoparticles and MPc complexes employed.

Table 3.1: List of synthesized nanoparticles with their absorption maxima and size in PBS pH 7.4.

^a Nanoparticle	^b Abs max (nm)	Size (nm) (Polynomial)	Size (nm) ^d (XRPD)	^e Abb.	No.
TGA capped CdTe QDs	550	3.2	2.2	TGA1	1a(i)
TGA capped CdTe QDs	600	3.7	3.4	TGA2	1a(ii)
MPA capped CdTe QDs	500	2.3	2.2	MPA1	1b(i)
MPA capped CdTe QDs	595	3.6	3.7	MPA2	1b(ii)
CYS capped CdTe QDs	530	3.0	2.7	CYS1	1c(i)
CYS capped CdTe QDs	578	3.5	-	CYS2	1c(ii)
CYS capped CdTe QDs	580	3.6	3.4	CYS3	1c(iii)
OH capped Magnetite	316, 360	^c 10 (TEM)	14	MNH	2a
APES capped Magnetite	285, 358	-	14	MNS	2b

^aTGA = thioglycolic acid; MPA = mercaptopropionic acid; CYS = L-cysteine; APES = 3-aminopropyltriethoxysilane. ^bAbs max = absorption maxima; ^cTEM = transmission electron microscope, ^dXRPD = X-ray diffraction and ^eAbb. = abbreviation.

Table 3.2: List of synthesized water-soluble MPcs.

MPc complex	Abbreviation	No.
Zinc(II)tetrasulfophthalocyanine	ZnPcS ₄	33
Aluminium(III)tetrasulfophthalocyanine	AlPcS ₄	34
Silicon(IV)tetrasulfophthalocyanine	SiPcS ₄	35
Germanium(IV)tetrasulfophthalocyanine	GePcS ₄	36
Zinc(II)tetracarboxyphthalocyanine	ZnTCPc	37
Aluminium(III)tetracarboxyphthalocyanine	AlTCPc	38
Silicon(IV)tetracarboxyphthalocyanine	SiTCPc	39
Germanium(IV)tetracarboxyphthalocyanine	GeTCPc	40
Zinc(II)octacarboxyphthalocyanine	ZnOCPc	41
Aluminium(III)octacarboxyphthalocyanine	AlOCPc	42
Silicon(IV)octacarboxyphthalocyanine	SiOCPc	43
Germanium(IV)octacarboxyphthalocyanine	GeOCPc	44
1,(4)-Tetra (2-diethylmethylaminoethylsulfanyl) phthalocyaninato zinc (II) tetra iodide	α -TZnPcQ	47b
2,(3)-Tetra (2-diethylaminoethylsulfanyl) phthalocyaninato zinc (II)	β -TZnPcQ	48b
Octa (2-diethylaminoethylsulfanyl) phthalocyaninato zinc (II)	β -OZnPcQ	49b

Table 3.3: List of synthesized aryloxy- and aminoalkanethio-substituted MPcs.

MPc complex	Abbreviation	No.
1,(4)-(Tetraphenoxyphthalocyaninato) tin (IV)	α -SnPcPh	45a
1,(4)-(Tetra-tert-butylphenoxyphthalocyaninato) tin (IV)	α -SnPcTbtPh	45b
1,(4)-(Tetra [4-(benzyloxy)phenoxy]phthalocyaninato) tin (IV)	α -SnPcBzPh	45c
2,(3)-(Tetraphenoxyphthalocyaninato) tin (IV)	β -SnPcPh	46a
2,(3)-(Tetra-tert-butylphenoxyphthalocyaninato) tin (IV)	β -SnPcTbtPh	46b
2,(3)-(Tetra [4-(benzyloxy)phenoxy]phthalocyaninato) tin (IV)	β -SnPcBzPh	46c
1,(4)-Tetra (2-diethylaminoethylsulfanyl)phthalocyaninato zinc (II)	α -TZnPc	47a
2,(3)-Tetra (2-diethylaminoethylsulfanyl)phthalocyaninato zinc (II)	β -TZnPc	48a
Octa (2-diethylaminoethylsulfanyl) phthalocyaninato zinc (II)	β -OZnPc	49a

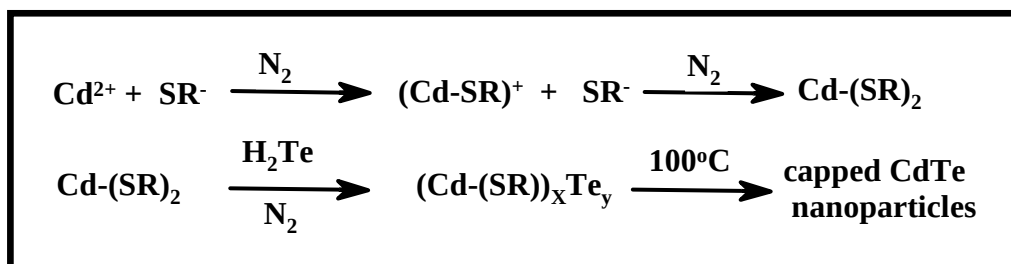
3.1 Synthesis and characterization of nanoparticles

The nanoparticles (quantum dots (QDs) and magnetic iron oxide nanoparticles (MN) used in this thesis were synthesized and characterized as reported before and their spectroscopic characterizations were consistent with literature [40,281,312,313].

3.1.1 Mercaptocarboxylic acid capped CdTe quantum dots (QDs)

The synthesis and purification of mercaptocarboxylic acid capped CdTe QDs were carried out via a modified method adopted from literature [40], Scheme 3.1 and Figure

1.8. Appreciable yields of the QDs were obtained and the QDs were characterized using UV-Vis and IR spectroscopies and by X-ray powder diffraction (XRPD).



Scheme 3.1 Synthesis of CdTe quantum dots.

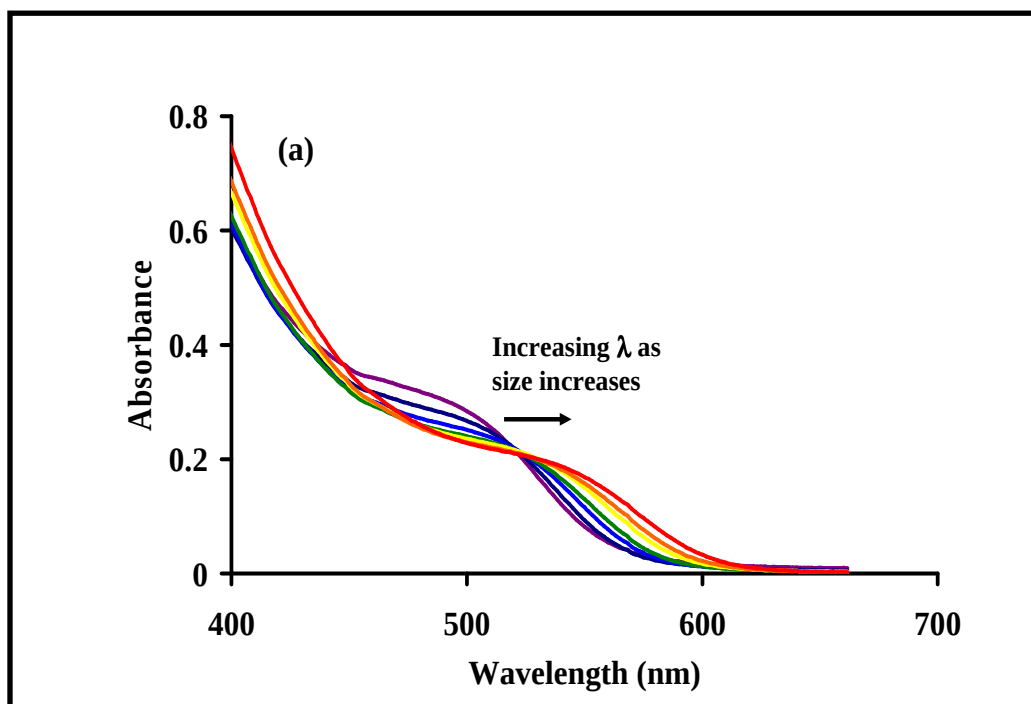
The QDs were synthesized in aqueous medium to give hydrophilic conjugates capped with carboxylic acid thiols, as opposed to the more common synthesis in organic media [224]. The adjustment of the pH of the precursor solution is dependent on the capping thiol, however for the QDs synthesized in this work, pH 12 worked well for all the cappings. In few cases, on adjustment of pH of the precursor solution, turbidity of the solution was observed due to incomplete solubility of the Cd thiolate complexes. This however did not have an effect on the synthesis since complete solubility occurred on applying temperature. The formation of the CdTe QDs is accompanied by a change of the solution color (orange, yellow or red), depending on the thiol cappings used. These colours gave way to other colours or became darker with increased growth of the QDs. Figure 3.1c inset shows a change in colour as size increases.

The electronic absorption spectra of CdTe quantum dots began to appear after 5-10 mins of refluxing. The spectra continued to shift to longer wavelengths with refluxing time and the reaction was stopped when the desired wavelength was attained. Growth rate was generally slow compared to those grown in organic medium [40] because of the low temperature of growth (100°C). The thioglycolic acid capped CdTe QDs (TGA), grew at

a much slower rate than the L-cysteine, (CYS) and 3-mercaptopropionic acid (MPA) capped ones, inferring that the rate of growth is dependent on the nature of the thiol cappings. All synthesized QDs were highly soluble in water.

The IR spectra showed pronounced vibrations between 3300 and 3500 cm^{-1} characteristic of O-H for all the QD types, C-H vibrations were observed at $2873\text{--}2960\text{ cm}^{-1}$, asymmetrical stretches of C=O were observed between 1530 and 1590 cm^{-1} . The L-cysteine capped QDs also showed an extra band at 3118 cm^{-1} which can be assigned to NH_2 vibration.

The normalized absorption spectra of the QDs, Figure 3.1, show typical [40] broad peaks in the visible region with tails extending to about 700 nm . The absorption spectra of the synthesized QDs indicate that the CdTe QDs have a wide range of absorption with their



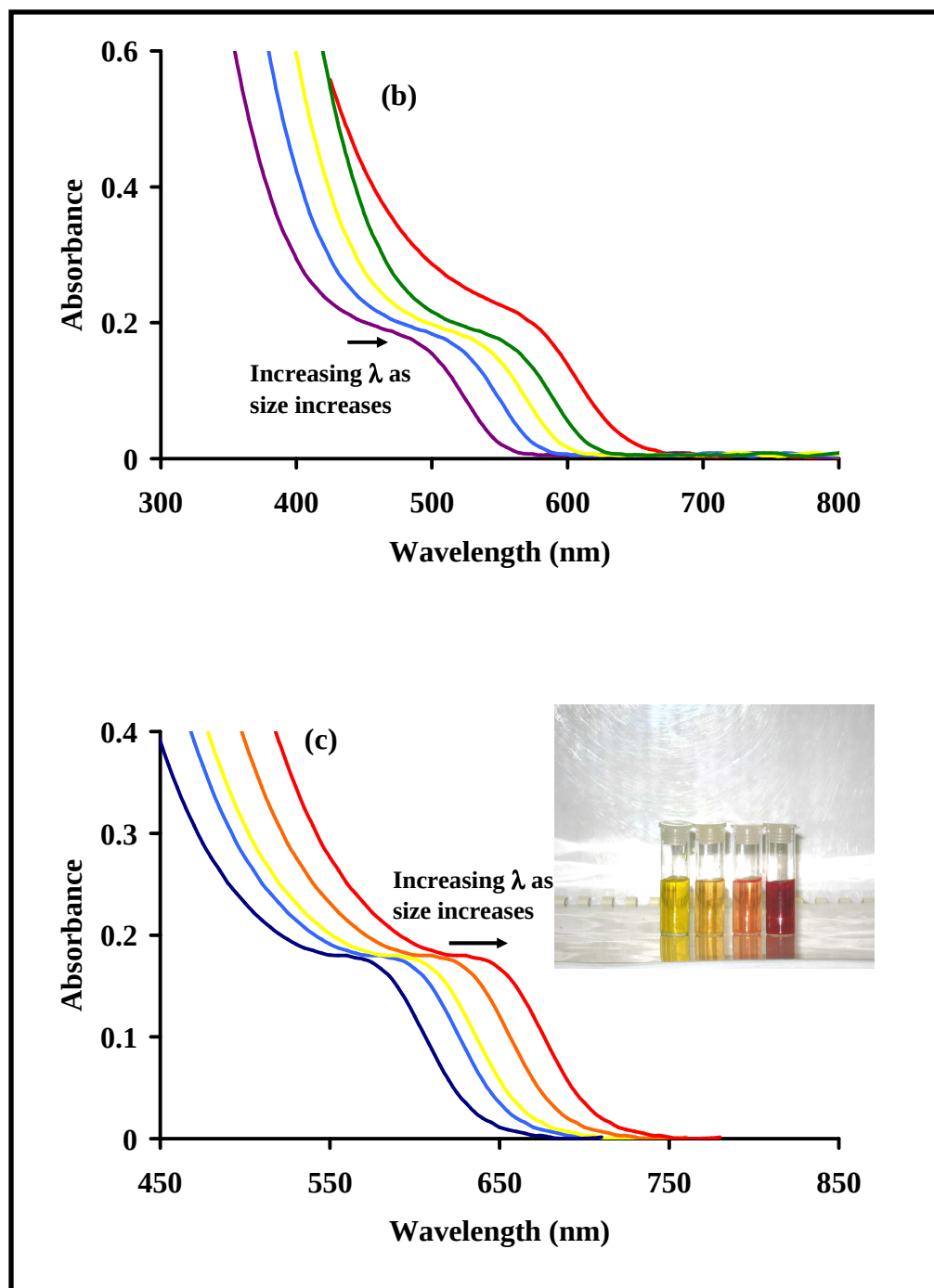


Figure 3.1: Electronic absorption spectra of synthesized CdTe quantum dots capped with mercaptopropionic acid (a), L-cysteine (b) and thioglycolic acid (c) as synthesized in aqueous medium, $[QD] = \sim 1.3 \times 10^{-6}$ M. Inset in (c) shows change in colour as size increases.

absorption peak maxima ranging from 500 nm to 600 nm as shown in Figure 3.1 (Table 3.1). The absorbance maxima are well resolved for TGA capped ones, inferring narrow size distribution of the synthesized QDs. The absorbance maxima shift to longer wavelength with increasing size of the QDs as a result of quantum confinement.

Two types of QDs are presented in this work, depending on their absorption region, hence their size and the overlap of the emission spectra with the absorption spectra of the MPcs studied. The smaller QDs which absorb between 500 and 550 nm (sizes 2.3 to 3.2 nm) are represented with subscript 1 after the capping thiol as follows: TGA1, MPA1 and CYS1. Those with more red shifted absorption spectra (hence larger size, 3.5 to 3.7 nm) ranging from 578 to 600 nm are represented with a subscript 2 after the capping thiol as follows: TGA2, MPA2 and CYS2 (Table 3.1).

XRPD can provide information both about the crystal-structure and nanocrystalline properties of the QDs. Figure 3.2a shows the X-ray diffraction patterns of the synthesized CdTe QD nanoparticles. The diffraction peaks are broad and weak, but the main peaks centred at approximately $2\theta = 25^\circ$, 40° and 47° correspond well to the three most intense peaks for bulk CdTe (ZnS-type structure, $2\theta = 23.8^\circ$, 39.3° , and 46.5°) as they appear on the simulated pattern obtained from crystal structure data using PLATON [321]. Following literature methods [89], the particle-diameter, d , was estimated using the Scherrer Equation 3.1 (same as Equation 1.4):

$$d(\text{\AA}) = \frac{k\lambda}{\beta \cos\theta} \quad (3.1)$$

The particle-sizes determined by XRPD, using the peak at 25° are shown in Table 3.1. Sizes of the QDs were also estimated using the polynomial fitting function in Equation 3.2 [217].

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84) \quad (3.2)$$

where λ is the absorption maxima of the QDs. The fitting function is not valid for sizes of quantum dots outside the size range of 1 to 9 nm [217]. The error in the determination was ± 0.05 .

The values for the MPA- and CYS-capped QDs are in reasonable agreement with the particle-sizes obtained by polynomial except for TGA1 where the value is much smaller when determined by the XPRD method (2.2 nm) compared to estimation (3.2 nm) by the polynomial fitting. CYS2 diffraction peaks were very broad and further analysis was difficult. For the purpose of the work in this thesis, the values obtained using the polynomial fitting which is accepted in literature [217], were employed.

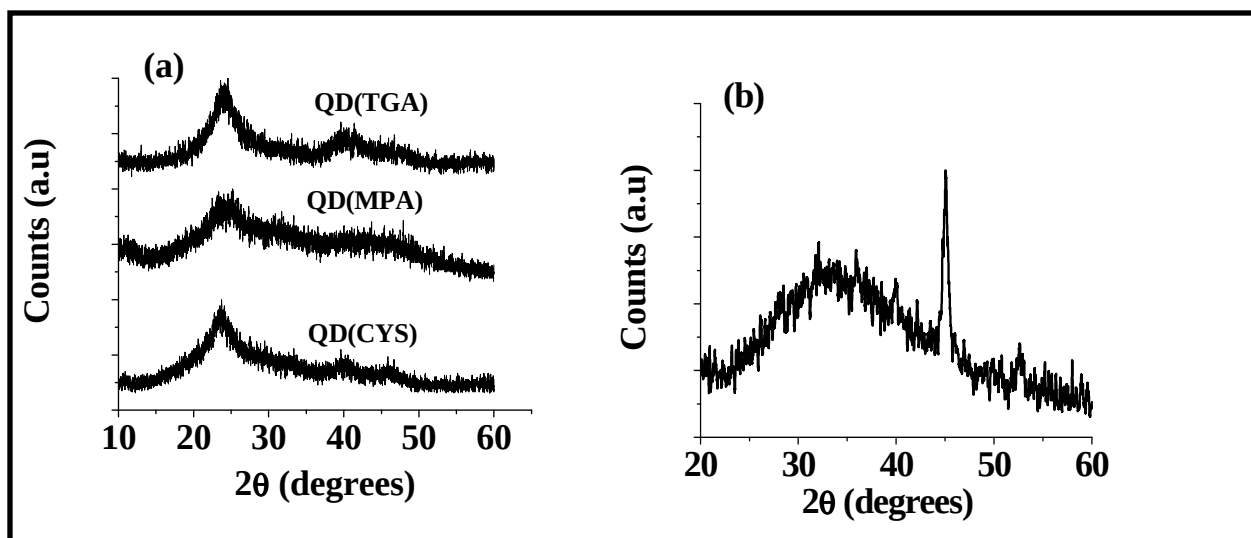


Figure 3.2: X- ray diffractograms of the different mercaptocarboxylic acid stabilized CdTe quantum dots (a) and magnetic iron oxide nanoparticle (b).

3.1.2 Magnetic iron oxide nanoparticles

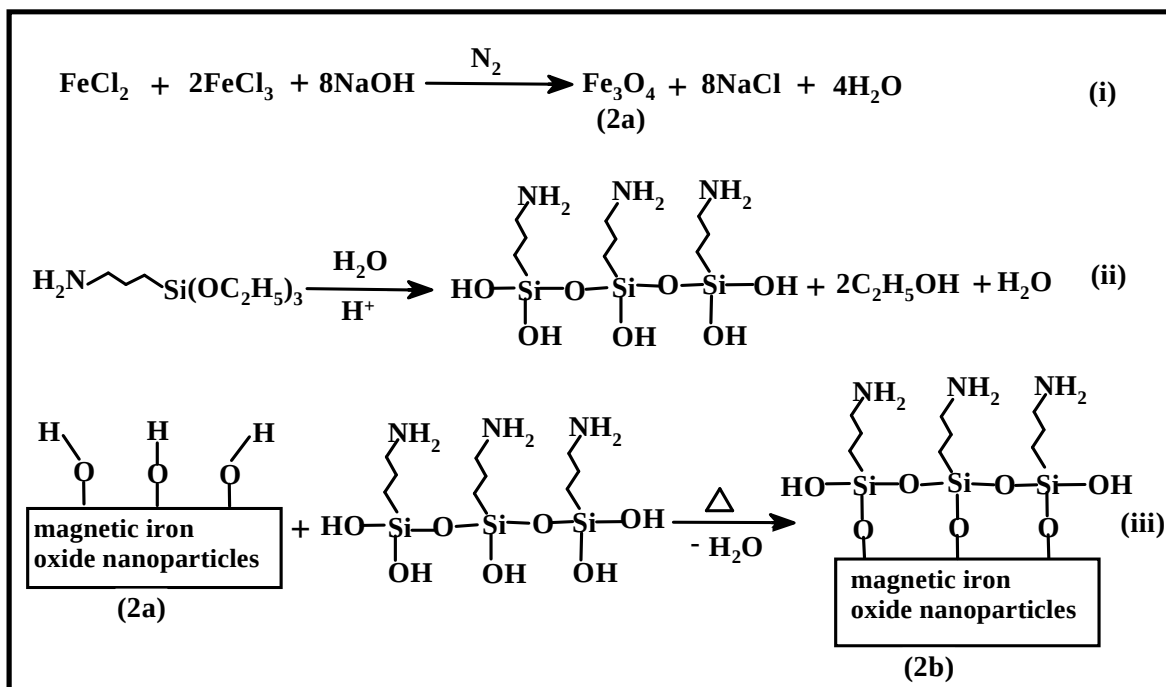
The synthesis and purification of magnetic iron oxide nanoparticles with surface hydroxyl groups, MNH (**2a**), was carried out by coprecipitation process via a synthetic

route adopted from literature [281,312], Scheme 3.2. Magnetic iron oxide nanoparticles capped with 3-aminopropyltriethoxysilane (APES) MNS (**2b**), was also obtained by coprecipitation, firstly, **2a** was formed, then silanization reaction on the nanoparticle surface as shown in Scheme 3.2 (iii) [313] followed to result in **2b**. The silane capping was synthesized as shown in Scheme 3.2 (ii). Appreciable yields were obtained in both cases and were characterized using UV-Vis and IR spectra giving results that are consistent with literature [313,322].

The coprecipitation process of obtaining MNH (**2a**) was carried out in aqueous medium under an inert condition since magnetic iron nanoparticles can undergo oxidation processes in the presence of air, Scheme 3.2 (i). The silanization process is a bit complex but by working in an acidic aqueous medium that acts as catalyst, hydrolysis and condensation reactions first occur in which the alkoxide groups are replaced by hydroxyl groups Scheme 3.2 (ii) and secondly, dehydration as well as adsorption onto the metal oxide surface occurs in which the silanol groups associates with the magnetic iron oxide nanoparticles forming a covalent bond with hydroxyl groups as shown in Scheme 3.2 (iii). The particles obtained in both routes were black and exhibited strong magnetic response. This silane capping should slow down the corrosion of MNS and help in its attachment to other molecules through its amino groups shown in Scheme 3.2.

The presence of iron oxide in MNH (**2a**) was evident by the bands from 635 to 420 cm^{-1} (Fe-O); O-H stretch was also observed at 3402 cm^{-1} . In MNS (**2b**) there was a shift of the O-H stretch to 3450 cm^{-1} with the Fe-O band occurring at 635 cm^{-1} and 583 cm^{-1} . These shifts may be due to the change in environment of the particles after APES capping. Additionally, bands due to the siloxane bonds were evident between 1261 and 986 cm^{-1} .

Figure 3.3 shows the transmission electron microscopic (TEM) image of **2a** reflecting the size and size distribution of the particles. The image shows that these particles have size of about 10 nm (Table 3.1) with narrow size distribution.



Scheme 3.2: Synthesis of iron oxide nanoparticles.

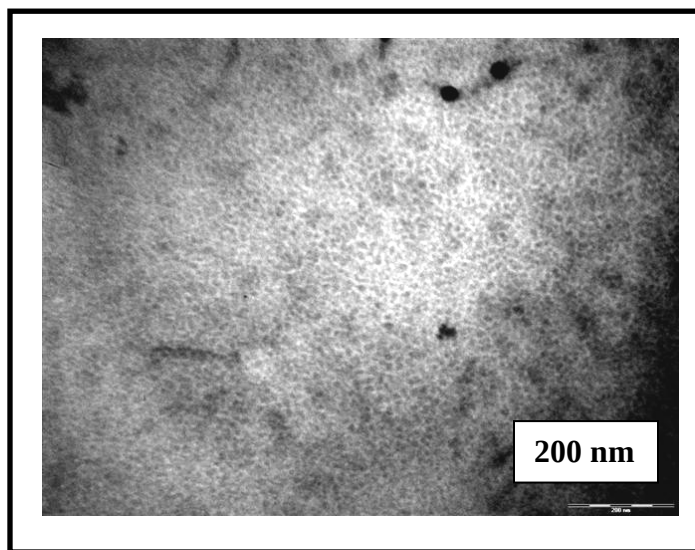


Figure 3.3 Transmission electron microscope images of magnetic iron oxide nanoparticles, MNH (2a). Magnification = 100 000. Burnt in scale bar = 200 nm.

The XRPD patterns of the iron nanoparticles in MNS (**2b**) is shown in Figure 3.2b The observed XRD peaks (at $2\theta = 45.2^\circ$ and 52.6°) are consistent with characteristic diffraction peaks in iron oxide nanoparticles [323]. The broad diffraction peak (at about $2\theta = \pm 30^\circ$) may be due to the presence of the silanol groups on the iron oxide nanoparticles. The particle size estimated from the strongest reflection at 45.2° using Scherrer's formula gave a value of about 14 nm as seen in Table 3.1 with no significant difference between **2a** and **2b** which is consistent with literature [313].

The electronic absorption spectra of the iron oxide nanoparticles are shown in Figure 3.4. The absorption spectra were broad with two absorption peaks observed at 285 and 358 nm for **2b** and unresolved peaks (probably due to extended period of exposure to air during measurements leading to oxidation) between 250 and 400 nm for **2a**. These peaks are in agreement with literature [322,324].

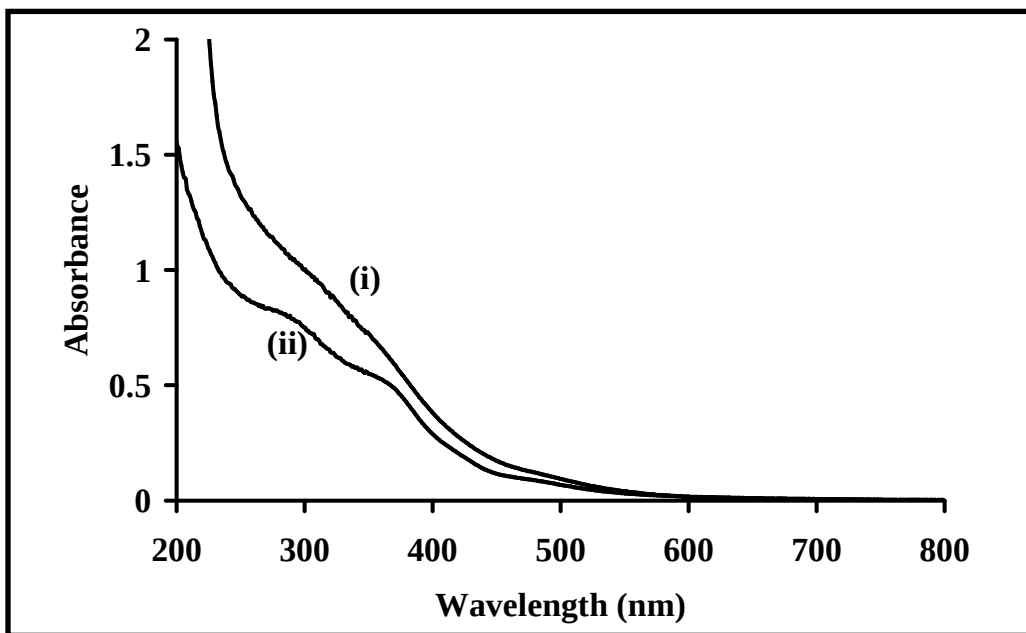


Figure 3.4: Electronic absorption spectra of magnetite capped with (i) OH, MNH (**2a**) and (ii) 3-aminopropyltriethoxysilane, MNS (**2b**) in PBS pH 7.4.

3.2 Metallophthalocyanines

3.2.1 Unsubstituted and tetrasulfonated MPcs (Scheme 3.3)

Chloroaluminium(III) phthalocyanine (**31**) and zinc(II) phthalocyanine complexes (**32**) were synthesized and characterized as it has been reported before [314,315] these complexes can also be purchased.

Figure 3.5 shows the ground state electronic absorption spectra of complexes **31** and **32** recorded in DMSO. Typical monomeric Q bands at 680 nm (**31**) and 672 nm (**32**) with B bands at 357 nm (**31**) and 337 nm (**32**) were observed.

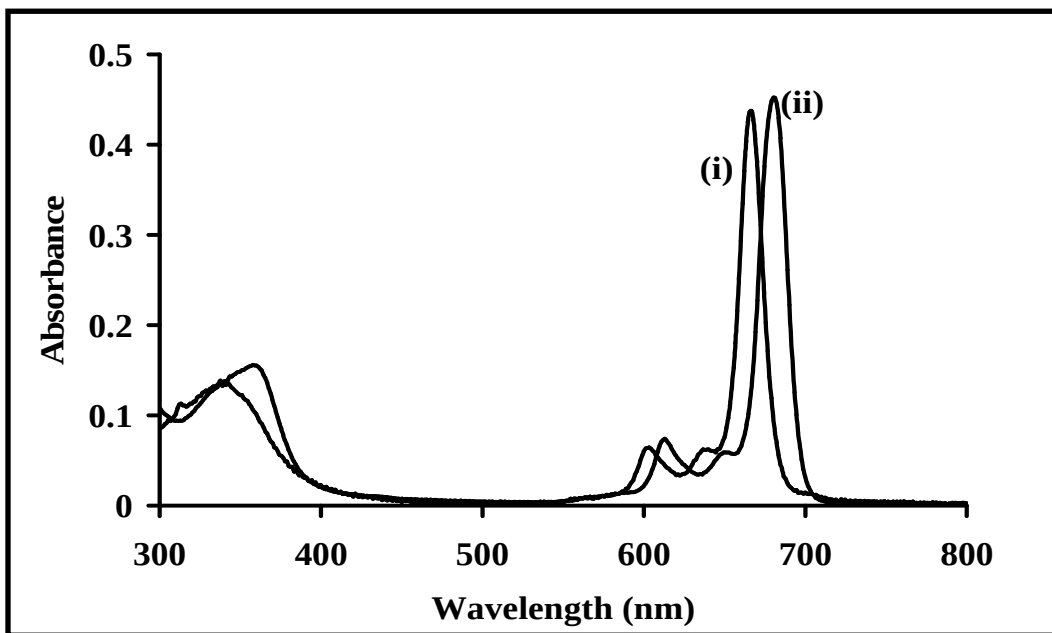
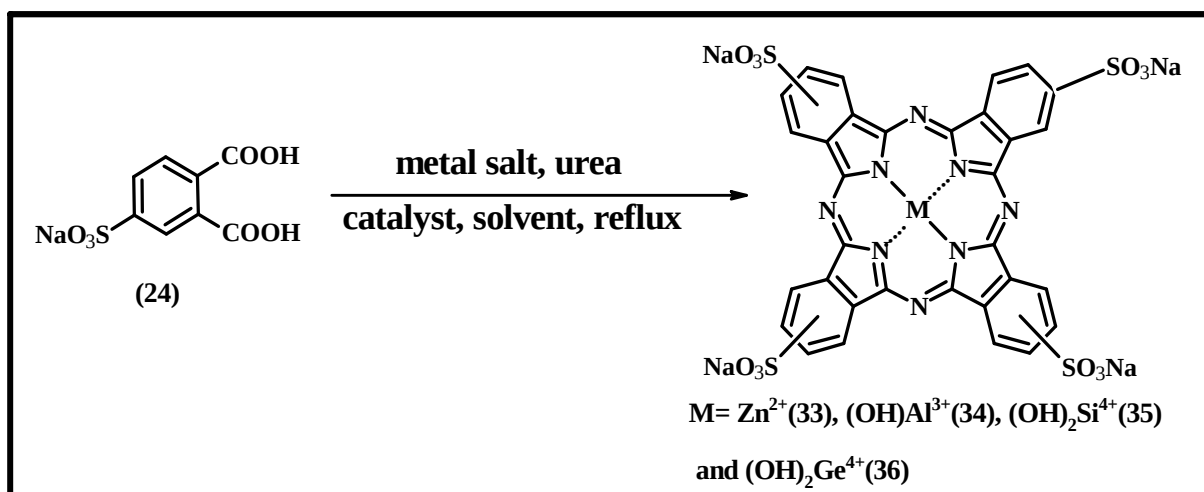


Figure 3.5: Electronic absorption spectra of (i) ZnPc (**32**) and (ii) ClAlPc (**31**) in DMSO. Concentration $\sim 10^{-6}$ M.

The tetra sulfonated MPc complexes (MPcS₄) were synthesized using literature methods [150,151] as shown in Scheme 3.3. Much has been reported on the zinc (**33**) and aluminium (**34**) complexes [234,325]. High yields of the complexes were obtained.

The characteristic S=O vibrations for MPcS₄ complexes were observed in the 1030 –



Scheme 3.3: Synthetic route to tetra sodium salt of Zn²⁺, (OH)Al³⁺, (OH)₂Si⁴⁺ and (OH)₂Ge⁴⁺ tetrasulfophthalocyanine (MPcS₄) [150,151].

1045 cm⁻¹ region in the IR spectra. The O-H band appeared at 3462 cm⁻¹ for AlPcS₄ (34), 3500 and 3533 cm⁻¹ for SiPcS₄ (35) and GePcS₄ (36) respectively. The bands due to M-O vibrations were very weak and were observed at 834 cm⁻¹ (Si-O) and 639 cm⁻¹ (Ge-O) for SiPcS₄ and GePcS₄ respectively. These spectral assignments are consistent with literature reports [150,151,302,326].

MPcS₄ complexes are soluble in water since they are negatively charged. They are generally known to exist as aggregates in equilibrium with monomers in aqueous solutions. The ground state electronic absorption spectra of the MPcS₄ complexes shown in Figure 3.6 confirms that the complexes are aggregated in aqueous medium with the formation of two main bands at ~ 680 nm due to the monomeric species and ~ 640 nm due to the aggregated species. AlPcS₄ (34) however showed much less aggregation.

Aggregation in MPc complexes is due to a coplanar association of rings, resulting in splitting and broadening of spectra, with a blue shifted peak at ~ 630 nm being due to the aggregate. These dimers are not chemically bonded but exist as loosely associated species

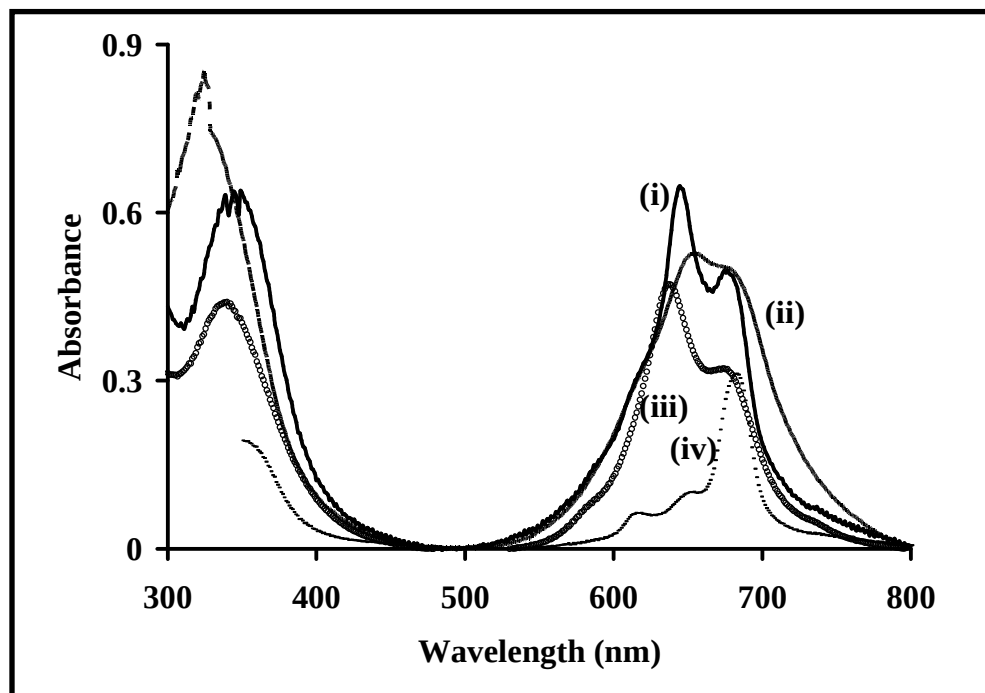


Figure 3.6: Electronic absorption spectra of the tetrasulfonated MPc complexes in PBS pH 7.4; (i) GePcS₄ (36) (ii) SiPcS₄ (35), (iii) ZnPcS₄ (33) and (iv) AlPcS₄ (34).

Concentration $\sim 10^{-6}$ M.

which can be dissociated by surfactants or in non-aqueous solvents. They are believed to be a result of association between the peripheral substituents of the phthalocyanine, which hold adjacent rings together in space. Also, water has been found to distinctively change the spectra of sulfonated compounds [125,212,308]. In this work, the unassociated species only began to appear at very low concentrations of about 10^{-7} M as shown with SiPcS₄ and GePcS₄ in Figures 3.7a and 3.7b respectively. Beer's law was obtained at concentrations lower than this value for these complexes.

Addition of a neutral surfactant drug carrier, cremophore EL (CEL), resulted in a decrease in the intensity of the band due to the aggregates with an increase in the intensity of the band due to the monomeric species (Figure 3.8 for SiPcS₄, (35)), which

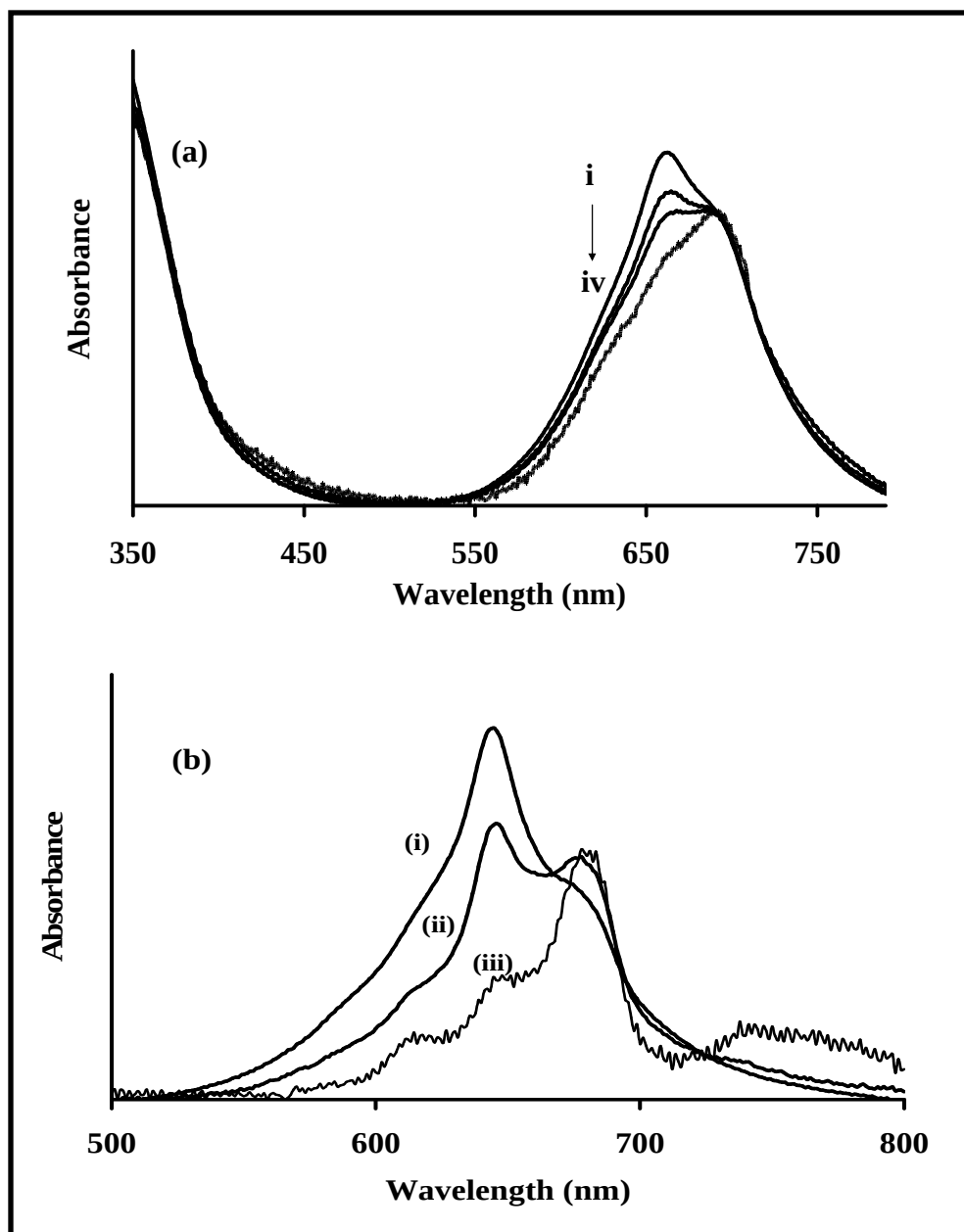


Figure 3.7: Electronic absorption spectra of SiPcS₄ (35) at (i) = 7.2×10^{-6} , (ii) = 3.1×10^{-6} , (iii) = 2.0×10^{-6} , (iv) = 5.1×10^{-7} M and (b) GePcS₄ (36) at (i) = 3.6×10^{-6} , (ii) = 1.2×10^{-6} , (iii) = 1.8×10^{-7} M in PBS pH 7.4.

confirms that the complexes are aggregated in aqueous solution with Q band maxima given in Table 3.4. The disaggregation of GePcS₄ (36) however occurred with time, Figure 3.9, and the final spectrum (dotted line) still showed some aggregation suggesting

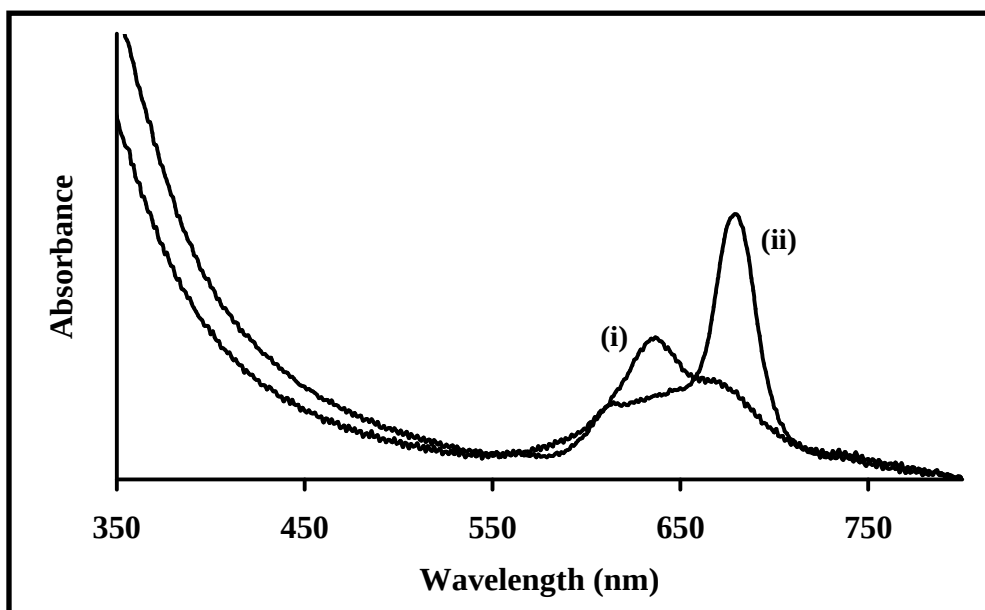


Figure 3.8: Electronic absorption spectra of 1.8×10^{-6} M SiPcS₄ (35) in PBS pH 7.4 (i) and (ii) in the presence of 4×10^{-3} M CEL.

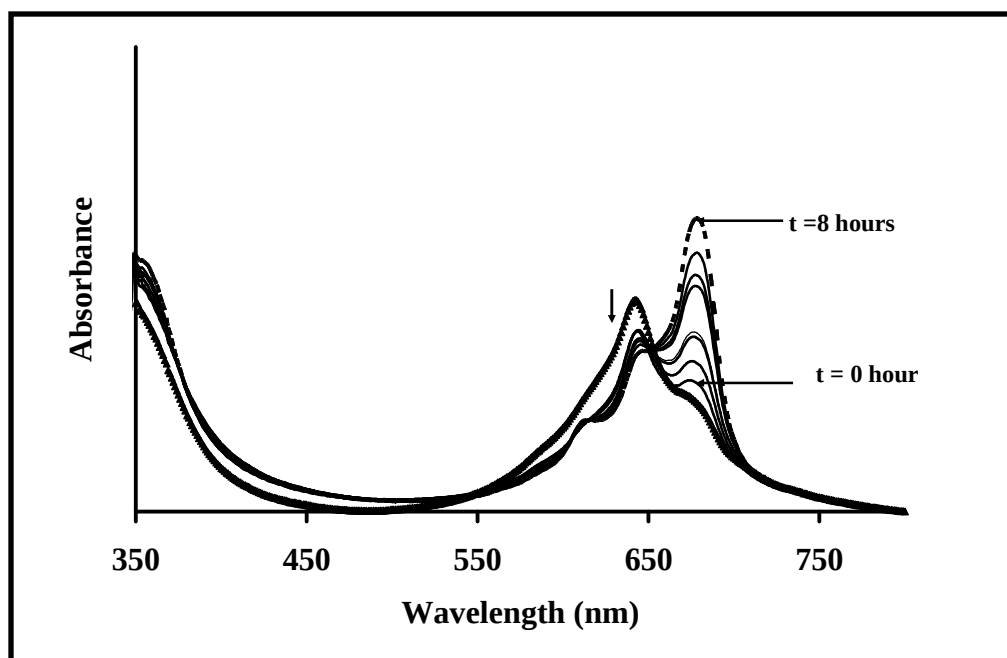


Figure 3.9: Electronic absorption spectrum of GePcS₄ (36) (1.7×10^{-6} M) (thick black line) disaggregating with time in PBS pH 7.4 in the presence of 4×10^{-3} M CEL, $t = 0$ to 8 hours. Dotted line shows the final spectrum.

Table 3.4: Spectral properties of sulfonated, carboxylated, quaternized and aminoalkanethio-substituted MPcs in aqueous and non-aqueous media.

Complexes	^a Solvent	^b λ_Q /nm	Log ϵ	Complex	^a Solvent	λ_Q /nm	Log ϵ
ZnPcS ₄ (33)	PBS	676,638	4.92	ZnOCPc (41)	PBS	693	5.25
	PBS+CEL	676	4.96		DMSO	707	5.18
	DMSO	680	^c 4.54	AlOCPc (42)	PBS	689	5.26
AlPcS ₄ (34)	PBS	680,636	5.23		DMSO	700	5.20
	PBS+CEL	680	5.23	SiOCPc (43)	PBS	691	5.10
	DMSO	682	5.01		DMSO	700	5.05
SiPcS ₄ (35)	PBS	679,636	4.96	GeOCPc (44)	PBS	697	5.15
	PBS+CEL	679	5.01		DMSO	703	5.12
	DMSO	679	4.44	47a	DMSO	717	5.30
GePcS ₄ (36)	PBS	680,646	4.83	48a	DMSO	696	5.19
	PBS+CEL	681	4.86	49a	DMSO	709	5.13
	DMSO	683	4.32	47b	PBS	653,692	4.96
ZnTCPc (37)	pH 10	694,642	4.84		PBS+CEL	703	5.02
	DMSO	690	5.00		DMSO	707	5.41
AlTCPc (38)	pH 10	682,646	4.98	48b	PBS	643,682	4.68
	DMSO	689	5.21		PBS+CEL	688	4.73
SiTCPc (39)	pH 10	702,640	4.11		DMSO	691	5.34
	DMSO	681	4.61	49b	PBS	661,700	4.85
GeTCPc (40)	pH 10	702,653	4.69		PBS+CEL	703	4.89
	DMSO	689	4.99		DMSO	707	5.37

^a CEL = cremophore EL, ^b λ_Q = wavelength of absorption, ^c[234].

that strong forces are responsible for the aggregation or that a high equilibrium between the monomer and the aggregated species occurs. It was also observed for GePcS₄ (**36**), that when the complex was left in aqueous solution for 5 days without the addition of the surfactant, disaggregation occurred, which suggests that it disaggregates by itself with time but since fresh solutions are needed for all experimental work, the results in this thesis are based on its aggregated form.

The increase in the low energy component of the Q band in the presence of CEL was used to calculate the degree of aggregation (% Agg) using Equation 1.5. SiPcS₄ (**35**) was estimated to have a value of 65.8% compared to GePcS₄ (**36**) (35.2%) or ZnPcS₄ (**33**) (49.1%) as shown in Table 3.5. The degree of aggregation for AlPcS₄ (**34**) was studied previously [155] and was found to be 37%. The high value of % Agg for **35** may lead to a low photoactivity of the complex in aqueous solution since aggregation diminishes the photosensitizing ability of MPc complexes. The low value of % Agg for **36** could be due to incomplete disaggregation which could not be achieved in CEL or organic solvent.

Equilibrium constant (K_D) for dimerization for SiPcS₄ (**35**) and GePcS₄ (**36**), calculated using Equation 1.11, given here as Equation 3.3 were found to be about the same except

$$Abs = \frac{[1 - \sqrt{(1 + 8K_D C)}][\epsilon_D/2 - \epsilon_M] + 2\epsilon_D K_D C}{4K_D} \quad (3.3)$$

for AlPcS₄ (**34**), Table 3.5, probably due to its less aggregated nature. K_D value for **34**, studied previously [213] in H₂O / 90% methanol was also found to be high (100×10^4). The values are high indicating that a strong association is occurring between the aggregates. The values of ϵ_D (Table 3.5) and ϵ_M (Table 3.4) are within the range reported for some MPc complexes [207,209].

The tetrasulfonated complexes showed strong monomeric Q band in DMSO, Figure 3.10

with absorption maxima given in Table 3.4, however, GePcS₄ (**36**) remains slightly broadened. ZnPcS₄ (**33**) and AlPcS₄ (**34**) show similar monomeric behaviour as SiPcS₄

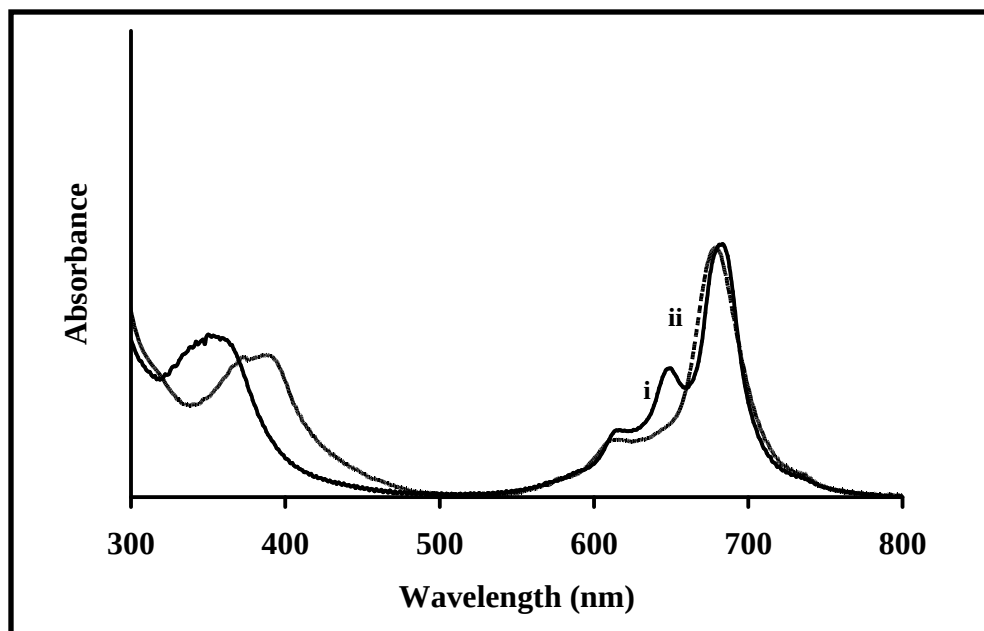


Figure 3.10: Electronic absorption spectra of the sulfonated MPc complexes in DMSO; (i) GePcS₄ (**36**) (ii) SiPcS₄ (**35**) (10^{-5} M).

Table 3.5: Aggregation parameters of sulfonated and cationic MPc complexes

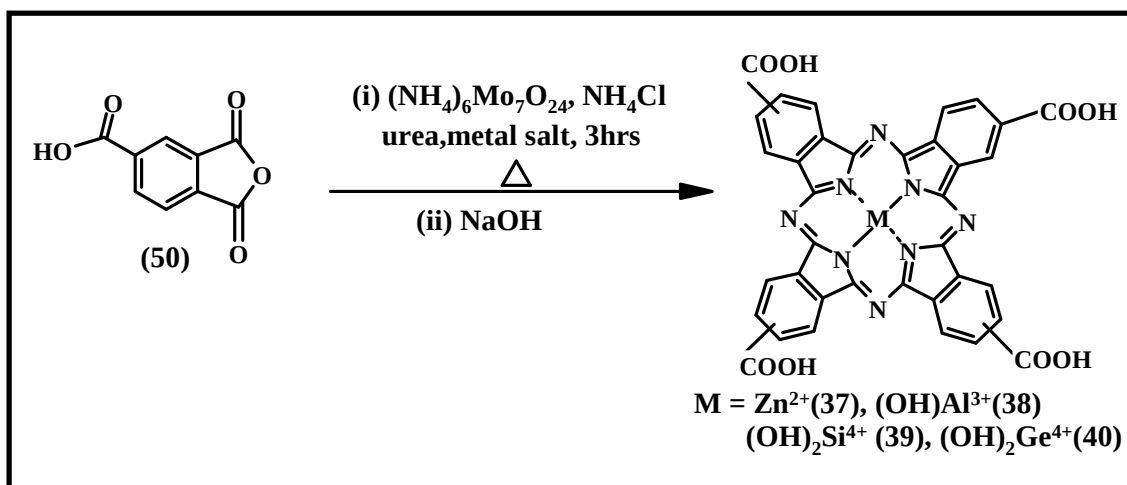
Complex	Solvent	%Agg	Log ϵ_D	$K_D (\times 10^4)$ $\text{dm}^3 \text{mol}^{-1}$
ZnPcS ₄ (33)	PBS+CEL	49.1	4.55	1.10
AlPcS ₄ (34)	PBS+CEL	37.0 ^a	-	15.0
SiPcS ₄ (35)	PBS+CEL	65.8	4.69	1.98
GePcS ₄ (36)	PBS+CEL	35.2	4.53	1.99
α -TZnPcQ (47b)	PBS+Methanol	54.1	4.29	1.01
β -TZnPcQ (48b)	PBS+Methanol	65.5	3.99	1.61
β -OZnPcQ (49b)	PBS+Methanol	73.4	4.14	1.82

^a [155]

(35). Aggregated MPcs are expected to disaggregate and exhibit monomeric behaviour in organic solvents [166,327], the behaviour of GePcS₄ (36) suggests that complete disaggregation was not achieved in DMSO for (36) which may be due to the fact that some of the forces responsible for the aggregation may be too strong to be broken by the organic solvent, DMSO.

3.2.2 Carboxy MPcs

The tetracarboxy metallophthalocyanine (MTCPC) complexes of zinc (37), aluminium (38) silicon (39) and germanium (40) were synthesized by direct condensation of trimellitic acid anhydride (50), urea and the respective metal chloride to form a tetra-amide with subsequent treatment with 1 M NaOH to form the MTCPC complexes (37-40) in moderate yields using established synthetic procedures according to Scheme 3.4 [316,317]. The complexes gave satisfactory spectroscopic characterization. Characteristic bands, O-H, C-O, C=O appeared at ~3400, 1700 and 1200 cm⁻¹ respectively for the complexes. The solubility of the MTCPC complexes was achieved in aqueous medium at pH 10 and the complexes were highly aggregated as seen from the broadness of their



Scheme 3.4: Synthetic route to tetracarboxymetallophthalocyanine (MTCPCs).

spectra, except for the AlTCpC (**38**) which showed much less aggregation as shown in Figure 3.11. Addition of a surfactant CEL, to the aqueous solutions of ZnTCpC (**37**) and

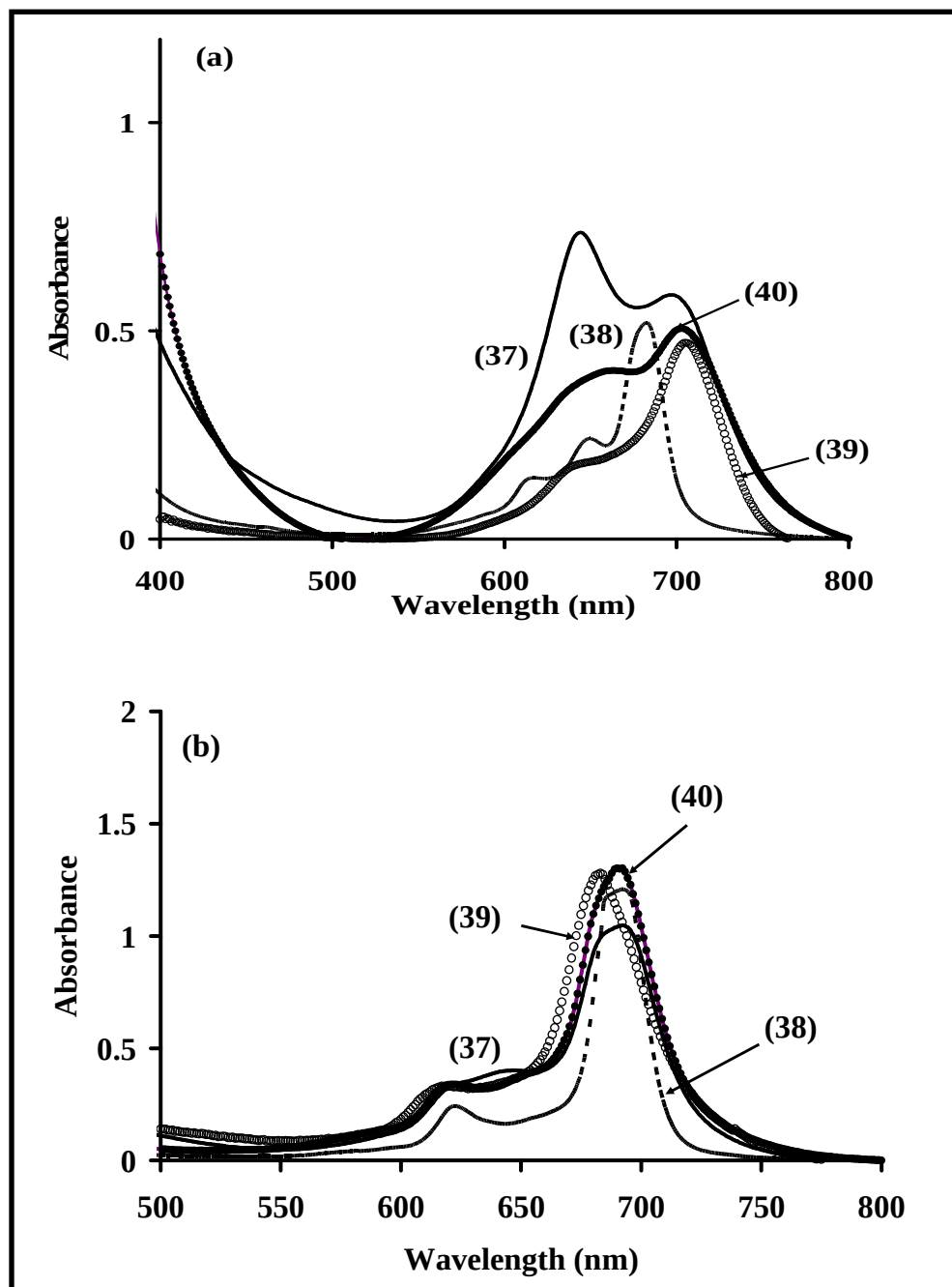


Figure 3.11: Electronic absorption spectra of MTCpC complexes 37-40 in pH 10 solution (a) and (b) DMSO ($\sim 10^{-6}$ M), **37** ZnTCpC; **38** AlTCpC; **39** SiTCpC and **40** GeTCpC.

AlTCpC (**38**) resulted in a decrease in the intensity of the band due to the aggregates with an increase in the intensity of the band due to the monomeric species (Figure 3.12 for ZnTCpC **37**), which confirms aggregation, though the MTCPc did not become totally monomeric. There was no noticeable change in the shape and intensity of the spectra of

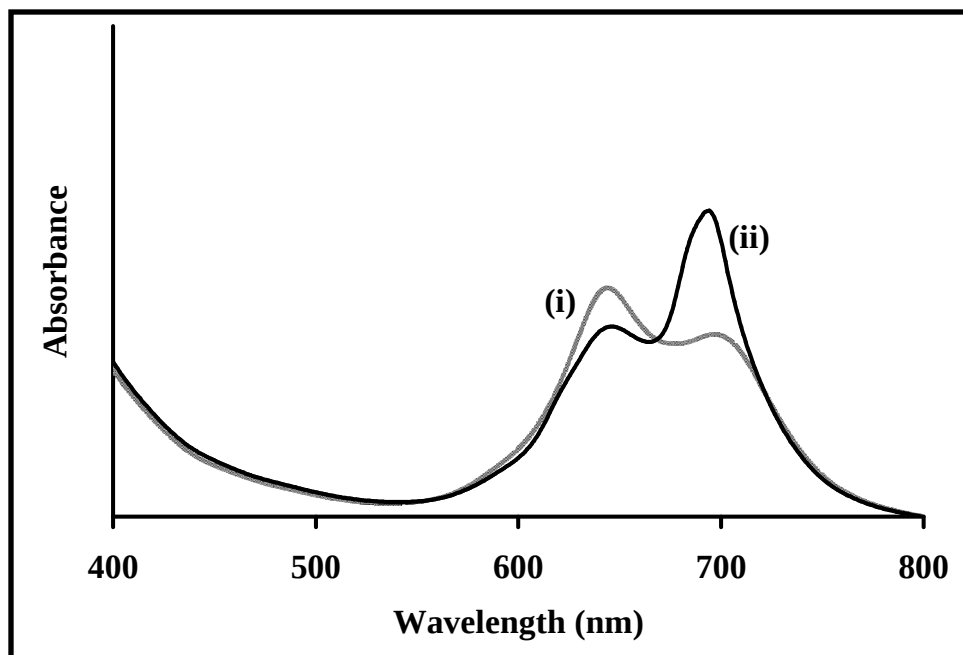
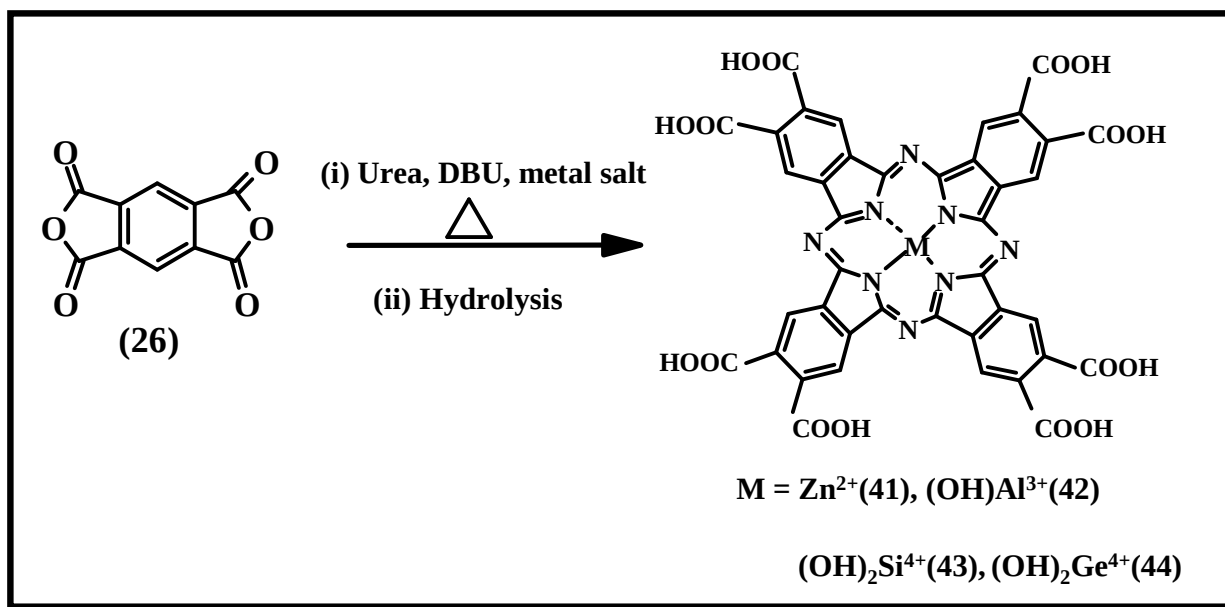


Figure 3.12: Electronic absorption spectra of 7.2×10^{-6} M ZnTCpC (**37**) in PBS pH 10 (i) and (ii) in the presence of 4×10^{-3} M CEL.

39 and **40** on addition of CEL; this would have suggested that these complexes are in their monomeric states as it has been reported before for Si and GePcS_{mix} [166] and that the broadness of their spectra may be due to distortion of symmetry [328]. However, when the MTCPc complexes were dissolved in DMSO, they showed more monomeric behaviour, Figure 3.11 (absorption maxima in Table 3.4) with some broadness still evident for some complexes. It can therefore be inferred that strong aggregation that can not be easily broken by a neutral surfactant occurs in these complexes. The absorption

maxima of the bands due to the monomeric species for these complexes were red shifted in aqueous medium, compared to their absorption maxima in DMSO, Table 3.4 with the exception of AlTCPc. The exciton coupling theory explains that aggregation of symmetrically substituted Pcs gives rise to pronounced spectral changes that extend from broadening to an observed splitting of the Q band [178], indicating presence of additional electronic levels of the aggregates and that there are few cases when symmetry forbidden transitions to the lower energy LUMO may occur (see Figure 1.20) to a small extent even though it is forbidden, thus resulting in a wide absorption spectrum or red-shifting of the spectrum [180]. This may explain the behaviour of these MTCPcs. Moreover, tetrasubstituted MPcs are known to be a mixture of constitutional isomers [148] hence their observed behaviour in solvents that allow coplanar association of the rings.

Syntheses of the octacarboxy metallophthalocyanine (MOCPC) complexes (**41-44**) were carried out using established methods from literature [152,153] (Scheme 3.5). Generally, low yields of the complexes were obtained. The FTIR data of the complexes showed characteristics bands of the complexes such as the O-H, C=O and C-O at ~ 3420 , 1705 and 1190 cm^{-1} which are in good agreement with reported values [153]. MOCPC complexes are characterized by their monomeric sharp Q bands with no aggregation Figure 3.13 which is in contrast to most water-soluble MPcs. MPcs octasubstituted with carboxylic groups at the periphery have been found to be monomeric in aqueous solution especially within the pH range of 6-10 [329, 330]. This was explained to be due to full ionization of the carboxylate groups at this pH range. However, a similar study with the phthalocyanine tetrasulfonate analogs showed that they remain aggregated at this pH range despite being ionized. It was therefore concluded that the monomerization



Scheme 3.5: Synthetic route to octacarboxymetallophthalocyanine (MOCPCs) [152,153].

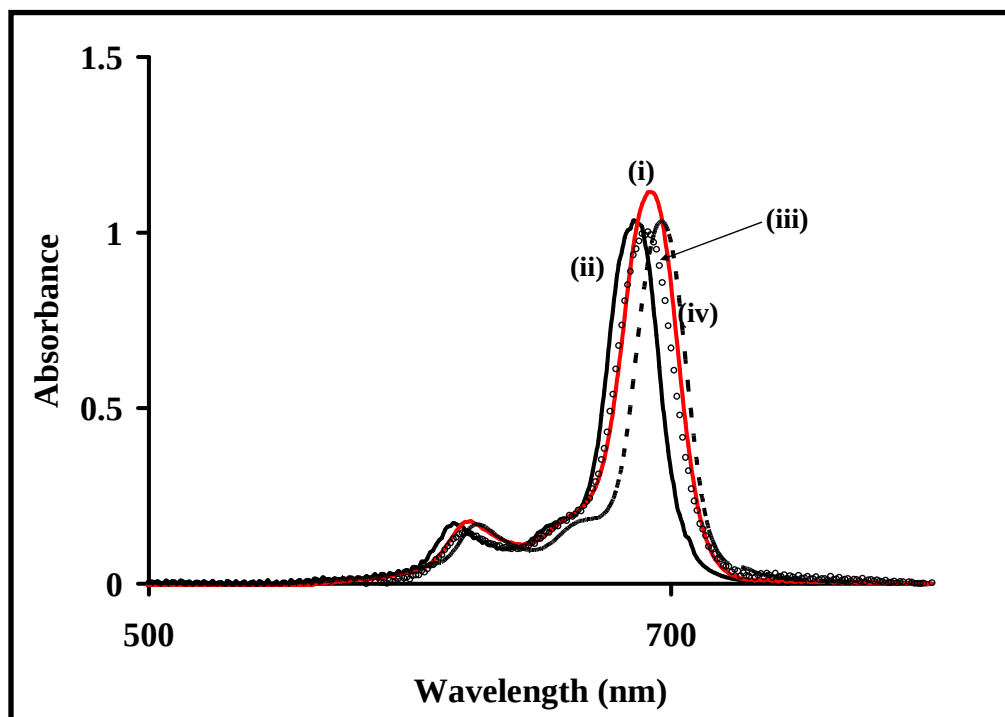


Figure 3.13: Electronic absorption spectra of the MOCPC complexes in PBS pH 7.4; (i) ZnOCPC (41), (ii) AlOCPC (42), (iii) SiOCPC (43) and (iv) GeOCPC (44) (10^{-6} M).

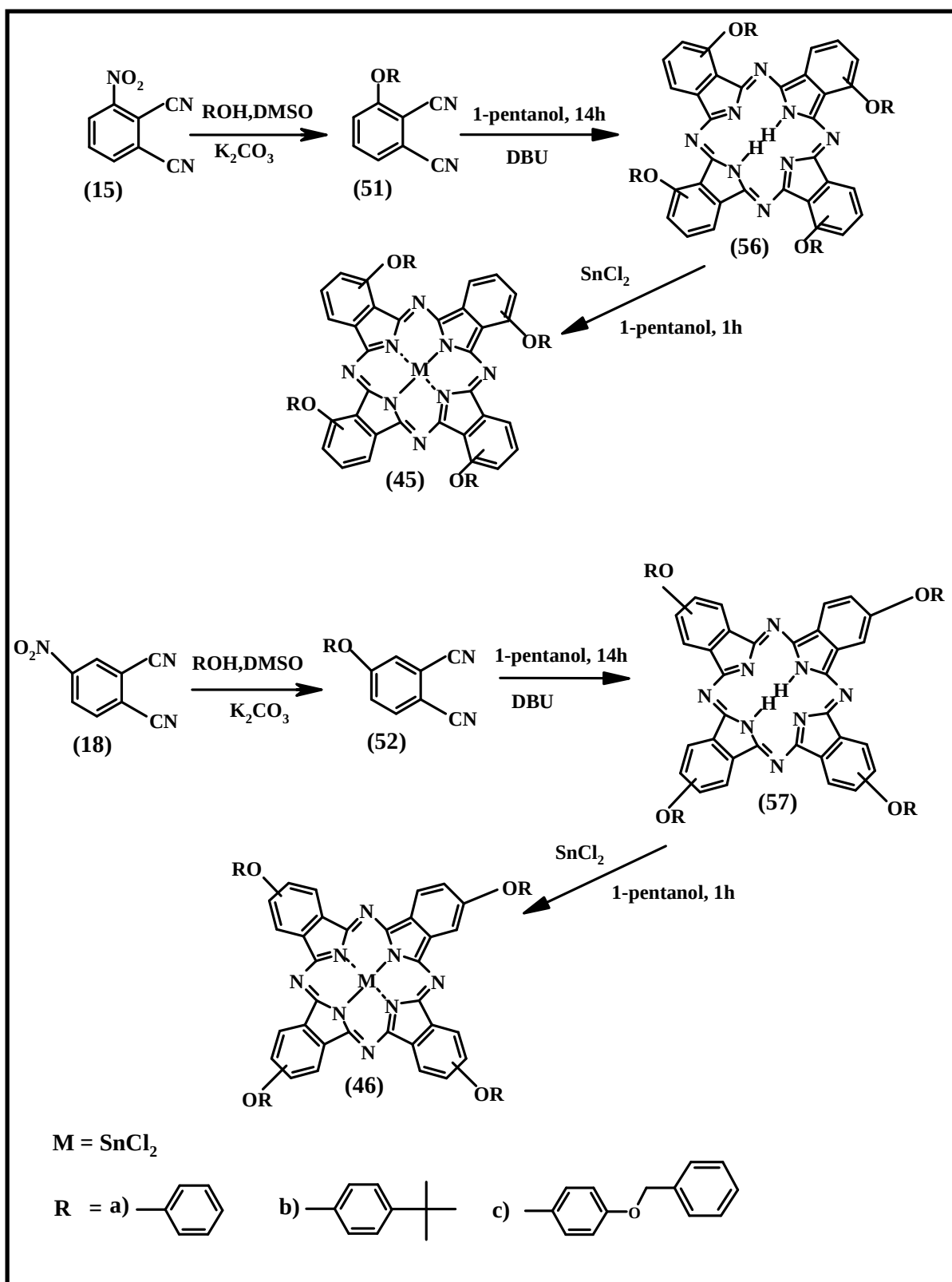
experienced with the phthalocyanine octacarboxylates may reside in the plurality of the substituents since it has eight peripheral carboxylate groups [329]. The MOCPCs showed monomeric behaviour both in PBS pH 7.4 and DMSO with absorption maxima shown in Table 3.4. The MOCPCs are red-shifted in DMSO compared to aqueous medium, thereby showing an opposite trend to the MTCPcs. The MOCPCs are also red-shifted by 11-19 nm respectively, when compared to their corresponding MTCPc complexes in DMSO, these red shifts are likely due to the greater number of substituents the octasubstituted complexes carry.

3.2.3 Aryloxy and aminoalkanethio-substituted metallophthalocyanine complexes

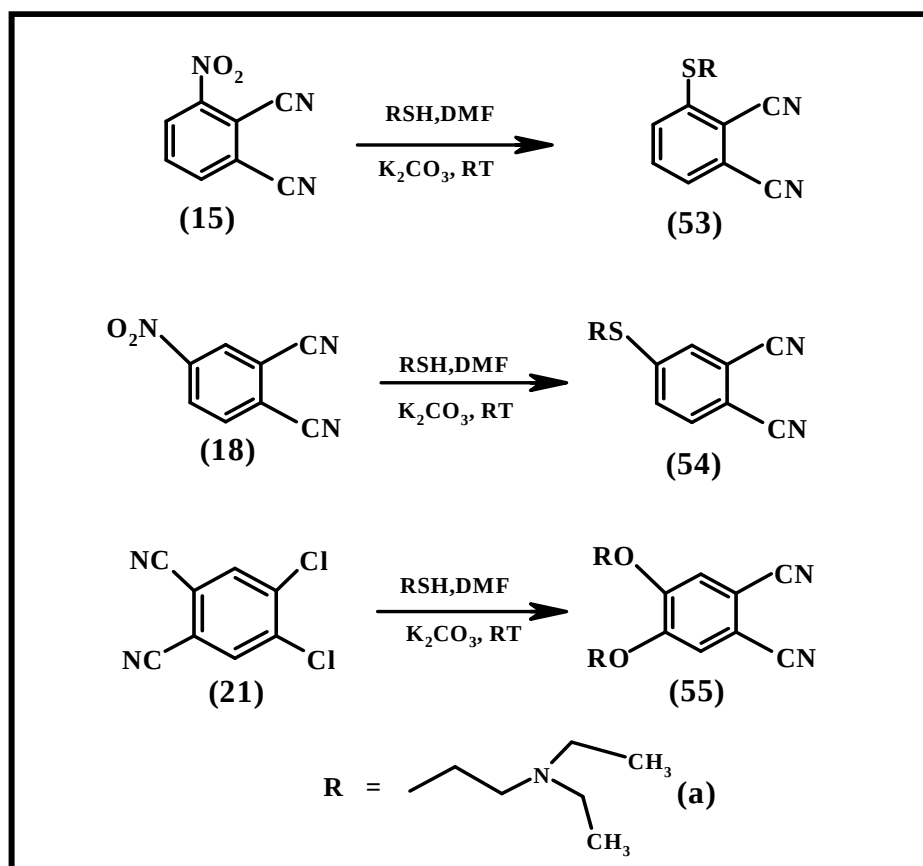
3.2.3.1 Phthalonitriles

The syntheses of monosubstituted: phenoxy, 4-*tert*-butylphenoxy, 4-(benzyloxy) phenoxy or diethylaminoethylsulfanyl phthalonitrile (**51a-c**, **52a-c**, Scheme 3.6, **53a** and **54a**, Scheme 3.7) and 4,5-disubstituted diethylaminoethylsulfanyl phthalonitrile (**55a**) Scheme 3.7, were achieved by base (K_2CO_3) catalysed nucleophilic substitution of nitro or chloride groups in the tetra (**15** or **18**) and octa (**21**) substituted phthalonitriles respectively using the appropriate substituent. The substitution was performed at room temperature under nitrogen according to published methods [160,318-320]. Satisfactory yields were obtained for these compounds.

The characteristic $C\equiv N$ stretches in the IR spectra were observed at $\sim 2300\text{ cm}^{-1}$ and the substituted phthalonitriles were pure by ^1H -NMR as shown in the experimental section with their proton NMR correctly corresponding to the number of expected protons.



Scheme 3.6: Synthetic routes to tin (IV) phthalocyanines tetra-substituted at the α (45a – c) and β (46a – c) positions.



Scheme 3.7: Synthetic routes to mono 53a, 54a and disubstituted 55a, diethyl aminoethylsulfanyl phthalonitrile.

3.2.3.2 Aryloxy substituted tin (IV) metallophthalocyanines

Peripherally and non-peripherally tetra substituted aryloxy metal free MPC complexes were synthesized by cyclotetramerization of the corresponding substituted phthalonitriles [100]. 4-Tetra-substituted phthalocyanines were obtained from 4-substituted phthalonitriles while 3-tetra-substituted phthalocyanines are obtained from 3-substituted phthalonitriles. The metal-free substituted phthalocyanines (**56a-c** or **57a-c**), were afforded in high yields by refluxing complexes **51a-c** or **52a-c** for 14 hrs in pentan-1-ol in the presence of DBU, a strong organic base, Scheme 3.6. The tin (IV) MPC complexes (**45a-c** or **46a-c**) were synthesized by the metallation of their corresponding metal free

analogues. Metallation proceeded by refluxing the metal-free derivatives in the presence of tin (II) chloride in pentan-1-ol for an average of 1 hr. A change in colour from blue to dark green and the total collapse of the split Q band for **56a-c** or **57a-c** to a single Q band indicated a complete reaction. A high boiling solvent (pentan-1-ol) was used to insert the metal into the core of the ring because tin is a large atom. The insertion method was employed because tin complexes are known to afford a lot of impurities when cyclotetramerization takes place in the presence of the metal salt [168].

In general, the synthesis of SnPc complexes using SnCl₂ may result in the formation of Sn(II)Pc or (Cl)₂Sn(IV)Pc species depending on the amount of SnCl₂ used in the reaction [302]. With excess SnCl₂, Sn(II)Pc derivatives are formed. In this work, a ratio of 1:1 (SnCl₂: **56a**, **56b**, **56c**, **57a**, **57b** or **57c**) was employed, resulting in the formation of the (Cl)₂Sn(IV)Pcs (**45a**, **45b**, **45c**, **46a**, **46b** and **46c**). The complexes were purified by column chromatography by making the eluent slightly polar using CH₂Cl₂: MeOH (30:1) (this allowed the mobility of the complexes on the silica gel column) to afford the MPcs with yields ranging from 30% to 55%. All the complexes were soluble in organic solvents such as CH₂Cl₂, CHCl₃, THF, toluene, and DMSO due to the presence of the substituents. The phenoxy, tert-butylphenoxy and benzyloxyphenoxy groups were tetra-substituted at the α and β positions of the ring for comparative purposes. The complexes were characterized by various spectroscopic methods; IR, UV-vis, ¹H NMR and elemental analysis and were in agreement with the predicted structures as shown in the experimental section (Chapter 2). The characteristic nitrile (C $\equiv$ N) stretch at $\sim$ 2230 cm⁻¹ of **51a-c** and **52a-c** disappeared upon formation of the phthalocyanine. Upon metallation, the N-H stretching frequency at $\sim$ 3300 cm⁻¹ disappeared. All the complexes showed

peaks between 1000 and 700 cm^{-1} which may be assigned to phthalocyanines skeletal vibrations [331]. The complexes showed characteristic vibrations due to ether groups (C–O–C) at 1231–1255 cm^{-1} , aliphatic CH stretching at ca. 2920–2996 cm^{-1} and aromatic CH stretching at ca. 3014–3038 cm^{-1} as shown in Figure 3.14 for complex **45b** ($\alpha\text{SnPcTbtPh}$).

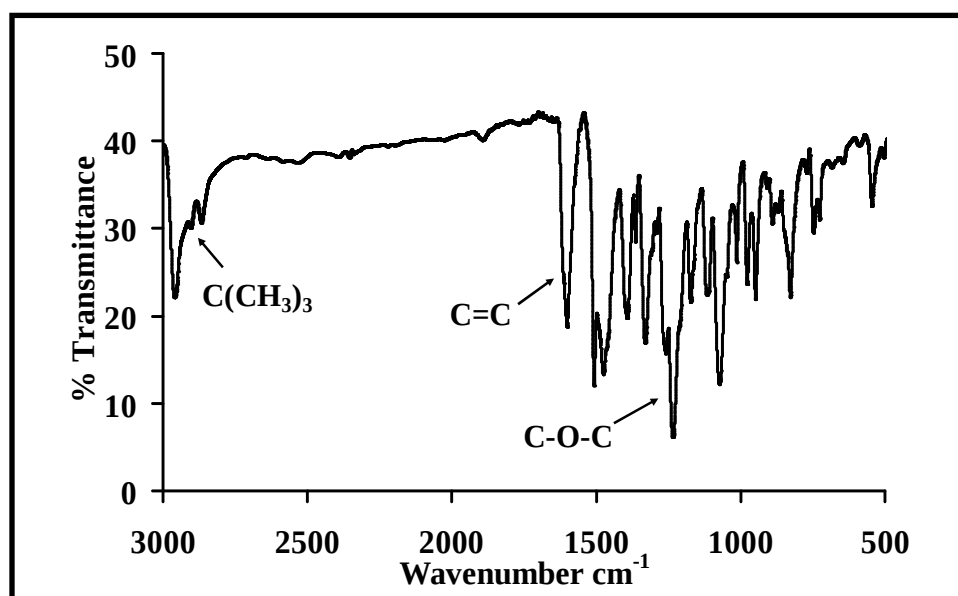


Figure 3.14: Infrared spectrum of $\alpha\text{SnPcTbtPh}$ (45b**).**

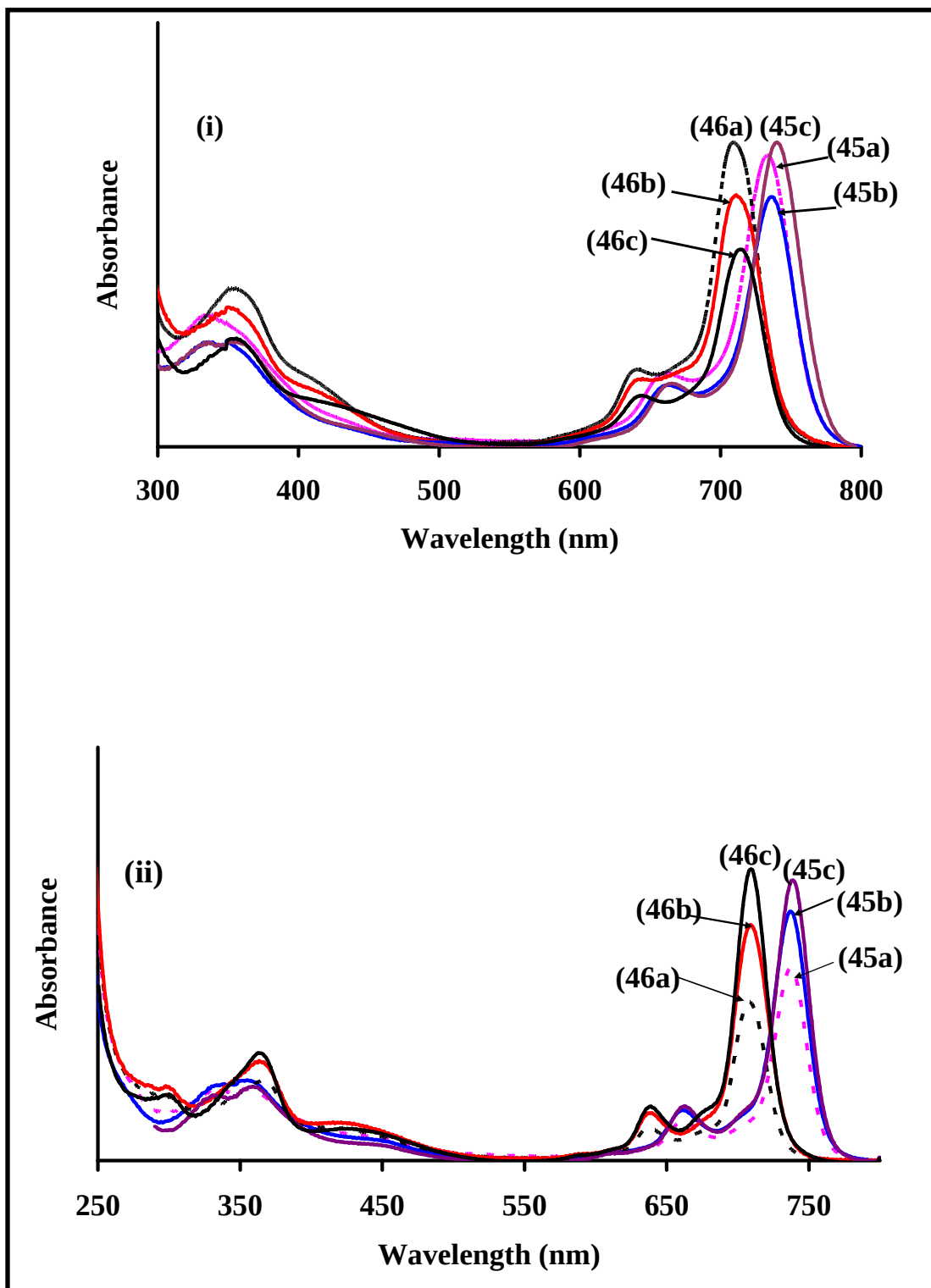
The ^1H NMR spectra for the MPc complexes were complex and similar. Although the presence of isomers for tetra-substituted complexes as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals [332], the observed spectra of the complexes were relatively well resolved. Complex **45a**, (αSnPcPh), showed three sets of multiplets at 8.95–9.37, 8.04–8.25 and 7.65–7.79 ppm for the phthalocyanine ring protons, integrating for four protons each. The phenyl protons were observed as multiplets at 7.16–7.46 ppm integrating for 20 protons. Complex **45b**, $\alpha\text{-SnPcTbtPh}$, also gave similar signals with the 3 sets of multiplets each integrating for 4 protons for Pc ring at 9.24–9.38, 8.89–9.08 and

8.01-8.25 ppm, 16 protons for phenyl at 7.55–7.80 ppm and a multiplet integrating to 36 protons for methyl (t-Bu) protons at 1.29-1.46 ppm. The ^1H NMR spectra of βSnPcPh (**46a**) and $\beta\text{SnPcTbtPh}$ (**46b**) showed similar spectral features as that of **45a** and **45b** with the methyl (t-Bu) protons occurring as a singlet in **46b** and integrating to 36 protons at 1.39 ppm. The resonances belonging to the aromatic protons were observed as multiplets between 8.08-9.37 and 7.06-7.44 ppm for complex **45c** ($\alpha\text{SnPcBzPh}$) and between 7.36-9.22 and 6.73-7.08 ppm for complex **46c** ($\beta\text{SnPcBzPh}$), integrating for a total of 48 protons for each complex as expected for aromatic protons. The protons were slightly more deshielded for the α substituted complexes.

The ground state electronic absorption spectra of the tin (IV) MPc complexes in various organic solvents showed monomeric behaviour evidenced by a single Q band, typical of metallated phthalocyanine complexes (Figure 3.15) [125]. The Q bands were observed in the near infrared region between 701 to 740 nm with the B bands between 332 and 364 nm in all the solvents Table 3.6. An additional broad band was observed between 400 to 460 nm, which may be due to charge transfer from the electron-rich ring to the central metal, this band was more pronounced in the β - substituted complexes compared to their α -substituted counterparts.

The Q bands of the α -tetra-substituted complexes (**45a**, **45b** and **45c**) were red-shifted by 22 - 27 nm in DMSO, when compared to the corresponding β -tetrasubstituted (**46a**, **46b** and **46c**) in the respective solvents. Bathochromic shifts are known to occur into the near infrared region on substitution of the Pc ring with electron-donating groups, with a greater effect observed when the substitution is at the non-peripheral (α) positions [333,334]. This has been documented [129] to be due to a greater destabilization effect

of the HOMO level at the α position compared to the β position since linear combinations of the atomic orbitals (LCAO) coefficient at the α positions of the HOMO



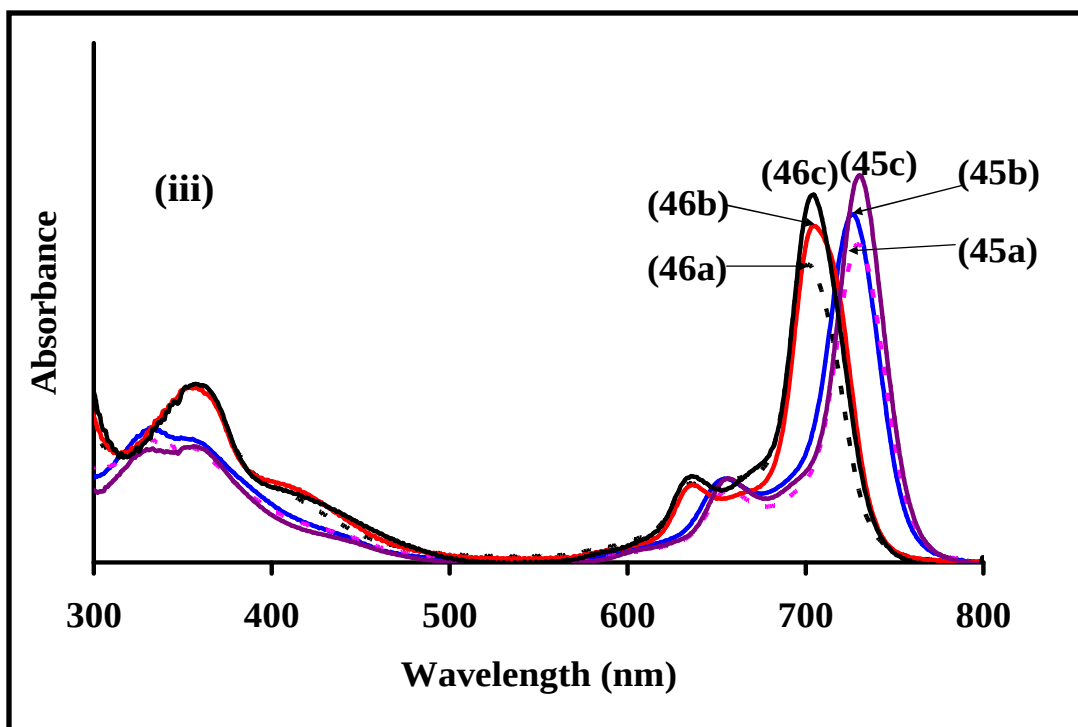


Figure 3.15: Electronic absorption spectra of α , 45a-c and β , 46a-c tetra-substituted phenoxy (a), tert-butylphenoxy (b) and benzyloxyphenoxy (c) complexes in (i) DMSO; (ii) CHCl_3 and (iii) THF ($\sim 4 \times 10^{-6} \text{ M}$).

level is greater than those at the β positions. This results in a decreased energy gap between the HOMO and LUMO levels and a subsequent bathochromic shift. The Q band maxima of the complexes were also found to increase in the order, phenoxy < tert-butylphenoxy < benzyloxyphenoxy- substituted derivatives in DMSO, Table 3.6. This may be due to the increase in electron donating ability of these substituents as we move from phenoxy to benzyloxyphenoxy. It can be observed from an overview of the complexes that the shortest Q band maximum absorption wavelengths are obtained in THF, while the longest are obtained in chloroform and/or DMSO, Table 3.6. This observation can be explained partly by considering the refractive indices of the solvents. It has been observed that red-shifting of absorption spectra is a function of the solvent's

Table 3.6: Spectral data of tin (IV) MPc complexes in different solvents.

Complex	Solvent	λ_Q /nm	λ_B /nm
α -SnPcPh (45a)	DMSO	733	339
	THF	727	333,357
	CHCl ₃	737	347
	DCM	732	345
	Toluene	730	332,357
α -SnPcTbtPh (45b)	DMSO	737	343
	THF	730	331,356
	CHCl ₃	737	347
	DCM	733	349
	Toluene	732	331,359
α -SnPcBzPh (45c)	DMSO	740	336,358
	THF	730	333,356
	CHCl ₃	739	331,359
	DCM	737	332,358
	Toluene	735	333,359
β -SnPcPh (46a)	DMSO	709	356
	THF	701	354
	CHCl ₃	709	366
	DCM	707	359
	Toluene	706	357

Table 3.6 contd.

Complex	Solvent	λ_Q / nm	λ_B /nm
β -SnPcTbtPh (46b)	DMSO	710	349
	THF	704	356
	CHCl ₃	710	363
	DCM	709	358
	Toluene	707	359
β -SnPcBzPh (46c)	DMSO	715	356
	THF	705	357
	CHCl ₃	709	364
	DCM	710	358
	Toluene	708	356

refractive index [177]. The B bands are broad in some cases due to the superimposition of the B₁ and B₂ bands in the 330-360 nm region [334]. The β substituted complexes exhibit a rarely observed N-band (Figure 3.15(ii)) in the UV transparent solvents; CH₂Cl₂ and CHCl₃. This arises from the deeper π levels due to LUMO transitions [334]. High molar extinction coefficients were obtained in DMSO and the complexes showed monomeric behaviour up to $\sim 1 \times 10^{-5}$ M in all solvents.

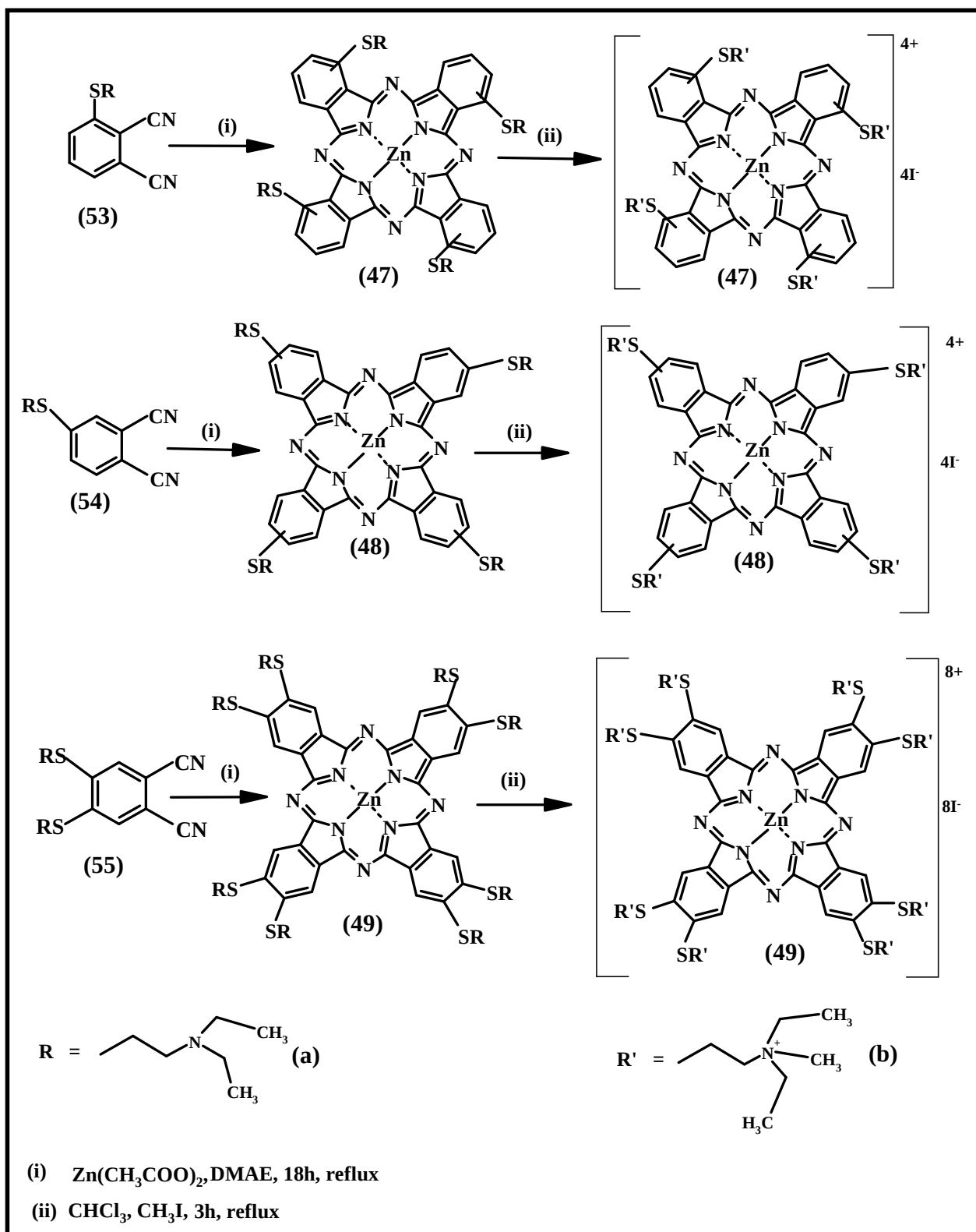
3.2.3.3 Aminoalkanethio-substituted zinc (II) metallophthalocyanines

Peripherally and non-peripherally tetra and peripherally octa 2-diethylaminoethanethio-substituted zinc metallophthalocyanine complexes were synthesized by

cyclotetramerization of the corresponding substituted phthalonitriles (**53a**, **54a** or **55a**) in the presence of zinc acetate (Scheme 3.8). The complexes (**47a**, **48a** or **49a**) were obtained in good yields. The 2-diethylaminoethanethio substituents on the complexes are suitable for conversion into quaternary ammonium groups which can increase the products' solubility in water. Compounds **47b**, **48b** or **49b** were obtained by methylation of **47a**, **48a** or **49a** respectively in CHCl_3 (Scheme 3.8) in good yields.

The non-ionic complexes (αTZnPc **47a**, βTZnPc **48a** or βOZnPc **49a**) were soluble in organic solvents such as THF, toluene, and DMSO and the ionic complexes (αTZnPcQ **47b**, βTZnPcQ **48b** or βOZnPcQ **49b**) were highly soluble in polar solvents like water, methanol and DMSO. The complexes were characterized by IR, UV-Vis, ^1H NMR and mass spectra which were found to be consistent with predicted structures as shown in the experimental section. The characteristic nitrile ($\text{C}\equiv\text{N}$) stretch at $\sim 2225\text{ cm}^{-1}$ of (**53a**, **54a** or **55a**) disappeared upon formation of the phthalocyanine. The ^1H NMR spectra of the complexes showed ring protons between 8.99 - 9.36 ppm with the substituent protons observed between 1.21 ppm and 4.09 ppm. Integration of the peaks correctly corresponded to the expected number of protons for each complex. The observed spectra of the complexes were relatively well-resolved except for the peaks corresponding to protons attached to the sulphur or nitrogen groups and this is consistent with literature [161]. **49a** and **49b** are known [160] and they gave satisfactory spectroscopic analyses as in literature.

The ground state electronic absorption spectra of (αTZnPc **47a**, βTZnPc **48a** or βOZnPc **49a**) and (αTZnPcQ **47b**, βTZnPcQ **48b** or βOZnPcQ **49b**) showed monomeric behaviour in DMSO evidenced by a single Q band, typical of metallated phthalocyanine

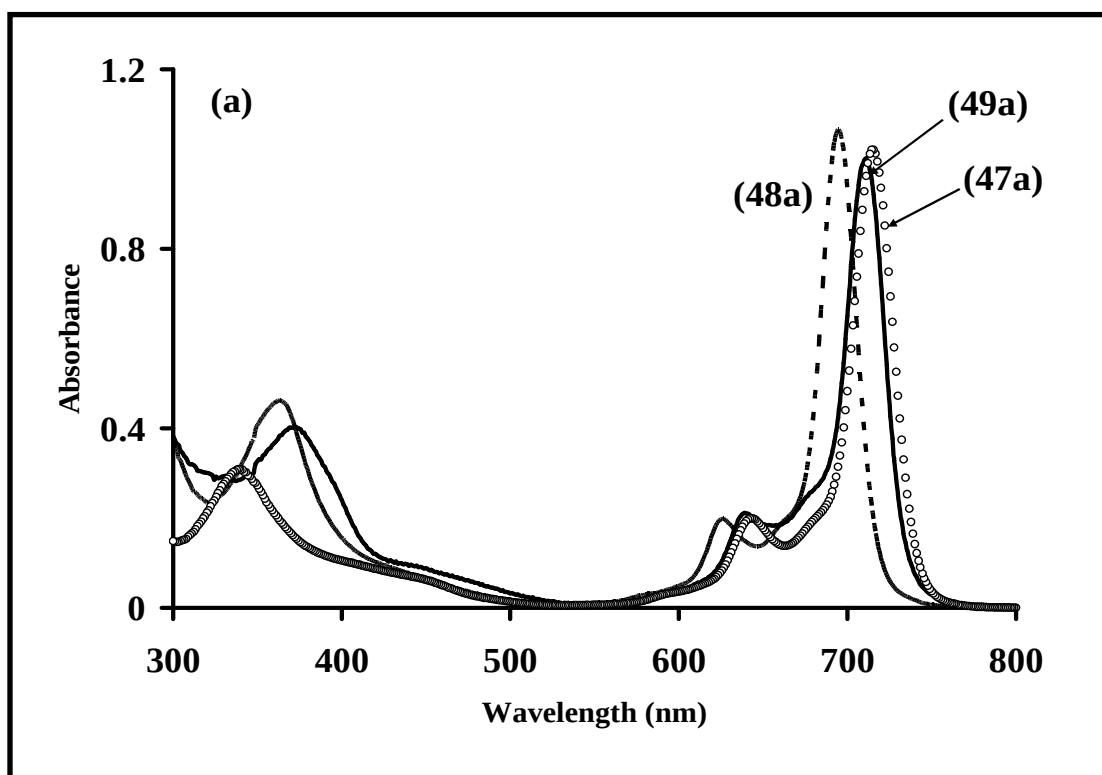


Scheme 3.8: Synthetic route to 2-diethylaminoethanethio- (a) and quaternized 2-diethylaminoethanethio- (b) substituted zinc (II) phthalocyanine complexes.

complexes (Figure 3.16a and b) [125]. The Q bands were observed in the near infrared region between 691 and 717 nm, Table 3.4 with the B bands between 340 to 380 nm in DMSO.

The Q bands of the α -tetrasubstituted complexes (**47a** and **47b**) are red-shifted by 16 and 21 nm, when compared to the corresponding β -tetrasubstituted (**48a** and **48b**) complexes in DMSO. Octa β substituted complexes **49a** and **49b**, showed red shifted spectra compared to the tetra β substituted complexes (**48a** and **48b**). The complexes showed monomeric behaviour up to $\sim 1 \times 10^{-5}$ M in DMSO.

On quaternization, blue shifts of about 2-10 nm was observed in complexes α TZnPcQ **47b**, β TZnPcQ **48b** or β OZnPcQ **49b** when compared to their corresponding non-ionic forms (α TZnPc **47a**, β TZnPc **48a** or β OZnPc **49a**) in DMSO (Table 3.4). This is due to the reduced electron donating ability of the nitrogen groups when quaternized. The



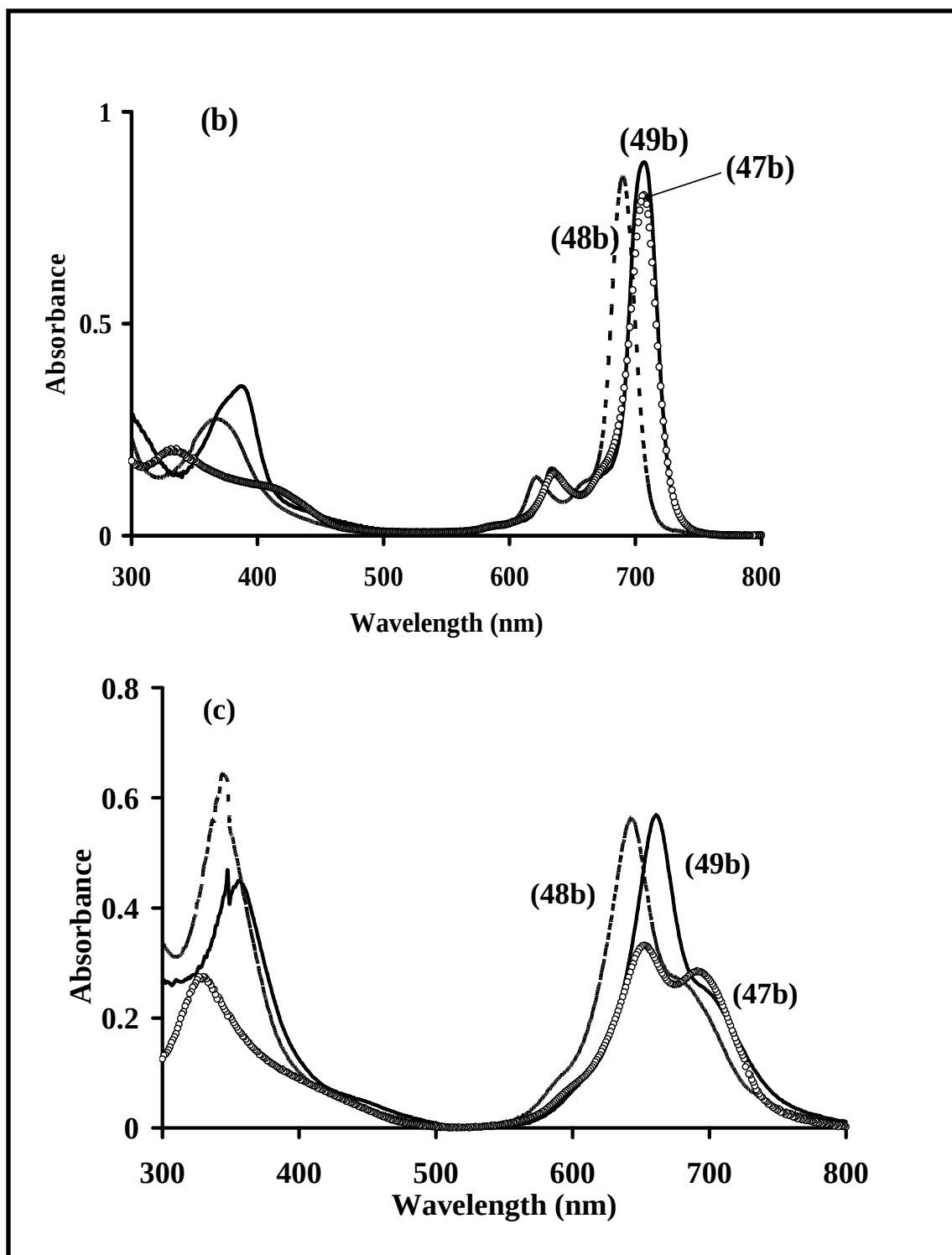


Figure 3.16: Electronic absorption spectra of: (a) 47a, 48a and 49a; (b) 47b, 48b and 49b in DMSO (5×10^{-6} M); (c) 47b, 48b and 49b in PBS pH 7.4 ($\sim 4 \times 10^{-6}$ M).

quaternized complexes, (**47b**, **48b** or **49b**) are highly soluble in aqueous medium but were aggregated Figure 3.16c with the formation of two main bands at $\sim 680 - 700$ nm (not well resolved for the β substituted complexes **48b** and **49b**) due to the monomeric species and $\sim 640 - 660$ nm due to the aggregated species, respectively. This must have been due to the coplanar association of the rings, resulting in splitting and broadening of spectra, with a blue shifted peak due to the aggregate. The presence of the bulky quaternized 2-diethylaminoethanethio substituent at the periphery of the Zn(II)-Pc significantly increases its solubility in aqueous medium, but is not so efficient in preventing aggregation of the Pc macrocycle. Metal ions like gallium and silicon, containing axial ligands in association with bulky substituents have been found to be more efficient in preventing aggregation of the Pc macrocycles [335,336]; buttressing the fact that aggregation can be dependent on the complexed metal ion. Addition of CEL, to the aqueous solution of α TZnPcQ **47b**, β TZnPcQ **48b** or β OZnPcQ **49b** resulted in a decrease in the intensity of the band due to the aggregates with an increase in the intensity of the band due to the monomeric species as shown for **47b** in Figure 3.17, which confirms that the complexes are aggregated in aqueous solution with Q band maxima given in Table 3.4. The addition of CEL caused ~ 11 nm red shift for the monomer peak in **47b** due to the disaggregation in water (this shift may have occurred in **48b** and **49b** also but it is not quite evident since their monomer peaks were not well resolved) Table 3.4. This shift may be due to the difference in media or existence of two or more different types of dimers in solution resulting in different positions and shapes of the absorption bands as has been observed before in sulfonated AlPc complexes [337]. It is also known that the electronic structure of phthalocyanines is perturbed when they are

aggregated, therefore leading to an alteration of the ground and excited state properties [338]. The disappearance of the peak due to the aggregates was however not complete for all the complexes as seen in Figure 3.17 for α TZnPcQ **47b**, by the persistent dimeric peak in the $\sim 640 - 660$ nm region. This suggests that strong forces are responsible for the aggregation. It is worth noting that complexes α TZnPcQ **47b**, β TZnPcQ **48b** or β OZnPcQ **49b** completely disaggregated in organic solvent (DMSO or methanol) Figure

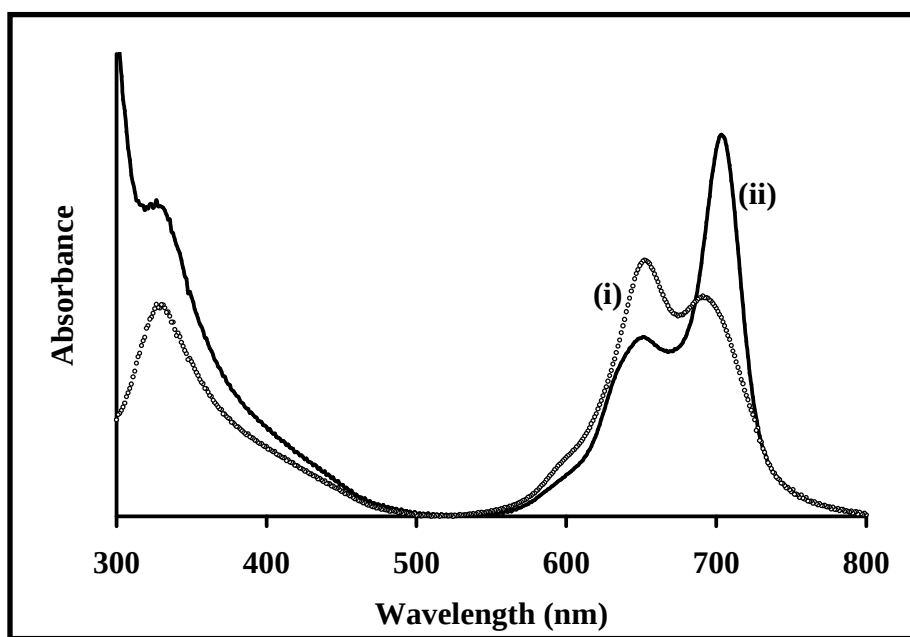


Figure 3.17: Electronic absorption spectra of (i) 3.95×10^{-6} M **47b** in PBS 7.4 and (ii) **47b** in the presence of 4×10^{-3} M CEL.

3.16b as it is expected since aggregated MPcs are expected to exhibit monomeric behaviour in organic solvents [166].

The cationic MPc complexes all exhibited high values of % Agg as shown in Table 3.5 with the α substituted complex having the lowest % Agg which may be due to reduced aggregation tendencies when substitution is at the non-peripheral positions [338]. The values of equilibrium constant (K_D) for the monomer/dimer equilibrium are high for the

complexes Table 3.5 indicating a strong association between the aggregates. These values are within the range for some MPc complexes [207,209]. The values of ϵ_D (Table 3.5) and ϵ_M (Table 3.4) are within the range reported for some MPc complexes [125,207,209].

3.3 Conclusions

Water-soluble (zinc, aluminium, silicon and germanium) sulfonated, tetracarboxy and octacarboxy MPc complexes were synthesized and characterized by spectroscopic methods. The complexes have intense absorption in the visible / near-IR region though most of the sulfonated and tetracarboxy MPc complexes are highly aggregated in aqueous solution but the addition of cremophore EL hindered aggregation for most of the complexes. The octacarboxy ones however exhibited monomeric behaviour. All the complexes exhibited improved monomeric behaviour in organic solvents (e.g. DMSO), furthermore, the synthesis, and spectroscopic characterization of unsubstituted aluminium and zinc phthalocyanines, aryloxy substituted SnPcs and aminoalkanethio-substituted ZnPc derivatives are presented. The latter were quaternized to result in water-soluble cationic complexes. These complexes were characterized by spectroscopic methods and exhibited interesting properties to allow for their possible use in various light driven applications. The synthesis of all the complexes gave reasonable yields, and spectroscopic methods satisfactorily confirmed the purity of the complexes.

CHAPTER 4

**PHOTOPHYSICAL,
PHOTOCHEMICAL
AND
PHOTOELECTROCHEMICAL
PROPERTIES**

This chapter deals with the photochemical and photophysical properties of the synthesized complexes. A selected number of octacarboxy MPCs are also investigated for their efficiency as photovoltaic cells.

4.1 Fluorescence Spectra and quantum yields

4.1.1 Nanoparticles (QDs and MN)

The normalized fluorescence emission spectra of the synthesized QDs (Figure 4.1 for MPA capped QDs (which is similar to others) are characterized by good symmetry, and are sufficiently narrow with full width at half maximum (FWHM) ranging from 46 to 60

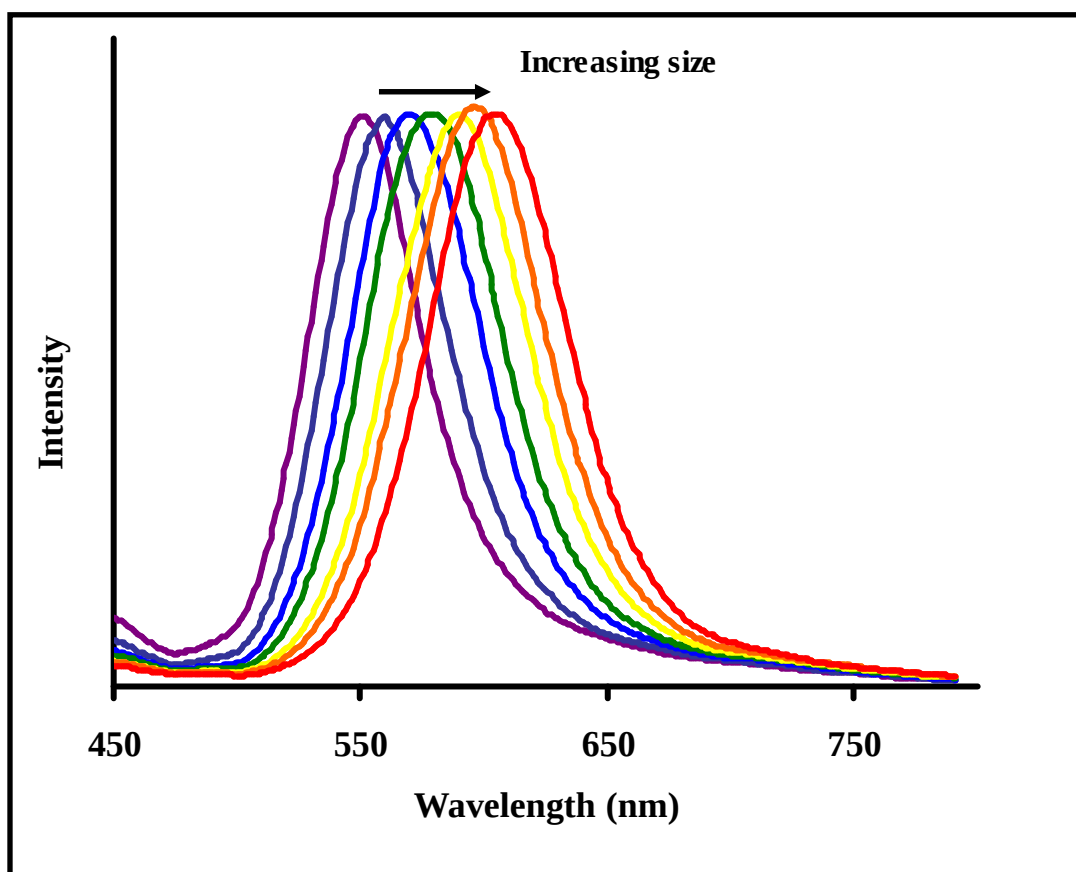


Figure 4.1: Fluorescence emission spectra of synthesized mercaptopropionic acid capped CdTe QDs showing increase in wavelength with increasing growth period as prepared in aqueous medium.

nm as shown in Table 4.1 for the different QDs. The QDs are photoluminescent in the visible region with the emission λ_{max} ranging from 550 to 649 nm, each having a Stokes' shift around 50 nm. The shift to lower band gap energies with increasing wavelength of the onset of absorption proves the quantum confinement effect in QDs [7]. The excitation spectra shows sharp peaks on the broad bands compared to the absorption spectra (Figure 4.2 for CYS1 **1c(i)**). This is probably due to the reported [40] inhomogeneous broadening which affects the excitation spectra more than the absorption spectra.

Table 4.1: Spectral properties and fluorescence quantum yields of thiol capped CdTe quantum dots (PBS pH 7.4).

^a QD	^b Emission λ_{max} (nm)	Size (nm)	Band gap (eV)	^c FWHM (nm)	$\Phi_{\text{F(QD)}}$
TGA1 (1a(i))	587	3.2	2.11	49	0.30
TGA2 (1a(ii))	632	3.7	1.96	48	0.62
MPA1 (1b(i))	550	2.3	2.25	46	0.19
MPA2 (1b(ii))	649	3.6	1.91	59	0.59
CYS1 (1c(i))	567	3.0	2.17	54	0.41
CYS2 (1c(ii))	626	3.5	1.98	58	0.09
CYS3 (1c(iii))	632	3.6	1.96	60	0.40

^aTGA = thioglycolic acid; MPA = 3-mercaptopropionic; CYS = L-cysteine capped QDs, ^b λ_{max} = wavelength maximum, ^cFWHM = full width at half height of spectrum

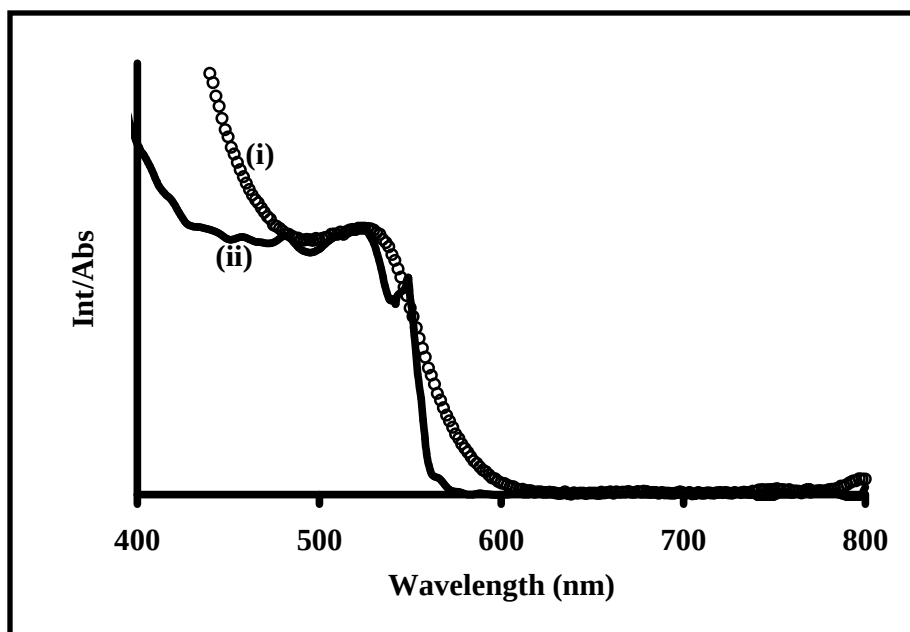


Figure 4.2: Absorption (i) and fluorescence excitation (ii) spectra of CYS1 taken as prepared in aqueous medium.

Fluorescence quantum yield values (Φ_F) values for the CdTe QDs were calculated using Equation 1.14 shown here as Equation 4.1 and listed in Table 4.1.

$$\Phi_F = \Phi_{F(\text{std})} \frac{F \cdot A_{\text{std}} \cdot n^2}{F_{\text{std}} \cdot A \cdot n_{\text{std}}^2} \quad (4.1)$$

The QDs have relatively high quantum yields compared to conventional dyes; except for CYS2 whose Φ_F was found to be lowest as shown in Table 4.1. Except for L-cysteine capped QDs, there is an increase in Φ_F values with increase in the size of QDs: compare TGA1 with TGA2 and MPA1 with MPA2. The observation of a decrease in Φ_F value for CYS2 compared to CYS1 may be ascribed to the structural differences in these QDs, with CYS2 probably having a less sulfur-enriched pre-surface layer, hence a low Φ_F value compared to CYS1.

The synthesized magnetic iron oxide nanoparticles (MNH, **2a** and MNS, **2b**) in this thesis did not show any appreciable fluorescence. Very low signals of fluorescence emissions were observed at about 450 and 540 nm as shown in Figure 4.3 on exciting at 260 nm (based on the λ_{max} of absorption shown in Figure 3.4). The appearance of many emission peaks has been reported before [339]. Higher emission intensity has previously been observed for iron nanoparticles [339,340]. The low or no emission intensity in this case may be due to the synthetic method used.

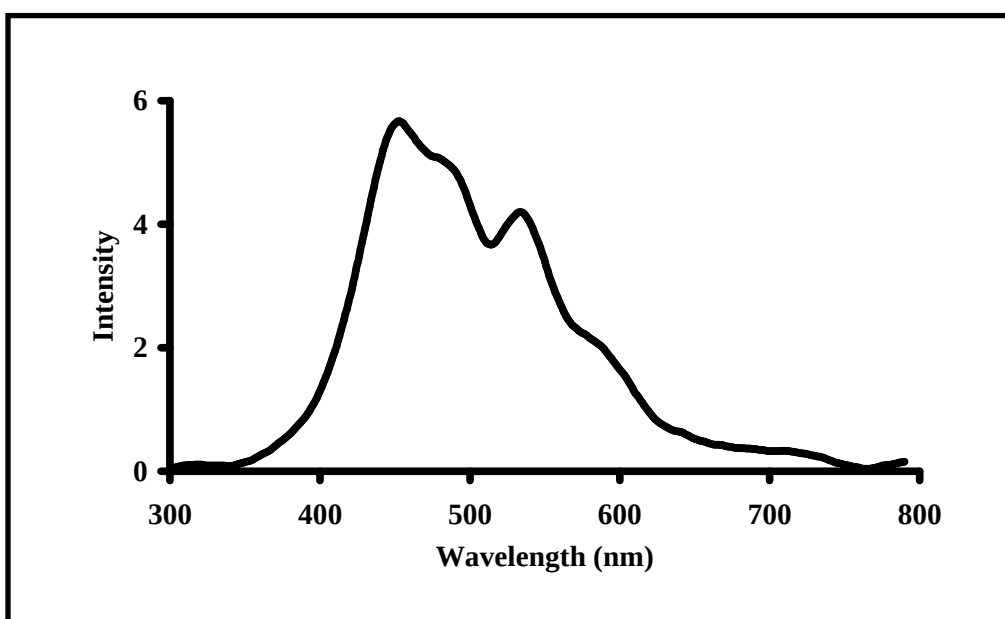


Figure 4.3: Fluorescence emission spectrum of magnetite capped with 3-aminopropyltriethoxysilane, MNS (2b) in PBS pH 7.4.

4.1.2 Phthalocyanines

4.1.2.1 Monomeric water-soluble metallophthalocyanines

The MOCPc complexes **41-44** were monomeric in solution as stated earlier and their absorption and fluorescence excitation spectra both in PBS 7.4 and in DMSO were

similar and both were mirror images of their fluorescence spectra which is typical of monomeric MPcs as shown in Figure 4.4 for SiOCPc (**43**).

The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for these complexes suggested that the molecules in the ground and excited states remained the same before and after excitation, and that it is the absorbing species that fluoresces.

The fluorescence quantum yields (Φ_F); determined using Equation. 4.1 are listed in Table 4.2. and are within the range for MPc complexes [236].

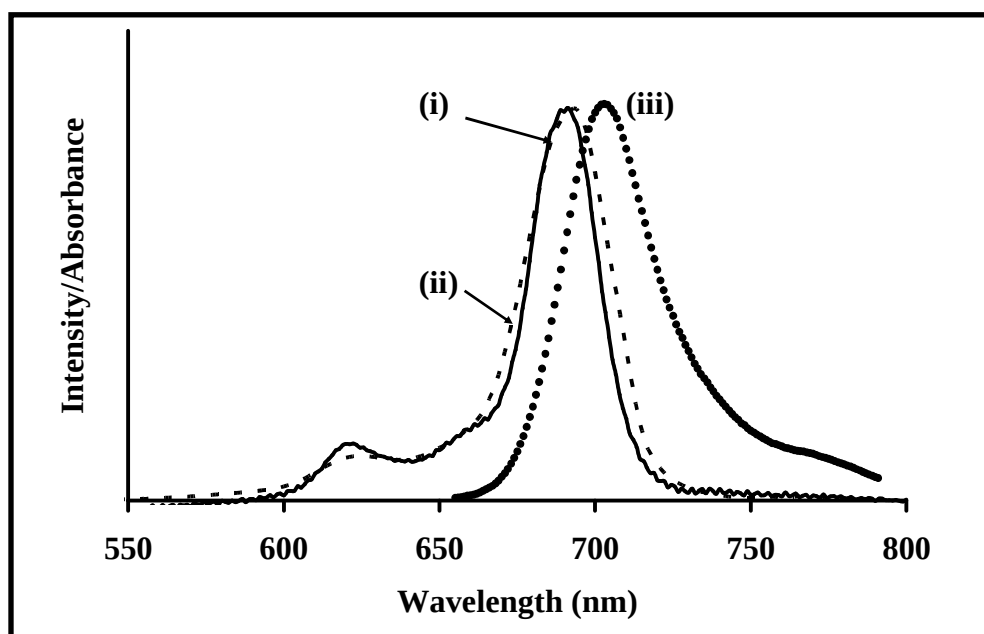


Figure 4.4: Normalized absorption (i) fluorescence excitation (ii) and emission (iii) spectra of SiOCPc (43**) in PBS pH 7.4 ($\lambda_{exc} = 640$ nm).**

A general decrease in the Φ_F values with increase in atomic number of the central metal was observed for complexes **41-44** both in PBS 7.4 and DMSO, which is consistent with the strengths of spin-orbit coupling induced by the respective central metals based on their relative atomic numbers. An aftermath of enhanced SOC is the reduction in the

Table 4.2: Fluorescence data of the complexes studied in aqueous or non aqueous media.

Complex	Solvent	λ_Q (nm)	λ_F (nm) ^a	λ_E (nm) ^b	Φ_F
ClAlPc (31)	DMSO	680	687	680	0.34
ZnPc (32)	DMSO	672	679	673	0.2 ^c
ZnPcS ₄ (33)	PBS	676,638	684	676	0.02
	PBS+CEL	676	681	676	0.10
	DMSO ^d	680	692	681	0.07
AlPcS ₄ (34)	PBS	680,636	689	680	0.13
	PBS+CEL	680	689	680	0.14
	DMSO	682	690	682	0.30
SiPcS ₄ (35)	PBS	679,636	692	679	0.01
	PBS+CEL	679	691	679	0.03
	DMSO	679	692	679	0.05
GePcS ₄ (36)	PBS	680,646	688	680	0.05
	PBS+CEL	681	689	681	0.09
	DMSO	683	691	683	0.12
ZnTCPc (37)	pH 10	694,642	696	694	0.01
	DMSO	690	703	690	0.16
AlTCPc (38)	pH 10	682,646	690	683	0.12
	DMSO	689	698	690	0.33
SiTCPc (39)	pH 10	702,640	710	706	<0.01
	DMSO	681	699	694	0.14
GeTCPc (40)	pH 10	702,653	707	703	<0.01
	DMSO	689	697	689	0.17
ZnOCPc (41)	PBS	693	702	693	0.23
	DMSO	707	714	707	0.24
AlOCPc (42)	PBS	689	694	689	0.27

Table 4.2 contd.

Complex	Solvent	λ_Q (nm)	λ_F^a (nm)	λ_E^b (nm)	Φ_F
	DMSO	700	708	700	0.44
SiOCpC (43)	PBS	691	703	691	0.24
	DMSO	700	720	704	0.27
GeOCpC (44)	PBS	697	704	697	0.13
	DMSO	703	713	704	0.19
α-SnPcPh (45a)	DMSO	733	747	740	0.008
α-SnPcTbtPh (45b)	DMSO	737	747	742	0.007
α-SnPcBzPh (45c)	DMSO	740	745	738	0.008
β-SnPcPh (46a)	DMSO	709	721	715	0.014
β-SnPcTbtPh (46b)	DMSO	710	723	717	0.010
β-SnPcBzPh (46c)	DMSO	715	719	713	0.011
α-TZnPc (47a)	DMSO	717	725	719	0.07
β-TZnPc (48a)	DMSO	696	707	697	0.13
β-OZnPc (49a)	DMSO	709	721	712	0.05
α-TZnPcQ (47b)	PBS	653,692	710	703	<0.01
	PBS+CEL	703	716	710	0.03
	DMSO	707	716	708	0.09
β-TZnPcQ (48b)	PBS	643,682	702	699	<0.01
	PBS+CEL	688	701	694	0.02
	DMSO	691	701	693	0.18
β-OZnPcQ (49b)	PBS	661,700	716	709	<0.01
	PBS+CEL	703	717	710	0.01
	DMSO	707	716	707	0.08

^a λ_F = emission wavelength, ^b λ_E = fluorescence excitation wavelength, ^{c,d}[234].

likelihood of fluorescence.

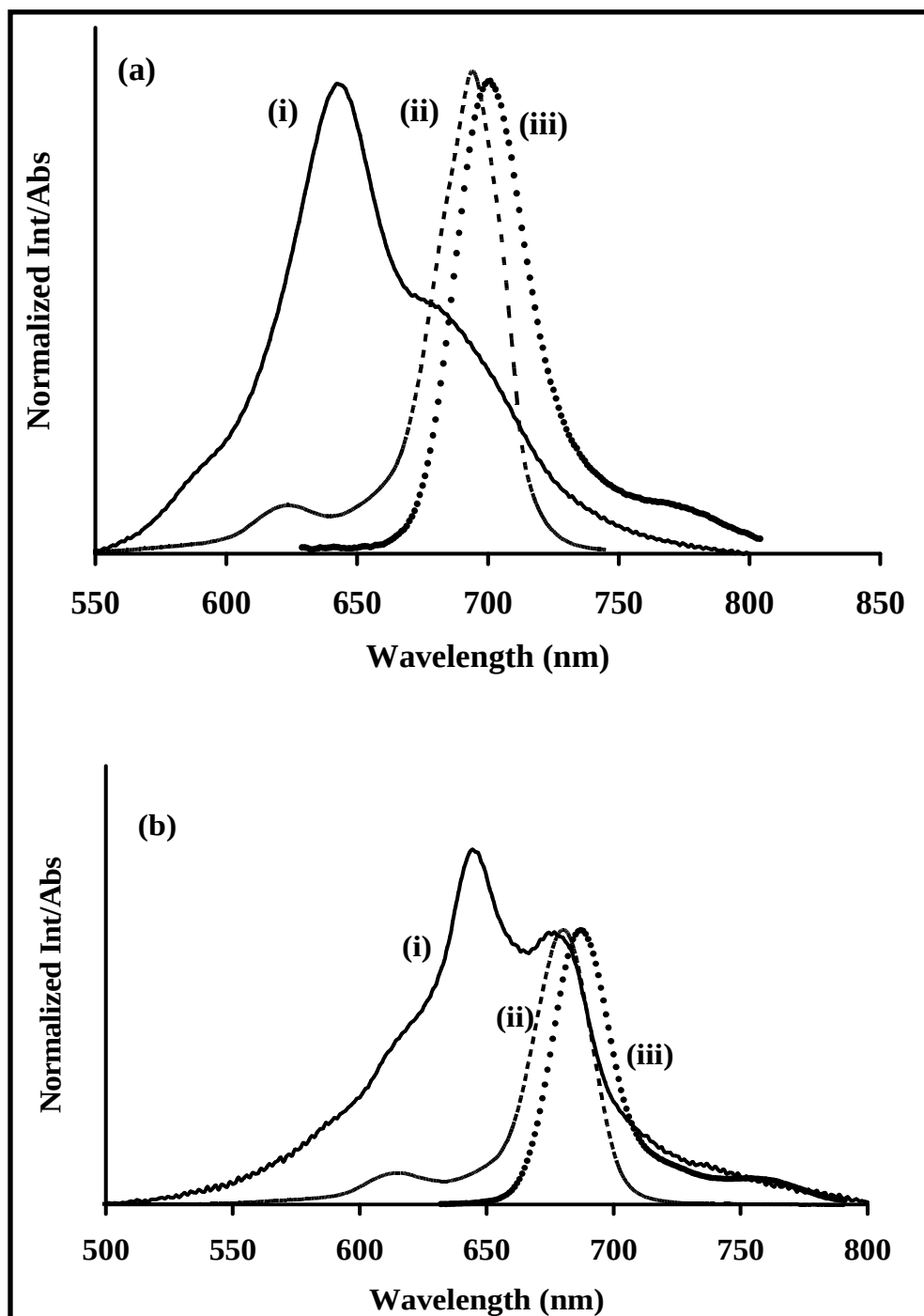
4.1.2.2 Aggregated water-soluble metallophthalocyanines

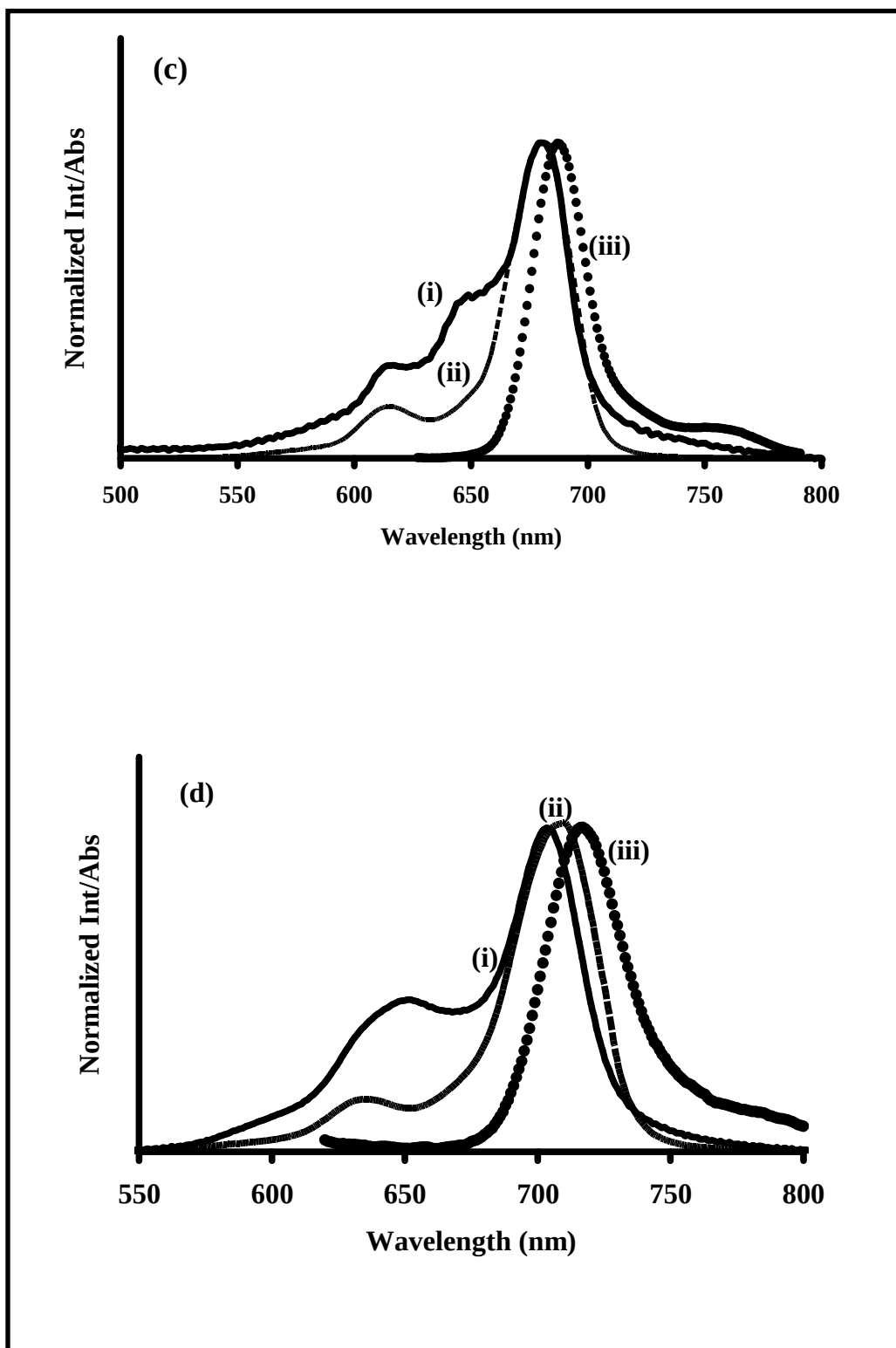
As stated earlier, the cationic (α -TZnPcQ **47b**, β -TZnPcQ **48b** and β -OZnPcQ **49b**) and tetra anionic (**33-40**, sulfonated and carboxy substituted) MPcs employed in this thesis were aggregated in aqueous medium, though the aggregation in the AlPc complexes (AlPcS₄, **34** and AlTCPC, **38**) was less pronounced. A lack of agreement was observed between the absorption and fluorescence excitation spectra of these complexes in aqueous medium, as shown in Figure 4.5 for the cationic β -TZnPcQ, **48b**, Figure 4.5a and anionic GePcS₄, **36**, Figure 4.5b complexes as examples. The high energy band associated with the dimer was not observed in the fluorescence excitation spectra suggesting that only the monomer fluoresces. It is widely known that dimers are generally non-photoactive [308]. In these cases, the maximum wavelengths of absorption of the monomers were similar to those of the fluorescence excitation.

The disaggregation induced by the surfactant, CEL reflected in the fluorescence properties of the MPcS₄ complexes, in that, the excitation spectra of the complexes were similar to the absorption spectra and mirror images to the fluorescence emission spectra in the presence of CEL. For GePcS₄ **36**, the absorption spectrum still had some aggregation even in CEL, hence some broadness was observed in its excitation spectrum, Figure 4.5c.

With the cationic complexes, **47b**, **48b** and **49b** in the presence of CEL, (Figure 4.5d for **47b**), the excitation spectra maxima were significantly different from that of the absorption spectra, also, the excitation spectra were fully monomeric suggesting that the absorbing species are somewhat different from the fluorescing species. In DMSO, where

the complexes show monomeric behaviour, as previously discussed, the absorption and fluorescence excitation spectra of the complexes were similar and were mirror images of their respective emission spectrum. However, for GePcS₄ (**36**), ZnTCPc (**37**) and SiTCPc





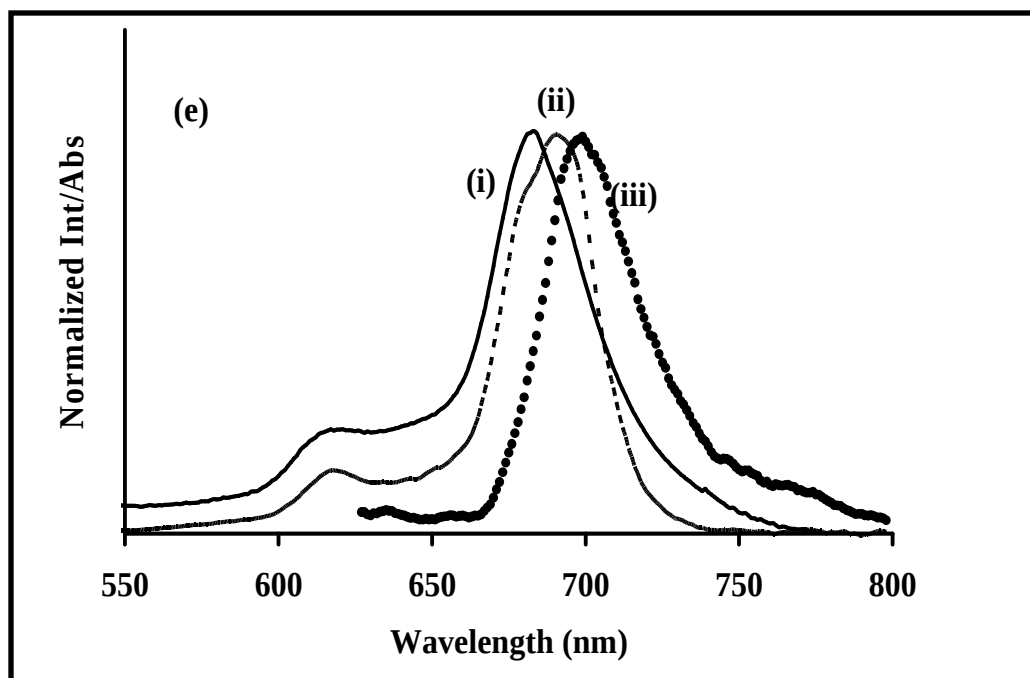


Figure 4.5: Normalized absorption (i), fluorescence excitation (ii) and emission (iii) spectra of (a) β -TZnPcQ (48b) and (b) GePcS₄ (36) in PBS pH 7.4; (c) GePcS₄ (36) and (d) α -TZnPcQ (47b) in the presence of cremophore EL in PBS pH 7.4 and (e) SiTCPc (39) in PBS pH 10 (λ_{exc} = 610 nm (a-d), 615 nm for (e)).

(39), only a single band was observed in their fluorescence excitation spectra in contrast with the slight broadness in their absorption bands (Chapter 3), **39** particularly behaved differently in that, the wavelength maxima (λ_{max}) of absorption and excitation spectra were different (Figure 4.5e) as shown in Table 4.2, suggesting a difference in the nuclear configuration of the ground and excited states.

The Stokes' shifts ($\lambda_{\text{ems}} - \lambda_{\text{exc}}$) between 6-20 nm were observed which is similar with known MPcs. In aqueous media where the complexes (MPcS₄ and cationic complexes) are aggregated, relatively low yields of fluorescence are obtained compared to MPcs in general [236], even in CEL where they are either totally (e.g. SiPcS₄ (35)) or partially (e.g. α -TZnPcQ (47b)) disaggregated, low Φ_{F} values were obtained, Table 4.2.

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 values of the complexes in the presence of CEL in in PBS pH 7.4 and in DMSO compared to that in PBS pH 7.4. The Φ_F values followed the trend PBS pH 7.4 < PBS pH 7.4 + CEL < DMSO for these complexes.

4.1.2.3 Monomeric non-water-soluble metallophthalocyanines

Similar fluorescence behaviour was observed for all the SnPc complexes (**45a-c** and **46a-c**) studied. The fluorescence excitation and emission spectra of the complexes are typical of phthalocyanine complexes, with Stokes' shifts ranging from 7 to 14 nm. Figure 4.6 shows the fluorescence excitation and emission spectra of complex **46a** (β -SnPcPh) in DMSO as an example.

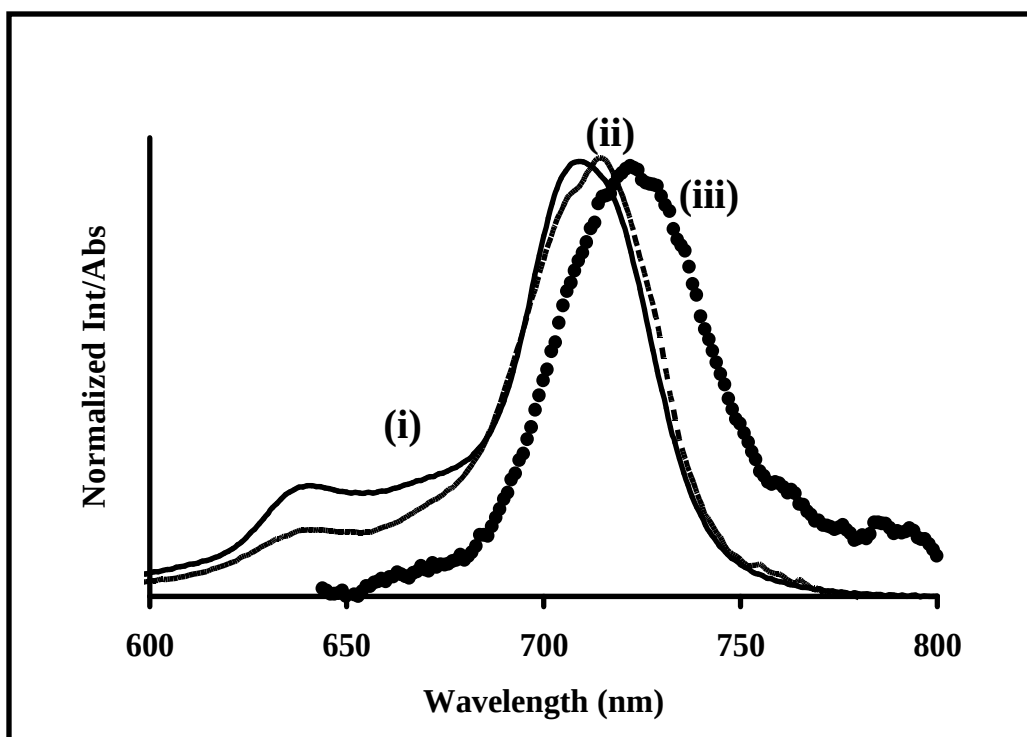


Figure 4.6: Normalized absorption (i), fluorescence excitation (ii) and emission (iii) spectra of β -SnPcPh (**46a**) in DMSO ($\lambda_{\text{exc}} = 625 \text{ nm}$).

The excitation spectra are similar to the absorption spectra and are mirror images to the fluorescence emission spectra for all complexes. However, the Q band maxima of the absorption and excitation spectra are different, with differences of between 5 and 7 nm, for **45a, b** and **46a, b**, Table 4.2. This was also observed for InPc derivatives bearing the same substituents as the SnPc complexes discussed in this work, but was not observed for the GaPc derivatives [232]. This behaviour may be due to the fact that Sn and In are metals with large atomic numbers that can be displaced from the core of the Pc ring on excitation hence, resulting in a loss of symmetry as it has been observed before in indium phthalocyanines [232]. For complexes **45c** (α -SnPcBzPh) and **46c** (β -SnPcBzPh), the difference in the wavelength maxima of the absorption and excitation spectra were only 2 nm, this proximity in λ_{max} of both spectra, suggests that the molecules in the ground and excited states remained the same before and after excitation. This could be explained by the fact that the bulky benzyloxyphenoxy substituent on the periphery of the complexes may shield the central metal from displacement on excitation, for **45c** and **46c**; similar fluorescence behaviour was observed for complexes α TZnPc **47a**, β TZnPc **48a** or β OZnPc **49a** in DMSO.

Φ_F values were very low for the SnPc derivatives in DMSO (Table 4.2) due to the increased strength of spin-orbit coupling induced by the presence of the central metal, Sn. Φ_F was found to be slightly higher in the β substituted complexes (**46a**, **46b** and **46c**) compared to the corresponding α substituted (**45a**, **45b** and **45c**) ones, suggesting less quenching of the excited singlet state by the former. Also with the 2-diethylaminosulfanyl substituted ZnPc derivatives in DMSO, the tetra- β substituted complex **48a** was also observed to have higher Φ_F compared to the tetra- α **47a** or octa- β

substituted **49a** complexes.

4.1.3 Fluorescence quenching of MTCPcs and MOCPCs by benzoquinone (BQ)

Fluorescence quenching studies were performed on tetra- and octa-carboxy substituted MPc complexes (**37-44**) by monitoring the decrease in the emission intensity of the complexes with increasing quencher concentration, i.e. [BQ] in DMSO. Figure 4.7 shows the spectral changes accompanying the fluorescence quenching of AlTCPC (**38**) by BQ in DMSO. There is a progressive decrease in fluorescence intensity as the concentration of BQ increases due to quenching of the excited state of the Pcs in the presence of BQ (the trend was characteristic of all the other complexes (**37-44**)). The fluorescence quenching of the MPc complexes by BQ obeyed Stern-Volmer kinetics as shown by the corresponding S-V plot (plot of F_0/F against [BQ] using Equation 1.17 now as Equation 4.2) (inset in Figure 4.7 for complex **38**).

$$\frac{F_0}{F} = 1 + K_{sv}[Q] \quad (4.2)$$

The S-V plots for all the MPc complexes employed gave straight lines, depicting diffusion controlled quenching mechanisms. No changes were observed in the absorption spectra of the complexes in the presence of BQ; hence the quenching mechanism can be said to be dynamic and not via the formation of non-fluorescent ground state complexes (static quenching). Quinones have high electron affinities, and their involvement in electron transfer processes is well documented [249]. The energy of the lowest excited state for quinones is known to be greater than the energy of the excited singlet state of

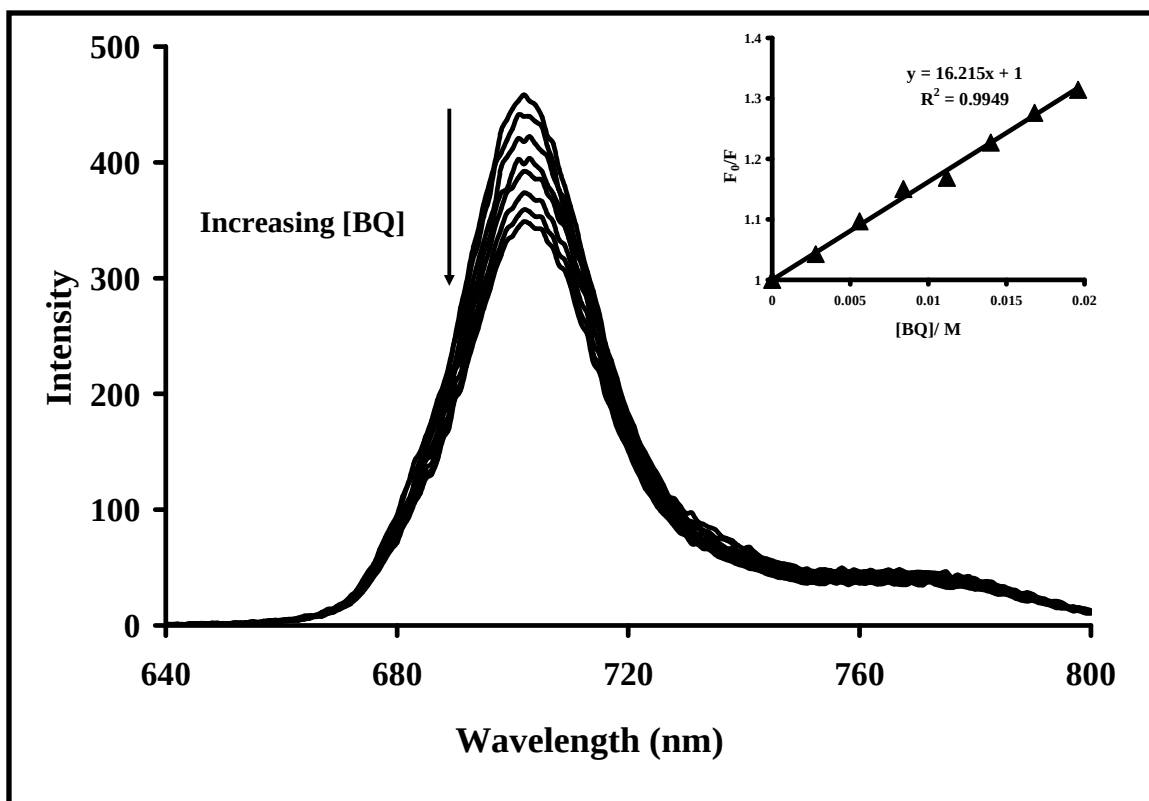
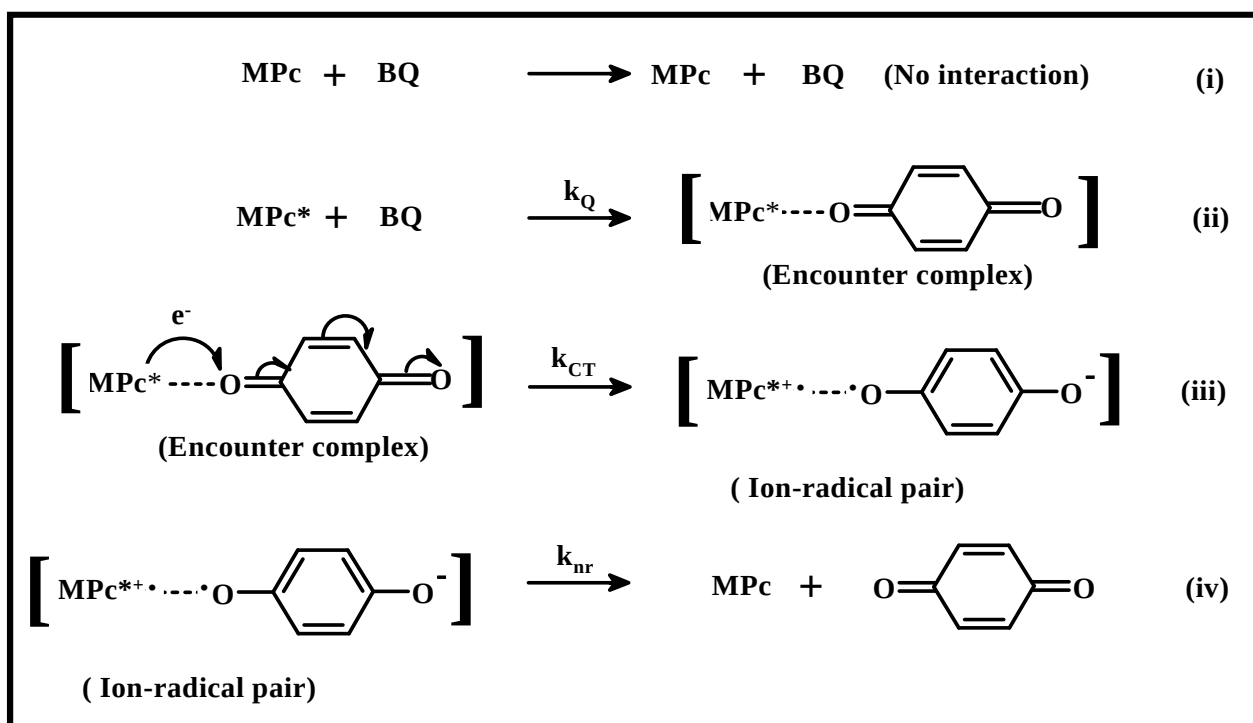


Figure 4.7: Fluorescence emission spectral changes of AlTCpC (38) (1.24×10^{-5} M) on addition of increasing concentrations of BQ in DMSO, [$\lambda_{\text{exc}} = 630$ nm].

MPC complexes [341], hence, energy transfer from the excited MPC to BQ is not likely to occur. Moreover, MPCs are known to be easily reduced [153]. Therefore MPC fluorescence quenching by BQ is via excited state electron transfer, from the MPC (electron donor) to the BQ (electron acceptor).

In Scheme 4.1, the mode of interaction of BQ with an excited MPC complex is explained. k_Q is the diffusion-controlled bimolecular quenching constant, k_{CT} , the charge transfer rate constant, and k_{nr} , the rate constant for the non-radiative decay of the non-fluorescent ion-radical pair, which also involves back electron transfer.

Stern-Volmer constants (K_{SV}) listed in Table 4.3, for fluorescence quenching of the carboxy substituted MPCs by BQ are within the same range for the MPC complexes



Scheme 4.1: Mechanism of charge transfer in MPc-quinone mixture.

studied in this work; this may be attributed to the similarity in structure and chemical nature of the MPc complexes. One expects the complexes to exhibit somewhat similar reduction potentials, substituent parameters (Hammett and Taft) and diffusion coefficients.

Bimolecular quenching constants (k_Q), calculated from Equation 4.3 (a combination of Equations 1.18-1.21) (assuming that collision efficiency, f , is unity) for the MPc

$$k_Q = f k_D \quad (4.3)$$

complexes were calculated using radii of MPcs estimated from the ACD/ChemSketch program in comparison with literature [342] and radius of BQ [343]. The values were found to be very close to the diffusion-controlled limits, $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, Table 4.3 reflecting the efficiency of the quenching. This is in agreement with the Einstein-Smoluchowski

approximation at room temperature for diffusion-controlled bimolecular interactions [309]. The values obtained were comparable to those observed with other phthalocyanines and quenchers [341].

Table 4.3: Fluorescence quenching and kinetic data of quenching of MPc complexes by BQ in DMSO.

	^a K _{SV} dm ³ mol ⁻¹	^b k _Q /dm ³ mol ⁻¹ s ⁻¹ (x 10 ⁹)	^c τ _F (MPc) (ns)	^d k _F /s ⁻¹ (x 10 ⁷)	^e k _{ISC} /s ⁻¹ (x 10 ⁸)	^f k _{IC} /s ⁻¹ (x 10 ⁷)
ZnTCPc (37)	13.04	5.66	2.3 (2.3)	6.96	3.57	0.87
AlTCPc (38)	16.22	5.58	2.9 (3.1)	11.3	1.92	3.78
SiTCPc (39)	13.49	4.85	2.8	5.04	2.37	5.76
GeTCPc (40)	18.35	5.03	3.7	4.66	2.25	0.27
ZnOCPc (41)	18.68	5.75	3.3 (3.5)	7.40	1.91	4.31
AlOCPc (42)	13.25	5.74	2.3 (1.8)	19.1	1.47	9.52
SiOCPc (43)	17.62	5.08	3.5 (3.8)	7.80	1.39	7.23
GeOCPc (44)	11.44	5.10	2.2 (2.7)	8.48	3.53	0.89

^aK_{SV} = Stern-Volmer constant; ^bk_Q = bimolecular quenching constant; ^cValues in brackets were obtained using PhotochemCAD software [243]; ^dk_F = rate constant for fluorescence (k_F = Φ_F/τ_F); ^ek_{ISC} = rate constant for intersystem crossing (k_{ISC} = Φ_T/τ_F); ^fk_{IC} = rate constant for internal conversion (k_{IC} = Φ_{IC}/τ_F).

Determination of MPcs fluorescence lifetimes from BQ-quenching data

Since the interactions of the excited states with BQ were diffusion-controlled, and k_Q is known, fluorescence lifetimes, τ_F values were determined (Equation 1.18 now given as

Equation 4.4, Table 4.3), and were found to be within the expected range for MPc derivatives [246,341].

$$K_{SV} = k_Q \cdot \tau_F \quad (4.4)$$

As this treatment is a relatively new dimension to the determination of τ_F [166], the results were compared with those obtained from familiar procedures of using Strickler-Berg equation. The values obtained from our treatment compare well with those obtained using the Strickler-Berg equation-adapted software (PhotochemCAD [243]), as given in Table 4.3. The fluorescence lifetimes range between 1.8 ns and 3.5 ns, and do not follow a well-defined trend among the MPc complexes studied. It was however not possible to detect τ_F for SiTCPC (**39**) and GeTCPC (**40**) using the Strickler-Berg equation-adapted software since their absorption spectra remained slightly broadened in DMSO or there were changes in their nuclear configuration on excitation. The Strickler-Berg equation is only valid for molecules that do not undergo geometric changes on excitation [167,244].

Rate constants for the intrinsic processes deactivating the excited singlet state (k_F , k_{ISC} and k_{IC}) are shown in Table 4.3. The rate constants of internal conversion were higher for the silicon and aluminium complexes within each set (octa or tetra carboxy), showing that there is a higher rate of quenching of the singlet excited state in these complexes. Larger rate constants for fluorescence (k_F) were observed for the MOCPC complexes compared to their corresponding MTCPCs, indicating a greater fluorescing ability of the former which may be due to their monomeric and isomeric nature. All the complexes exhibited large rate constants for intersystem crossing (k_{ISC}) indicating their high intersystem crossing ability to the triplet state.

4.2 Triplet state quantum yields and lifetimes

The efficiency of a phthalocyanine as a photosensitizer is determined by its triplet state quantum yield (Φ_T) and lifetime (τ_T). Table 4.4 gives the Φ_T values and τ_T in different solvents for the MPc complexes studied. These were determined by the laser flash photolysis system described in Chapter 2 and estimated using Equation 4.5, same as Equation 1.33.

$$\Phi_T = \Phi_T^{\text{Std}} \frac{\Delta A_T^{\text{Sample}} \cdot \epsilon_T^{\text{Std}}}{\Delta A_T^{\text{Std}} \cdot \epsilon_T^{\text{Sample}}} \quad (4.5)$$

Figure 4.8 shows the transient absorption spectrum and triplet decay curve (inset i) of **45a** (characteristic of all complexes). Inset ii shows a linear plot of $\ln A$ versus time.

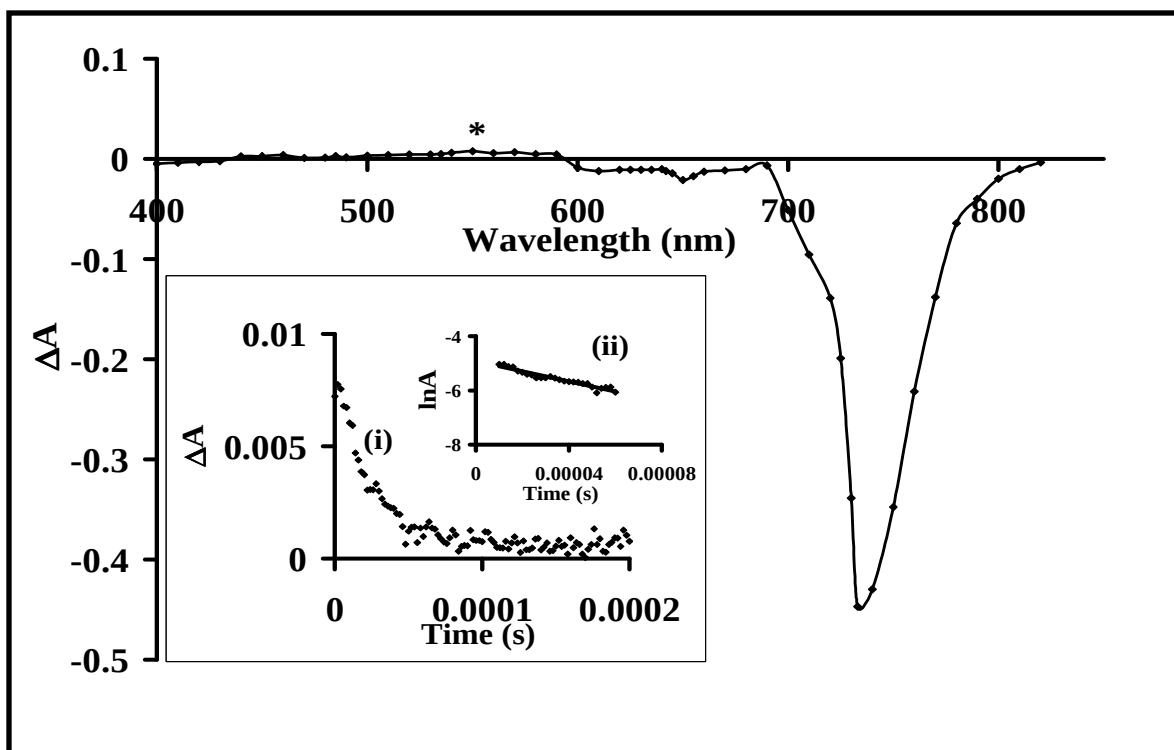


Figure 4.8: Transient absorption spectrum for α -SnPcPh (**45a**) in DMSO. Triplet state absorption at $\lambda = 550$ nm. (Inset: (i) Triplet decay curve of **45a** and (ii) Plot of $\ln A$ versus time for **45a**. $[45a] = \sim 1.4 \times 10^{-5}$ M. $\lambda_{\text{exc}} = 733$ nm.

The shape of the Q band at the triplet state is similar to the ground state absorption spectrum indicating that there is no change following excitation. The λ_{max} of absorption at the triplet state was determined for each complex and was centered at 550 nm for **45a** as shown with asterisk in Figure 4.8. In most cases, the triplet curve obeyed the second order kinetics. This is typical of MPCs due to the triplet-triplet recombination [344].

Φ_T values depended on heavy atom effect for all the complexes. In some cases, it also depended on aggregation. The aluminium and silicon complexes with lower atomic numbers had lower Φ_T values compared to zinc and germanium complexes in which the central metals have higher atomic numbers. With the tetrasulfonated complexes (**33-36**), the highest Φ_T values were obtained for GePcS₄ within the group in all the solvent media employed. Φ_T values were also found to be highest in all cases in DMSO since these complexes are slightly or fully monomeric in this solvent, and probably because intersystem crossing is favoured in DMSO than in aqueous solution. As expected, the presence of CEL gave increased Φ_T values since the MPCs₄ complexes are fully or partially disaggregated in this case and monomers have greater tendencies to undergo intersystem crossing because less energy is lost through internal conversion [166]. The increase in Φ_T values is complemented by a decrease in Φ_F values in these complexes, Table 4.4. The Φ_T values followed the trend PBS 7.4 < PBS 7.4 + CEL < DMSO except for AlPcS₄ (**34**) which may be due to the fact that there was little or no aggregation in this complex. The same trend was observed for the cationic complexes α TZnPcQ **47b**, β TZnPcQ **48b** and β OZnPcQ **49b** which were also aggregated in aqueous medium while α TZnPc **47a**, β TZnPc **48a** and β OZnPc **49a** precursors to **47b**, **48b** and **49b** maintained high Φ_T values in DMSO. Complexes **37 - 40** (MTCPs) also had higher Φ_T values in

Table 4.4: Triplet state quantum yields and lifetimes of the MPcs studied in different solvents.

Complex	Solvent	Φ_T	$\tau_T/\mu s$	Φ_{IC}	Φ_F
CIAIPc (31)	DMSO	0.20	720	0.46	0.34
ZnPc (32)	DMSO	0.65 ^a	350 ^b	0.15	0.20 ^b
ZnPcS ₄ (33)	PBS	0.56 ^c	180	0.42	0.02
	PBS+CEL	0.59	210	0.31	0.10
	DMSO ^c	0.88	470	0.05	0.07
AlPcS ₄ (34)	PBS	0.36	560 ^d	0.51	0.13
	PBS+CEL	0.40	590	0.46	0.14
	DMSO	0.38	1335	0.32	0.30
SiPcS ₄ (35)	PBS	0.49	200	0.50	0.01
	PBS+CEL	0.57	270	0.40	0.03
	DMSO	0.67	310	0.28	0.05
GePcS ₄ (36)	PBS	0.61	180	0.34	0.05
	PBS+CEL	0.70	240	0.21	0.09
	DMSO	0.84	640	0.04	0.12
ZnTCPc (37)	pH 10	0.31	50	0.68	0.01
	DMSO	0.82	240	0.02	0.16
AlTCPc (38)	pH 10	0.29	200	0.59	0.12
	DMSO	0.56	340	0.11	0.33
SiTCPc (39)	pH 10	0.35	30	0.64	<0.01
	DMSO	0.66	210	0.16	0.14
GeTCPc (40)	pH 10	0.45	41	0.54	<0.01
	DMSO	0.82	260	0.01	0.17
ZnOCPc (41)	PBS	0.50	160	0.27	0.23
	DMSO	0.62	480	0.14	0.24
AlOCPc (42)	PBS	0.32	450	0.41	0.27

Table 4.4 contd.

Complex	Solvent	Φ_T	$\tau_T/\mu s$	Φ_{IC}	Φ_F
	DMSO	0.34	1270	0.22	0.44
SiOCPc (43)	PBS	0.34	90	0.42	0.24
	DMSO	0.48	760	0.25	0.27
GeOCPc (44)	PBS	0.62	240	0.25	0.13
	DMSO	0.79	480	0.03	0.19
α -SnPcPh (45a)	DMSO	0.79	50	0.20	<0.01
α -SnPcTbtPh (45b)	DMSO	0.76	40	0.23	<0.01
α -SnPcBzPh (45c)	DMSO	0.69	30	0.30	<0.01
β -SnPcPh (46a)	DMSO	0.89	40	0.10	0.014
β -SnPcTbtPh (46b)	DMSO	0.75	40	0.24	0.010
β -SnPcBzPh (46c)	DMSO	0.71	30	0.28	0.011
α -TZnPc (47a)	DMSO	0.66	190	0.27	0.07
β -TZnPc (48a)	DMSO	0.71	180	0.16	0.13
β -OZnPc (49a)	DMSO	0.75	200	0.20	0.05
α -TZnPcQ (47b)	PBS	0.15	20	0.85	<0.01
	PBS+CEL	0.17	90	0.80	0.03
	DMSO	0.63	200	0.28	0.09
β -TZnPcQ (48b)	PBS	0.28	70	0.72	<0.01
	PBS+CEL	0.34	110	0.64	0.02
	DMSO	0.57	210	0.25	0.18
β -OZnPcQ (49b)	PBS	0.17	40	0.83	<0.01
	PBS+CEL	0.32	60	0.67	0.01
	DMSO	0.60	220	0.32	0.08

^a[307], ^b[234], ^c[308], ^d[325].

DMSO compared to pH 10. The Φ_T values of the monomeric water-soluble MPcs (MOCPcs) were observed to be lower compared to the MPcS₄ complexes both in PBS pH 7.4 and DMSO; they are also lower compared to MTCPcs in DMSO.

The SnPc derivatives exhibit high Φ_T values for the phenoxy (**45a**, **46a**) and *tert*-butylphenoxy (**45b**, **46b**) substituted derivatives due to the large atomic number of the Sn central metal, but the values were lower in the benzyloxyphenoxy substituted derivatives (**45c** and **46c**). These values were comparable to other MPcs with the same substituent, though different metals [232,238]. The Φ_T values were found to decrease in the order phenoxy substituted (**45a** and **46a**) > *tert*-butylphenoxy substituted (**45b** and **46b**) > 4-benzyloxyphenoxy substituted (**45c** and **46c**) derivatives. This could be due to the concept of the “loose bolt” effect [268] for the *tert*-butyl phenoxy and benzyloxyphenoxy substituted SnPc complexes (**45b** and **46b**; **45c** and **46c**). The effect is associated with the vibrations of the bonds set off by the parent molecule in a similar way as a loose bolt in a moving part of the machine, which tends to be set in motion by the other moving parts of the machine. The σ C–H bonds of these bulkier substituents may show this effect. The effect increases the rate of internal conversion as electronic energy is lost through C–H vibrations [268], hence lower Φ_T values. The “loose bolt” effect is expected to be less pronounced in the phenoxy substituted SnPc complexes (**45a** and **46a**) since they have less C–H bonds.

Triplet lifetimes, τ_T were determined by fitting the data with OriginPro 7.5 software. Enhanced ISC results in high Φ_T and decreased τ_T in complexes **45a-c** and **46a-c** compared to MPcs in general [236] and to the standard ZnPc ($\Phi_T = 0.65$ [307]), Table 4.4. It is expected that central metals with high atomic numbers and diamagnetic

properties will exhibit high Φ_T values and short triplet state lifetime τ_T values. The trend of the triplet state lifetime τ_T values, is however not dependent on central metals only but also on substituents. The tetrasulfonated and octacarboxy derivatives had longer lifetimes compared to their corresponding unsubstituted derivatives in DMSO (AlPc, **31** (720 μ s), AlPcS₄, **34** (1335 μ s), AlOCPc, **42** (1270 μ s) which may mean that the dissipation of energy by the anionic complexes at the excited triplet state is less efficient compared to that of the unsubstituted MPcs.

The τ_T values for MTCPcs and MOCPCs were generally short in aqueous medium compared to in DMSO. SiOCPc (**43**) was odd in that in aqueous medium, it exhibited very short τ_T compared to its other counterparts with the same substituent (**41**, **42**, **43**), but its τ_T was high in DMSO.

For complexes that have aggregation that can be broken with CEL in aqueous medium (**33-36**, **47b**, **48b** and **49b**), there is a striking increase in τ_T in the order, PBS 7.4 < PBS 7.4 + CEL < DMSO as seen in Table 4.4. The lowest τ_T values exhibited in PBS 7.4 are likely due to the fact that water quenches the triplet states of MPcs as has been reported before [234]. Values of τ_T in DMSO are high; this may be attributed to the fact that the absorption of DMSO at the region of the energy of the triplet states of MPcs (~ 1108 nm) is not as intense as that of water [234]. This stresses the effect of solvent on τ_T . The increase in τ_T values in the presence of CEL compared to PBS alone may be due to the reduction in the exposure of the phthalocyanine to the aqueous medium because of the presence of the CEL.

Following laser irradiation, for the determination of triplet state yield and lifetime (Φ_T and τ_T) values, the spectra for both (Cl)AlPc (**31**) and AlPcS₄ (**34**) in DMSO changed as

shown in Figure 4.9a for **31**. No transformation of the water-soluble **34** was observed in aqueous medium. The changes involved a decrease in the Q band and increase in the

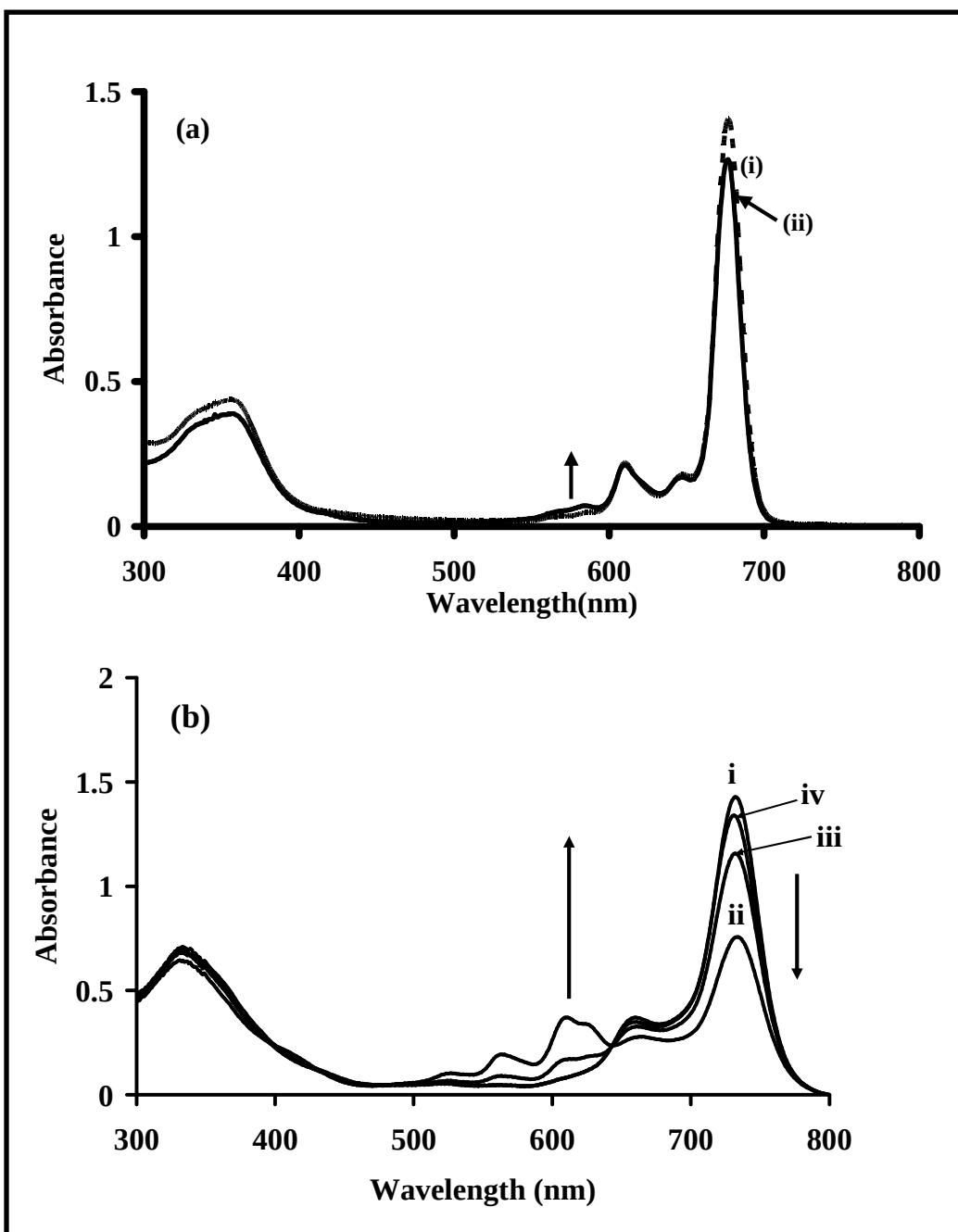
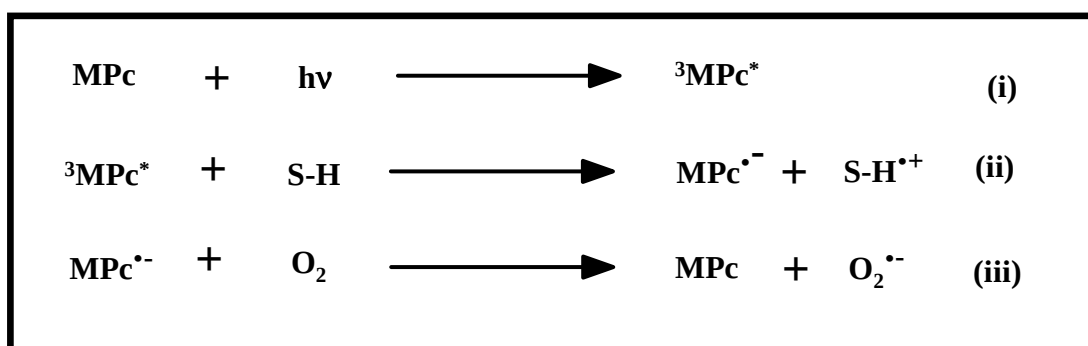


Figure 4.9: Absorption spectral changes of AlPc (**31**) (a) and α -SnPcPh (**45a**) in DMSO (b) before (i), and after (ii) laser irradiation at 7 mJ. (iii) and (iv) shows spectra of **45a** on exposure of laser irradiated solution to air for 2 and 5 minutes respectively.

absorption near 580 nm region. There was also a change in the absorption spectra for complexes **45a-c** and **46a-c**, as shown in Figure 4.9b for α -SnPcPh (**45a**). A decrease in the Q band and increases in the 500 to 650 nm region, with an isosbestic point at 640 nm was observed as shown for **45a**. These increases disappeared gradually on exposure of the solution of the MPc complexes to air and the Q band increased in intensity suggesting that the emerged bands were due to reduction products of the complexes. This type of transformation has been observed before during photodegradation of pyridinoporphyrazines [301] using visible light. The ease of reduction of SnPc complexes in the presence of light is well documented as stated in the introduction [167,304]. The first ring reduction in MPc complexes was characterized by a decrease in the Q band and the formation of weak bands between 500 and 600 nm [345]. Also, only ring reduction is expected in AlPc complexes. Thus during laser irradiation, the AlPc and SnPc complexes were partly transformed to an anion ($\text{Pc}^{\cdot-}$). The mechanism for the photoreduction of MPc complexes in the presence of light has been suggested to involve H atoms from the solvent (S-H) during the production of $\text{Pc}^{\cdot-}$ [232,301], equations i to iii of Scheme 4.2. Considering the fact that no spectral changes on exposure to laser light were observed with the unsubstituted and tetrasulfonated ZnPc counterparts, a likely reason for the



Scheme 4.2: Mechanism of photoreduction of MPcs in the presence of light.

phototransformation in the AlPc complexes could be probably due to the fact that AlPc containing a trivalent central metal is more easily reduced than ZnPc. However, there were no significant spectral changes on exposure of the AlPc complexes to unfiltered white light or white light filtered to remove UV light (used for photobleaching and singlet oxygen quantum yield determinations). The laser light has a much larger intensity than the white light. The effect of laser energy on the phototransformation of AlPc derivatives to the Pc^{-3} species was investigated. It was observed that phototransformation increased with laser energy as judged by the decrease in the Q band absorption, Table 4.5. Thus the formation of the Pc^{-3} increased with increase in laser energy whereas, the triplet lifetimes increased (and Φ_T decreased) with decrease in laser energy, Table 4.5. Thus the increase in Pc^{-3} was directly related to the decrease in triplet lifetime as laser energy increased. The presence of paramagnetic species such as Pc^{-3} is expected to result in the decrease in triplet lifetime, but an increase in triplet yield [165], as observed in Table 4.5.

The assumption that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet states of the complexes allows for

Table 4.5: Effects of laser energy on absorbance (A), triplet lifetime and quantum yield for AlPc (31) in DMSO.

Laser energy (mJ)	τ_T (μs)	Φ_T	ΔA (Q band)
3.5	720	0.20	0.08
5.3	620	0.29	0.12
6.7	510	0.30	0.12
7.0	510	0.31	0.13

calculation of quantum yields of internal conversion, Φ_{IC} which were obtained from Equation 4.6

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \quad (4.6)$$

From Table 4.4, considering the aggregated water-soluble MPc complexes (**33-40**, **47b**, **48b** and **49b**), it is observed that Φ_{IC} values were generally high due to aggregation, which is due to the dissipation of electronic energy by the aggregates. Φ_{IC} values decreases in the order, PBS 7.4 > PBS 7.4 + CEL > DMSO which suggests that molecules are more photoactive in DMSO than in aqueous solution. The decrease in Φ_{IC} values in the presence of CEL is due to its monomerizing effect on these complexes. Generally Φ_{IC} values were higher in aqueous medium compared to DMSO which may also be due to the fact that water has a lower viscosity compared to DMSO. Within the MPcS₄ complexes, Φ_{IC} was least in GePcS₄ due to its higher photosensitizing ability. The Φ_{IC} values for the organic soluble SnPc and aminoalkanethio-substituted MPcs were generally low (≤ 0.2) showing that the photoactivity of the complexes is high in DMSO.

4.3 Singlet oxygen and photodegradation quantum yields

4.3.1 Singlet oxygen quantum yields

Energy transfer between the triplet state of MPcs and ground state molecular oxygen leads to the production of singlet oxygen. 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 for photochemical reactions. Therefore, singlet oxygen quantum yield, Φ_{Δ} which is the efficiency of singlet oxygen generation, should depend on the triplet state quantum yield and lifetime, the efficiency of energy transfer,

which depends on the energy of the triplet state and the ability of the substituents to quench the triplet state amongst other factors.

Determination of Φ_{Δ} involved the use of singlet oxygen quenchers; DPBF in DMSO and ADMA in aqueous medium. The decay of DPBF or ADMA in the presence of singlet oxygen generated from the photoexcited MPc were monitored at 417 and 380 nm and they are shown in Figures 4.10a and 4.10b for ClAlPc, **31** (DPBF) or GeOCPC, **44** (ADMA) respectively. Equation 4.7 (Equation 1.36) was used in the calculations.

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \cdot \frac{R I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} I_{\text{abs}}} \quad (4.7)$$

The singlet oxygen quantum yields of the complexes under study in different solvent media are presented in Table 4.6. In general the Φ_{Δ} values are expected to be related to Φ_T values. Considering the aggregated water-soluble MPcs (**33-40** and **47b**, **48b** and **49b**), an efficient production of Φ_{Δ} in all solvent media was observed relative to the triplet state yields. Low values of Φ_{Δ} (Table 4.6) were obtained in cases where low Φ_T (Table 4.6) values are also obtained. There is a slight improvement in Φ_{Δ} values in CEL. The Φ_{Δ} values were however unexpectedly low for GePcS₄ (**36**) and SiTCPc (**39**) in DMSO in comparison with their triplet state quantum yields, which may be connected to the fact that these complexes are not fully disaggregated even in DMSO as mentioned in Chapter 3. SiTCPc, **39** behaved differently in most cases (e.g excitation spectra) and its relatively short triplet lifetime (compared to its Φ_T), may also be a reason for its low production of Φ_{Δ} since efficient energy transfer from its triplet state to ground state molecular oxygen may not have been plausible within the short triplet lifetime.

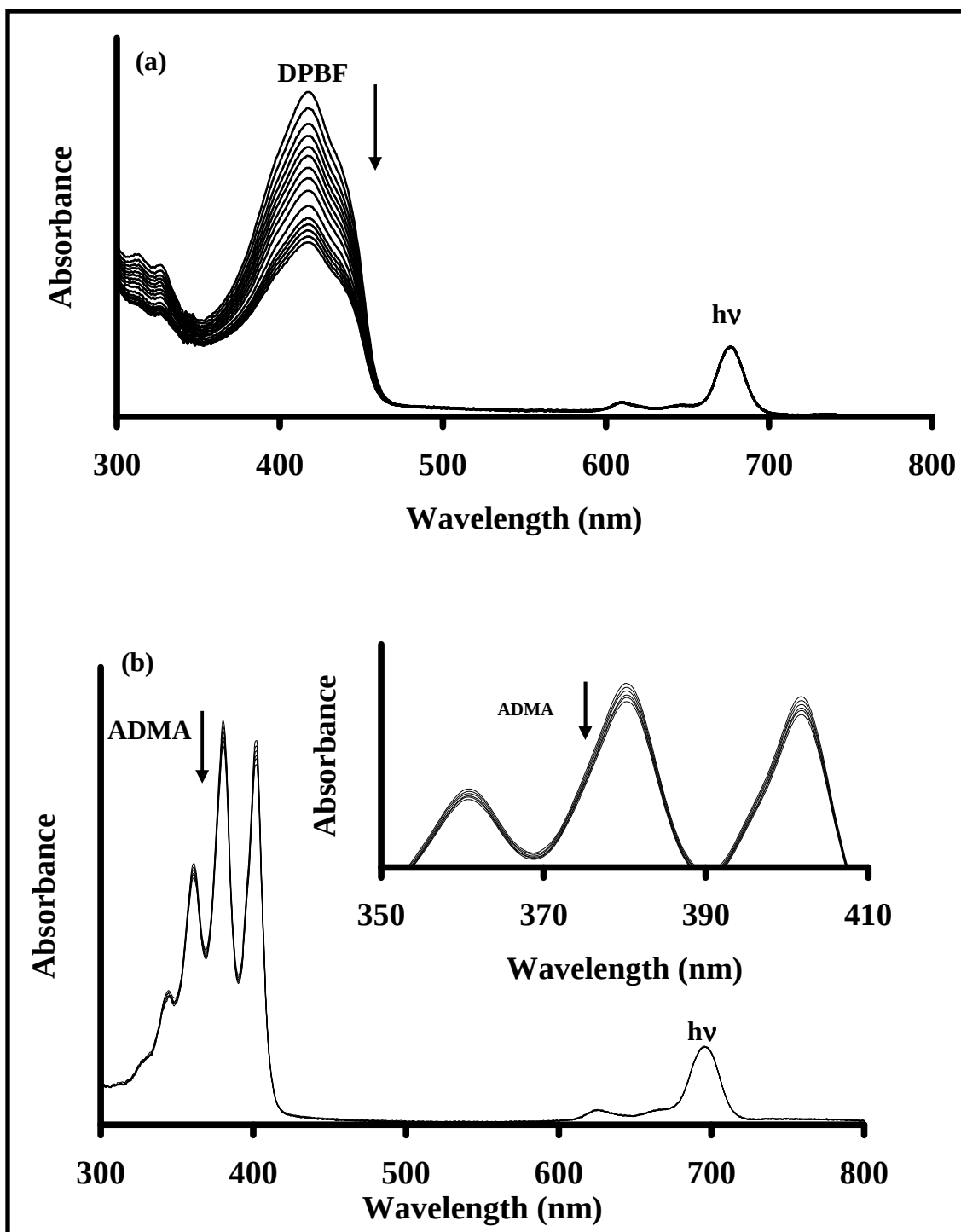


Figure 4.10: Photodegradation of DPBF observed in the presence of (Cl)AlPc (31) in DMSO during Q band irradiation of 31 $[31] = 8.2 \times 10^{-7}$, $[DPBF] = 4.8 \times 10^{-5}$ M (a) and (b) ADMA observed in the presence of GeOCPc (44) in PBS pH 7.4 during Q band irradiation of 44. $[44] = 2.7 \times 10^{-6}$ M, $[ADMA] = 8.0 \times 10^{-5}$ M.

Table 4.6: Singlet oxygen (Φ_{Δ}) and photodegradation (Φ_P) quantum yields of studied MPc complexes in different solvents.

Complex	Solvent	Φ_{Δ}	Φ_T	S_{Δ}	$\Phi_P (\times 10^{-5})$
ClAlPc (31)	DMSO	0.29	0.20	1.45	0.12
ZnPc (32)	DMSO	^a 0.67	0.65 ^b	1.03	4.53
ZnPcS ₄ (33)	PBS	0.23	0.56 ^c	0.41	2.21
	PBS+CEL	0.51	0.59	0.86	9.77
	^d DMSO	0.46	0.88	0.52	4.03
AlPcS ₄ (34)	PBS	0.34	0.36	0.94	0.24
	PBS+CEL	0.41	0.40	1.03	3.56
	DMSO	0.38	0.38	1.00	0.32
SiPcS ₄ (35)	PBS	0.50	0.49	1.02	4.48
	PBS+CEL	0.55	0.57	0.96	5.82
	DMSO	0.68	0.67	1.01	8.62
GePcS ₄ (36)	PBS	0.64	0.61	1.05	3.66
	PBS+CEL	0.68	0.70	0.97	5.54
	DMSO	0.31	0.84	0.34	8.57
ZnTCPc (37)	pH 10	0.30	0.31	0.97	2.20
	DMSO	0.84	0.82	1.02	26.4
AlTCPc (38)	pH 10	0.26	0.29	0.90	0.94
	DMSO	0.35	0.56	0.63	10.6
SiTCPc (39)	pH 10	0.31	0.35	0.89	2.64
	DMSO	0.17	0.66	0.26	2.15
GeTCPc (40)	pH 10	0.43	0.45	0.96	2.66
	DMSO	0.73	0.82	0.89	14.5
ZnOCPc (41)	PBS	0.32	0.50	0.64	2.65
	DMSO	0.56	0.62	0.90	12.1
AlOCPc (42)	PBS	0.12	0.32	0.38	0.26

Table 4.6 contd.

Complex	Solvent	Φ_{Δ}	Φ_T	S_{Δ}	$\Phi_P (\times 10^{-5})$
AlOCPc (42)	DMSO	0.32	0.34	0.94	8.47
SiOCPc (43)	PBS	0.22	0.34	0.65	86.3
	DMSO	0.33	0.48	0.69	96.6
GeOCPc (44)	PBS	0.31	0.62	0.51	2.12
	DMSO	0.63	0.79	0.75	7.03
α-SnPcPh (45a)	DMSO	0.58	0.79	0.73	41.0
α-SnPcTbtPh (45b)	DMSO	0.74	0.76	0.97	43.1
α-SnPcBzPh (45c)	DMSO	0.75	0.69	1.08	61.7
β-SnPcPh (46a)	DMSO	0.73	0.89	0.82	27.9
β-SnPcTbtPh (46b)	DMSO	0.65	0.75	0.87	17.9
β-SnPcBzPh (46c)	DMSO	0.73	0.71	1.01	42.9
α-TZnPc (47a)	DMSO	0.64	0.66	0.97	66.2
β-TZnPc (48a)	DMSO	0.68	0.71	0.96	66.1
β-OZnPc (49a)	DMSO	0.62	0.75	0.83	94.0
α-TZnPcQ (47b)	PBS	0.10	0.15	0.67	9.30
	PBS+CEL	0.12	0.17	0.71	12.2
	DMSO	0.51	0.63	0.81	18.1
β-TZnPcQ (48b)	PBS	0.15	0.28	0.54	10.9
	PBS+CEL	0.26	0.34	0.76	19.0
	DMSO	0.62	0.57	1.09	16.6
β-OZnPcQ (49b)	PBS	0.10	0.17	0.59	5.10
	PBS+CEL	0.24	0.32	0.75	7.70
	DMSO	0.49	0.60	0.82	17.1

^a[310], ^b[307], ^c[308], ^d[234]

For the SnPc complexes, Table 4.6 shows that even though α -SnPcBzPh (**45c**) had the lowest Φ_T value, its Φ_Δ was not the lowest, its low Φ_T value may be due to the photoreduction occurring following laser irradiation. Though photoreduction occurred in all the SnPc complexes, it may have been enhanced in the benzyloxyphenoxy substituted derivatives **45c** and **46c** due to more electron donating ability of this substituent compared to the phenoxy or tert-butylphenoxy substituents (**45a**, **46a**, **45b** and **46b**).

S_Δ (Equation 4. 8) which represents the efficiency of quenching of the triplet excited state

$$S_\Delta = \frac{\Phi_\Delta}{\Phi_T} \quad (4.8)$$

by singlet oxygen, was observed to be near unity for the complexes (Table 4.6), suggesting efficient quenching of the triplet state by singlet oxygen for these complexes except for GePcS₄ (**36**) and SiTCPC (**39**) in DMSO and ZnPcS₄ (**33**) in PBS which is likely connected to the aggregation in these samples. ClAlPc (**31**), also had a value higher than unity due to the photo transformation that occurred with this sample on irradiation with laser light.

The phenoxy and tert-butylphenoxy substituted Sn complexes (**45a**, **45b**, **46a** and **46b**) (Table 4.6), exhibited an efficient quenching of the triplet state by singlet oxygen considering their S_Δ values. However, S_Δ values were slightly higher than unity in the benzyloxyphenoxy substituted Sn complexes (**45c** and **46c**) due to the low Φ_T values obtained for these complexes as a result of photoreduction following laser irradiation as discussed above. Photoreduction was not experienced during Φ_Δ determinations because of the presence of oxygen during such determination.

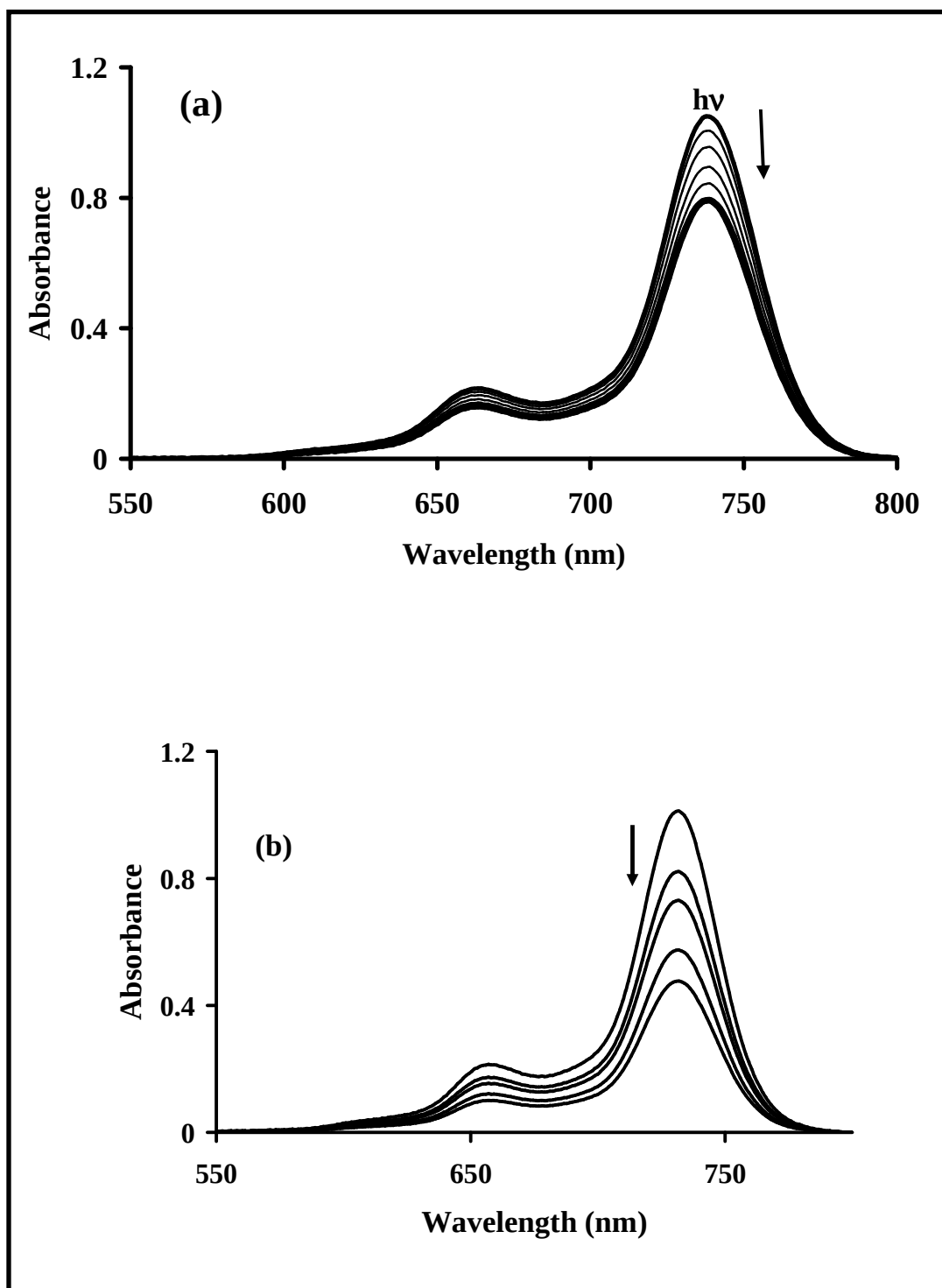
4.3.2 Photodegradation (photobleaching) quantum yields

The stability of MPc complexes in the presence of light plays an important role in their functionality and therefore it is vital to determine the stability of these complexes when exposed to light and determine any possible pathways of degradation. 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 [293,327]. Photodegradation is identified by a reduction in the intensity of the Q band absorption without formation of new peaks and it is easily monitored by UV/Vis spectroscopy. Typical spectral changes observed during photodegradation of MPcs are shown in Figure 4.11a for α -SnPcBzPh, **45c** and used with Equation 4.9 (Equation 1.36) to calculate photodegradation quantum yields (Φ_p).

$$\Phi_p = \frac{(C_0 - C_t)VN_A}{S.t.I_{abs}} \quad (4.9)$$

From Table 4.6, it is observed that Φ_p for the MPc complexes were higher in DMSO and CEL than in PBS pH 7.4. This implies that photodegradation is dependent on singlet oxygen; the highest Φ_Δ values were obtained in DMSO, hence the high Φ_p values. There were however exceptions; GePcS₄ (**36**) in DMSO where the Φ_Δ was unexpectedly low, had a high Φ_p value which therefore implies that for this complex in DMSO, the degradation occurs because the triplet state is sufficiently long lived (Table 4.4), implying that Φ_p also depends on τ_T values. Also, SiTCPC (**39**) again behaved differently by having lower Φ_p value in DMSO compared to aqueous medium, which is an opposite trend to what is observed in other MPc complexes.

The AlPc complexes had the lowest Φ_P values in each group, considering complexes with the same substituents except with the tetracarboxy complexes where SiTCPc (**39**) had the



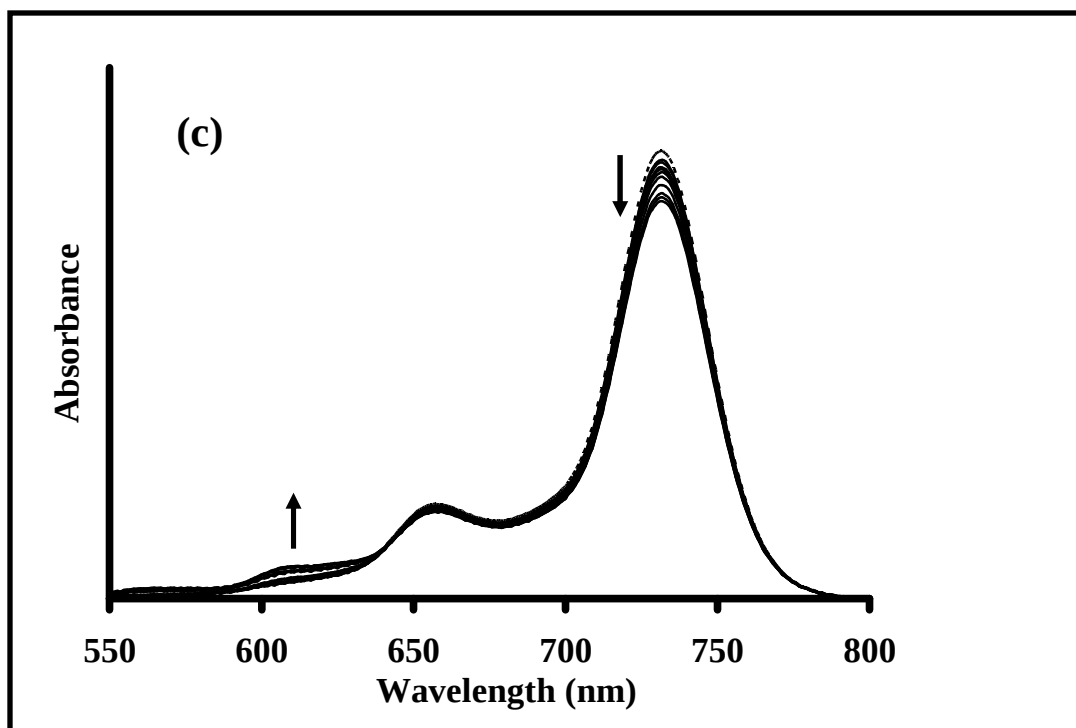


Figure 4.11: Photodegradation curves of α -SnPcBzPh (45c) in DMSO solution saturated with air (a), oxygen (10 minutes bubbling) (b) and argon (10 minutes bubbling) (c).

lowest Φ_P value in DMSO. In contrast, SiOCPC (43) was very unstable in the presence of light. In addition, the SnPc complexes (45a-c and 46a-c) and the aminoalkanethio-substituted complexes (47a, 47b, 48a, 48b, 49a and 49b) all exhibited approximately the same stability in DMSO with Φ_P in the order of 10^{-4} , which is higher than reported for some known MPc derivatives [236] but the values are in the range for GaPc and InPc with phenoxy and tert-butylphenoxy substituents. This confirms the fact that different substituents do have different effects on the stability of MPc complexes.

The photodegradation studies were done in air saturated solutions. No photoreduction (to other species absorbing in the visible region) of the complexes was observed during photodegradation studies.

In order to further confirm if the photoreduction that occurred after laser irradiation

(performed with argon saturated MPc solutions) also occurred during photodegradation, the latter experiments were repeated in solvent solutions that were oxygen or argon saturated for the SnPc complexes. Figures 4.11b and c show typical set of curves for each of these experiments for complex **45c** (α -SnPcBzPh). Similar results were obtained for other complexes. The photobleaching was very slow in argon purged solutions (due to some residual oxygen), Figure 4.11c, compared to solutions containing oxygen, Figure 4.11b. Bubbling with oxygen resulted in enhanced photodegradation Figure 4.11b due to the increased kinetics compared to in air only (Figure 4.11a) and in argon, Figure 4.11c. Figure 4.11c shows that in the presence of argon there was some photoreduction (as judged by increase in the absorption between 550 and 600 nm, as was observed for laser flash photolysis, but to a lesser extent in the former, further confirming photoreduction in these complexes in oxygen deficient environment. Figure 4.12 shows the kinetic plots for the photodegradation in the different media, and the results all point to the involvement of singlet oxygen in the photodegradation process.

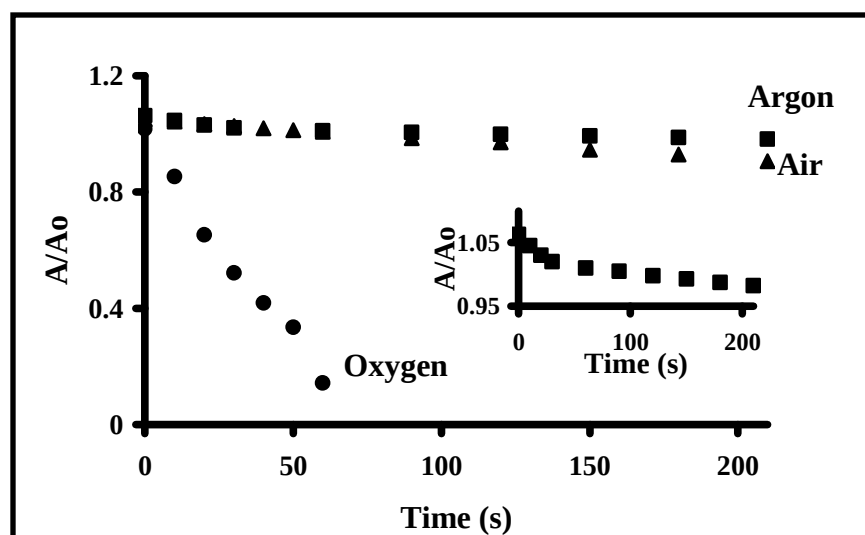


Figure 4.12: Kinetic plots for the photodegradation curves of α -SnPcBzPh (45c) in DMSO saturated with argon (Ar), air or oxygen (O_2). Inset: kinetic plot in argon saturated solution showing initial phototransformation.

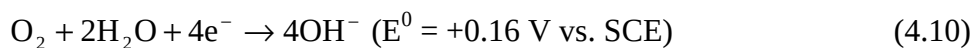
4.4 Photoelectrochemical processes

The comparative photoelectrochemical properties of aluminium, zinc and silicon octacarboxy phthalocyanines (MOCPs) (**41-43**) were investigated. The complexes were selected because they bore substituents that can allow proper chemical binding to the semiconductor oxide (ZnO) surface which requires the dye molecules to carry acid functionalities to allow for formation of covalent bonds to the hydroxide groups on the surface of the growing oxide. Hybrid thin films of the MOCPs (individually) and ZnO were prepared by the re-adsorption method. Time resolved photocurrent measurements of the prepared electrodes were determined. The efficiencies of the electrodes were also determined. The results are reported in terms of the incident photon to current conversion efficiency (IPCE), the amount of electrons in the external circuit divided by the amount of photons incident on the electrode. To provide an estimate of the sensitization efficiency of the dyes in the different electrodes, absorbed photon to current conversion efficiency (APCE), was also estimated. The re-adsorption of the dyes unto ZnO surface were carried in aqueous KOH solution (pH 10) because in this solvent, the complexes were in monomeric form and their adsorption on ZnO surface was optimum.

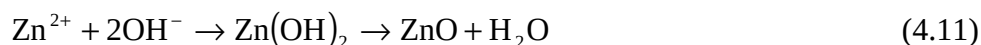
4.4.1 Electrodeposition of ZnO-Eosin-Y (ZnO-EY) hybrid films

Fabrication of thin films of metal chalcogens and metal oxides by electrochemical deposition is attractive because it is economically beneficial, harmless to the environment (because it is a low temperature process) and highly crystalline films can be obtained [346,347]. ZnO is an attractive material due to its electronic, mechanical, and thermal properties and can work well for fabrication of dye- sensitized solar cells (DSSCs) since

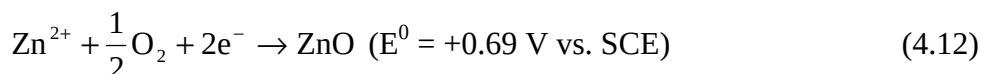
it is similar to the well known TiO_2 which is commonly used in DSSCs. ZnO films can be electrochemically deposited [346,348] and were prepared in this study by the reduction of oxygen as shown in Equations 4.10 to 4.12. The main reaction is the generation of hydroxide ions at the cathode;



The hydroxide ions produced are expected to react with Zn^{2+} and precipitate as zinc hydroxide. Following which, zinc hydroxide is dehydrated to ZnO [348,349].



The overall precipitation reaction of ZnO by reduction of oxygen is expressed in Equation 4.12;



Electrochemically induced crystallization of ZnO thin films in the presence of structure directing agents (SDA), e.g. eosin-Y followed by desorption of the SDA after electrodeposition and re-adsorption of a chosen sensitizer molecule from solution have been found to produce ideal monolayer adsorption films with high roughness factors which makes the sensitizer molecules like MPcs easily accessible in the ZnO pores, thereby appreciably increasing the photoelectrochemical efficiency of the electrodes [349-351].

Electrodeposition of ZnO -EY hybrid films was carried out at a potential of 1.0 V vs. SCE. A good indication for the film growth can be taken from plots of the observed current against time (Figure 4.13) which is typical of well deposited films in the presence of Eosin-Y [349-351].

A uniform thickness of 3 μm which is consistent with literature [349] was observed for the films as seen from the alphastep surface profile in Figure 4.14. The SEM image of the

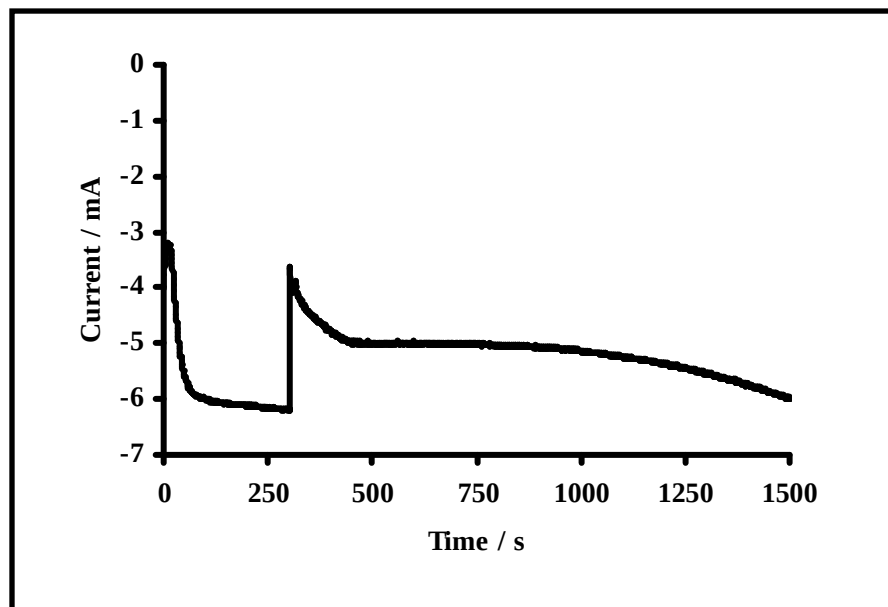


Figure 4.13: Current measured during the cathodic electrodeposition of ZnO-EY films from aqueous 5 mM ZnCl_2 , 50 μM Eosin-Y, O_2 saturated 0.1 M KCl at 70 $^\circ\text{C}$.

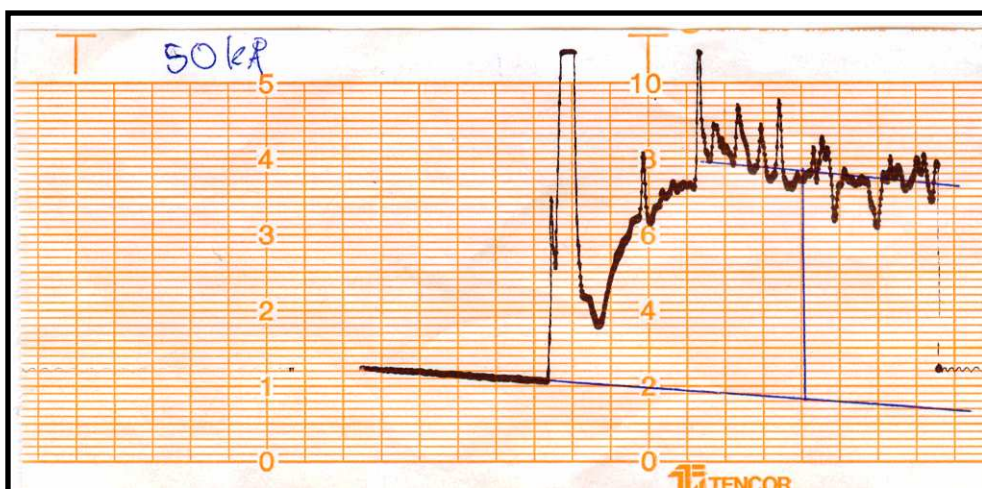


Figure 4.14: Alphastep surface profile of ZnO film.

ZnO films with EY and after its desorption from the film are shown in Figure 4.15. A change in morphology can be observed from the SEM images taken before (a) and after (b) the KOH treatment to extract the SDA from the surface of the film. Removal of SDA from the surface of ZnO increases the ZnO surface significantly with a finer morphology, which may be due to its porosity [349].

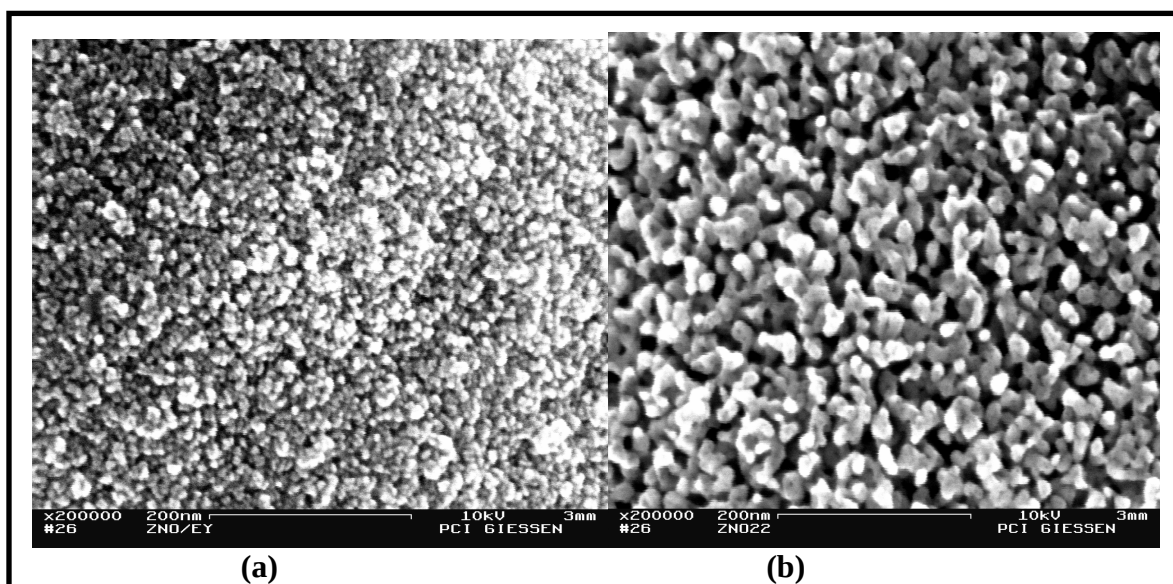


Figure 4.15: SEM images of one-step electrodeposited ZnO-EY hybrid thin film (a) and ZnO film (b) after extracting EY from ZnO surface in aqueous KOH. The data was provided by Prof. Dr. D. Schlettwein, Justus-Liebig University, Germany.

4.4.2 Dye loading and arrangement on ZnO

The desorbed ZnO thin film is translucent and milky white. The MOCPC dyes were loaded unto the ZnO films to furnish the film in blue (ZnOCPc) and green colours (AlOCPc and SiOCPc) respectively as shown in Figure 4.16 for ZnOCPc.

The electronic interaction within the hybrid films may lead to changes in the electronic structure of the dye molecules and can be studied by UV-vis absorption spectra. Figure

4.17 shows the absorption spectra of the ZnO/MOCPCs thin films compared with that of the pure ZnO thin film, and the aqueous solution of MOCPCs.

The desorbed ZnO thin film exhibits a wide range of absorption in the visible region with tail extending to about 800 nm with a sharp increase of the absorption below 380 nm attributed to the band gap absorption of ZnO. Gradual increase of absorption with decreasing wavelength is also observed due to light scattering (Figure 4.17a (iii)).

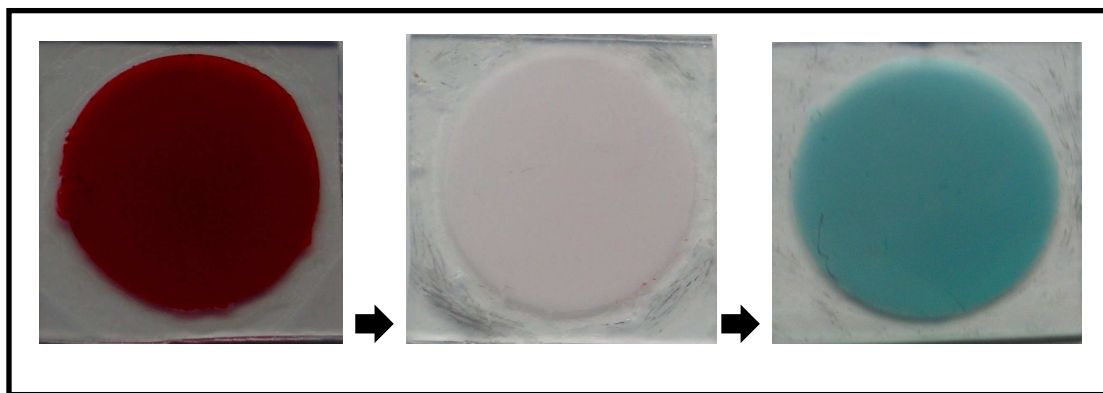


Figure 4.16: Images showing progress in change of color of ZnO films from electrodeposition (of ZnO/E-Y, red), followed by desorption of eosin-Y (white) and readsorption of ZnOCPC (blue).

As discussed in Chapter 3, the MOCPCs employed in this study are monomeric in aqueous solution Figures 4.17a-c with Q-band maxima at ~ 690 nm but they were slightly broadened in the ZnO films which is an indication of intermolecular electronic coupling in MPCs [352]. This may lead to different interactions of aggregated and non-aggregated dyes with the ZnO crystals. The UV-vis spectra in Figure 4.17 illustrate that the spectra of the re-adsorbed ZnO/MOCPC hybrid films are slightly red-shifted with Q-band maxima in Table 4.7 and broadened with the monomer still predominant. Such absorption character may be due to random intermolecular interaction leading to simple broadening

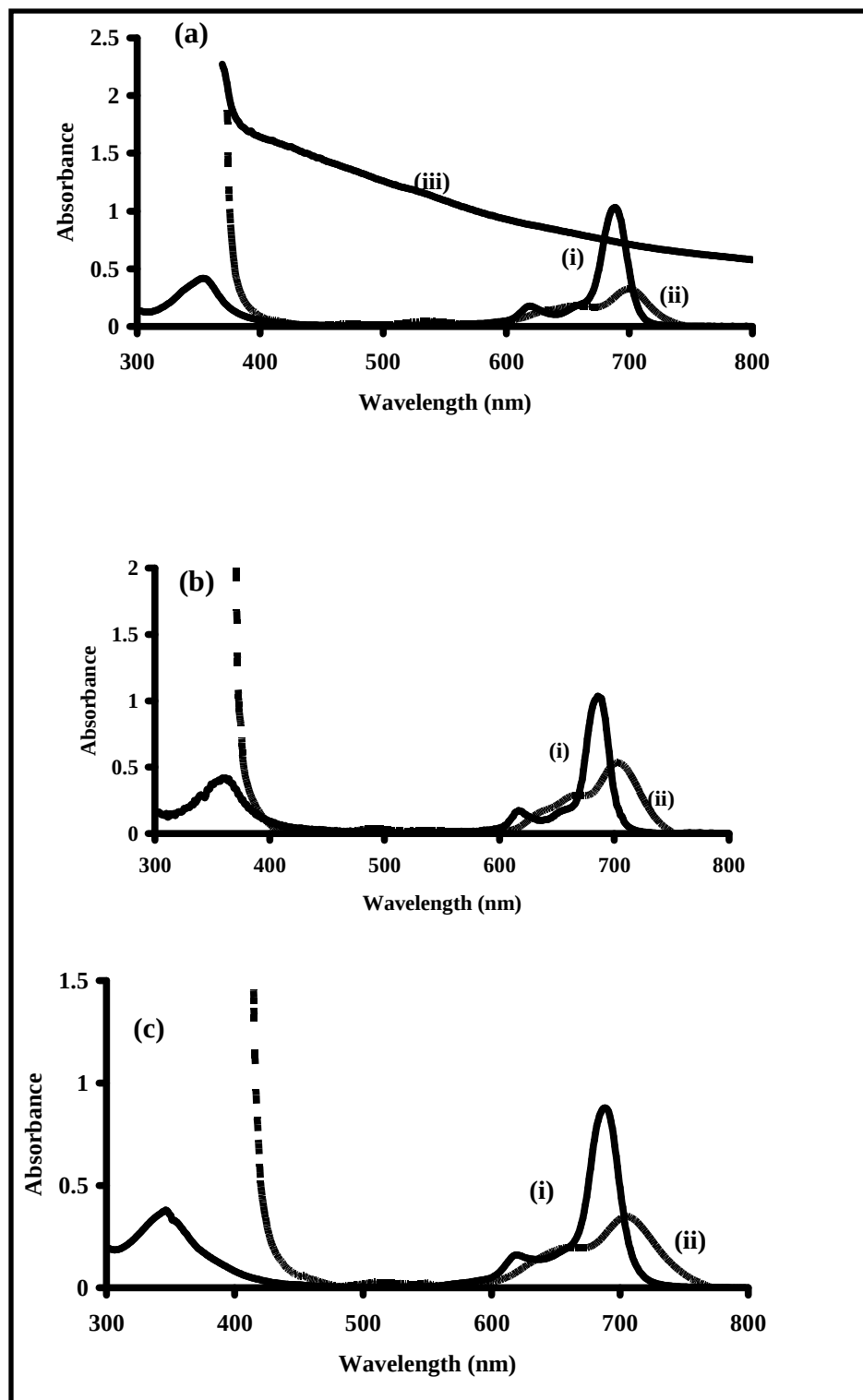


Figure 4.17: Absorption spectra of (i) of MOCpC in aqueous solution (pH 10), (ii) normalized or background corrected re-adsorbed ZnO/MOCpC thin film and (iii) ZnO thin film for ZnOCpC (a), AlOCpC (b) and SiOCpC (c).

Table 4.7: Spectral and photoelectrochemical data observed for MOCPc complexes at an incident photon flux of $10^{16} \text{ s}^{-1} \text{ cm}^{-2}$.

Complex	λ_Q (nm) (pH 10)	λ_Q (nm) (solid state)	Abs.	^a IPCE (%)	^b APCE (%)	Fill factor (%)	Eff (%)
ZnOCPc (41)	690	695	0.32	31.1	59.6	45.0	0.27
AlOCPc (42)	689	702	0.53	10.5	15.2	33.9	0.09
SiOCPc (43)	690	706	0.33	3.95	7.32	28.6	0.06

^aIPCE incident-photon-to-current-conversion efficiency, ^bAPCE absorbed- photon-to-current-conversion efficiency.

of the absorption spectrum. There is no indication for strong coupling of the chromophores as observed for ZnPcS₄ in ZnO [353], since the monomer peaks of the MOCPcs on ZnO still remains significant as against what was observed in the spectrum of ZnPcS₄ in ZnO where an additional absorption band was observed [353]. The observed red-shifting from that of monomeric MOCPcs in aqueous medium, suggests an electronic interaction of the MOCPcs with ZnO, because of the chemical attachment of the MOCPc to the ZnO surface. The red-shifting of the ZnO/MOCPc compared to the respective aqueous solution of MOCPc increased in the order ZnO/SiOCPc > ZnO/AlOCPc > ZnO/ZnOCPc. This may be due to the trivalent or tetravalent nature of the Al(III) or Si(IV) metal respectively, in the centre of the MOCPc molecule which allows axial OH coordination, that provides extra outlet for chemical attachment to the ZnO surface.

4.4.3 Photoelectrochemical measurements

4.4.3.1 Time-resolved photovoltage

Figure 4.18 shows the time-resolved photovoltage curves for the ZnO/MOCPCs. ZnO/ZnOCPC and ZnO/AlOCPC have the largest photovoltage of about 300 mV. Upon shutter closure, a monotonously slow decrease of the photovoltage was observed in ZnO/AlOCPC electrode (Figure 4.18 (iii)) during the decay period which may be due to a facile transfer of electrons from the electrolyte to the electrode. ZnO/AlOCPC was able to hold onto a high voltage value for a long time during the decay period whilst the photovoltage of ZnO/SiOCPC (Figure 4.18 (i)) and ZnO/ZnOCPC (Figure 4.18 (ii)) electrodes dropped immediately after the closure of the shutter.

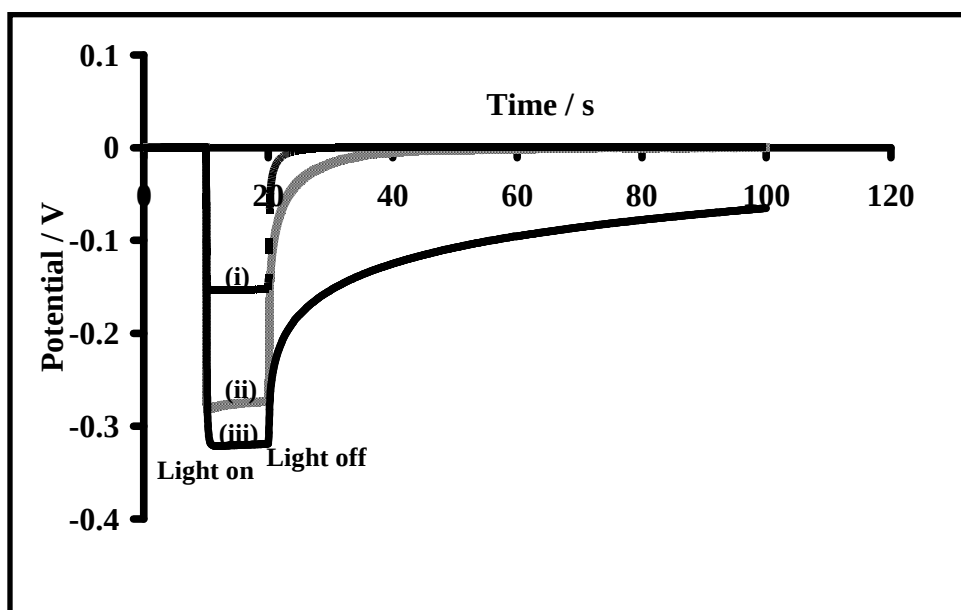


Figure 4.18: Time-resolved photovoltage transients of films of ZnO/SiOCPC (i) ZnO/ZnOCPC (ii) and ZnO/AlOCPC (iii) under illumination with white light in contact with 0.5 M tetrabutylammonium iodide and 0.05M iodine electrolyte in a 1: 4 by volume mixture of acetonitrile with ethylene carbonate.

4.4.3.2 Time-resolved photocurrent

Time-resolved photocurrent measurements were performed to analyze the kinetics of light induced charge transfer at the ZnO/MOCPC thin film electrodes and to discuss the role of charge-carrier recombination (Figure 4.19). The different MOCPCs showed transients of a stable anodic photocurrent upon irradiation of the electrodes with white light at an intensity of 100 mWcm^{-2} showing sensitization of the ZnO. These transients were similar in shape indicating similar relative rates of electron injection and re-reduction. An almost rectangular photocurrent response was obtained for the complexes especially with ZnO/SiOCPC with almost no overshoot when the light was switched on, suggesting small surface charging. The photocurrent increased monotonously at a significantly slow rate. The maxima of the photocurrents appear at about 100 ms after the beginning of illumination. This may be due to a slow electron transport in the nanocrystalline ZnO electrodes [354]. Even upon shutter closure, a slow decrease of the anodic photocurrent was observed which may be caused by continued detrapping of electrons and their collection at the back electrode even after the injection of electrons into ZnO had stopped. From this behavior, an assumption of a facile transfer of electrons from I_3^- to the MOCPCs can be concluded. However, smaller current densities were observed at ZnO/SiOCPC and ZnO/AlOCPC electrodes (Figure 4.19) compared to ZnO/ZnOCPC. This is probably due to occurrence of a faster charge transfer from ZnO/SiOCPC or ZnO/AlOCPC electrodes to the electrolyte whilst a faster and more efficient electron injection from ZnOCPC, as compared to SiOCPC or AlOCPC into ZnO led to the higher efficiency of the ZnO/ZnOCPC electrodes.

The more efficient charge transfer to the electrolyte from ZnO/SiOCPC or ZnO/AlOCPC

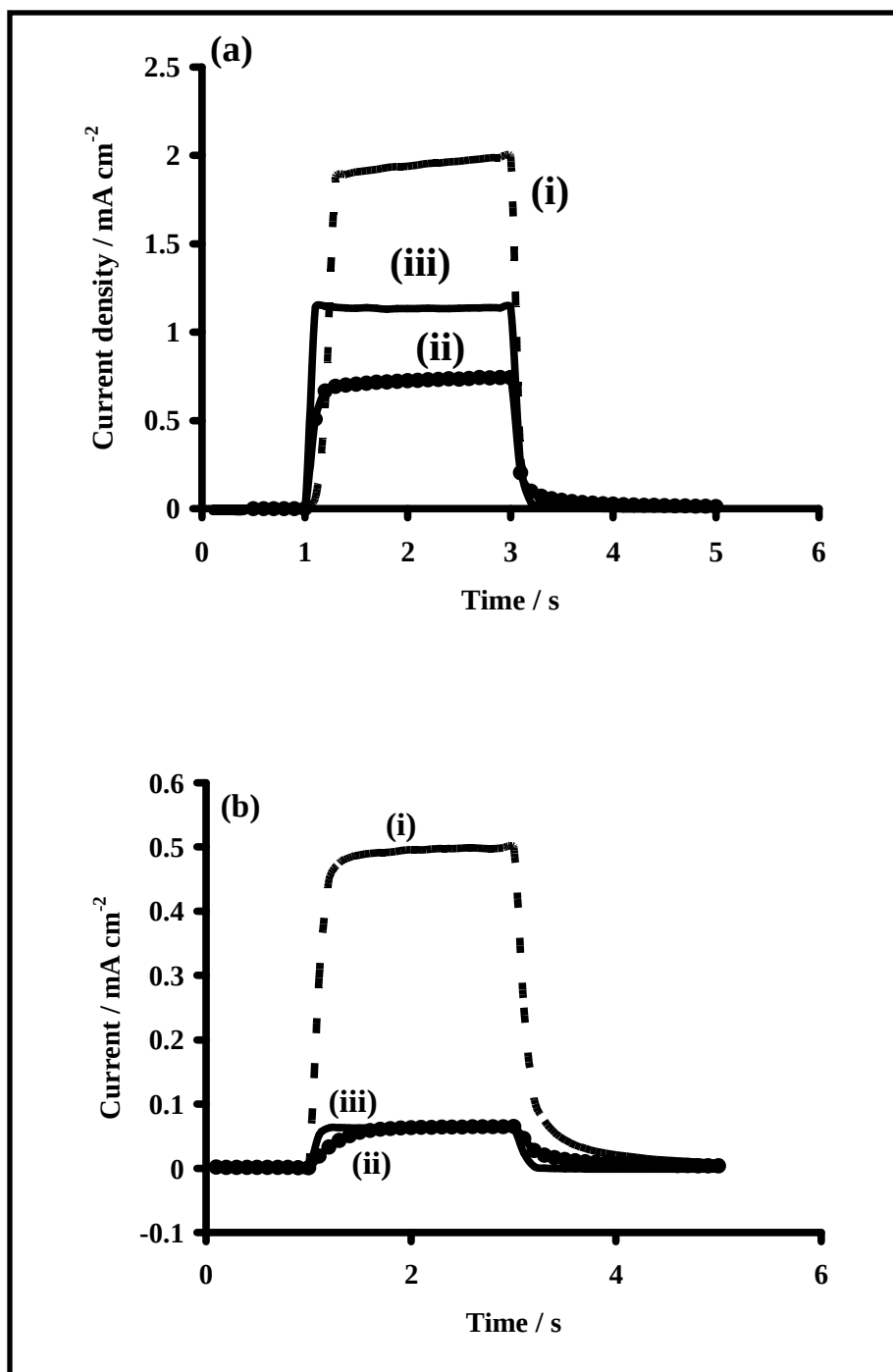


Figure 4.19: Time-resolved photocurrent transients of films of (i) ZnO/ZnOCPC, (ii) ZnO/AlOCPC and (iii) ZnO/SiOCPC under illumination with white light (a) in contact with 0.5 M tetrabutylammonium iodide and 0.05M iodine electrolyte in a 1 : 4 by volume mixture of acetonitrile with ethylene carbonate and (b) under illumination at the Q-band wavelength range part of the visible spectrum.

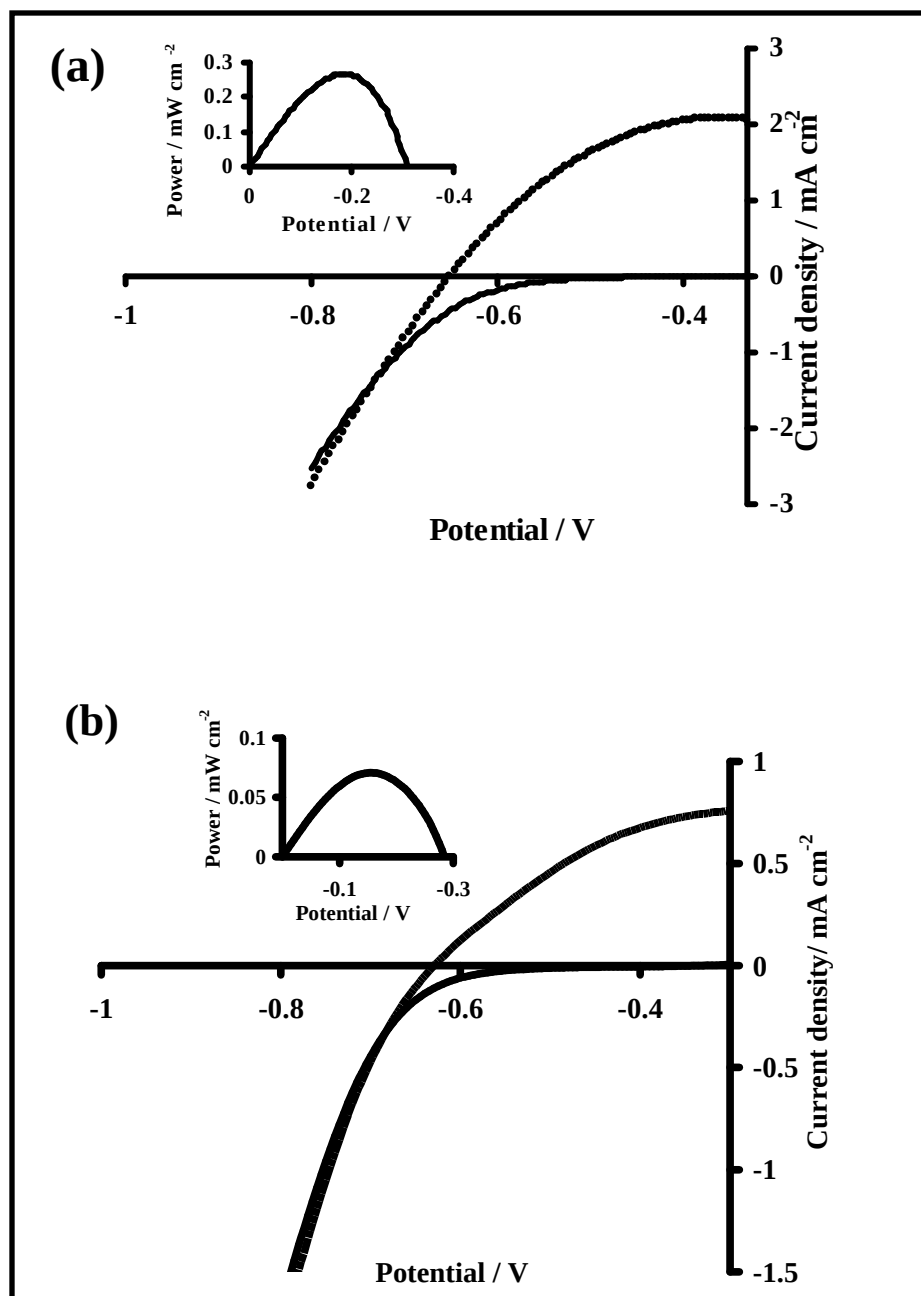
compared with ZnO/ZnOCPC electrode may be explained by differences in the chemical attachment of these MOCPc complexes to the ZnO surface.

These films were investigated further under illumination with the Q- band (700 nm) part of the visible spectrum where their maximum absorbances fall into (Figure 4.19b). Quite constant transient characteristics were observed for these electrodes. Due to a decreased light intensity, a slower increase in current density is observed caused by an increased relative trapping probability of injected electrons. The relatively higher photocurrent at ZnO/ZnOCPC confirms the considerably higher injection rate for this electrode. These transient curves were about a factor of three (for ZnOCPC and SiOCPC) or ten (for AlOCPC) smaller in current density due to the absence of the UV absorption.

Figure 4.20 shows the photocurrent-voltage characteristics of the ZnO nanocrystalline photoelectrochemical cells sensitized by MOCPcs. Clear photocurrents, photovoltages and diode characteristics are observed as expected for photovoltaic active cell structures. Faradaic characteristics are observed for the ZnO/ZnOCPC films which reflected in higher power (inset, Figure 4.20), fill factors and efficiencies (Table 4.7, Table 4.8). Power curves (inset, Figure 4.20) for the MOCPcs were plotted from the photocurrent-voltage characteristics and the efficiencies of the electrodes were estimated from these curves.

The incident- photon- to- current- conversion- efficiencies (IPCE), Table 4.7 were calculated as the ratio of the transferred electron density (calculated from Faraday's constant and the photocurrent at the working electrode) to the photon density (in the absorption maximum) incident on the cell during wavelength- dependent photocurrent measurements. The IPCE characterizes the overall efficiency of an electrode in its light

absorption, electron injection to the semiconductor, charge transport therein and hole transfer to the electrolyte. The IPCE values were generally low when compared to some organic sensitizers [355], but in comparison with known phthalocyanine complexes, the obtained IPCE values for the MOCPCs are very reasonable. The ZnO/ZnOCPC electrode proved to be the most efficient with the highest calculated IPCE value of 31.1% at an



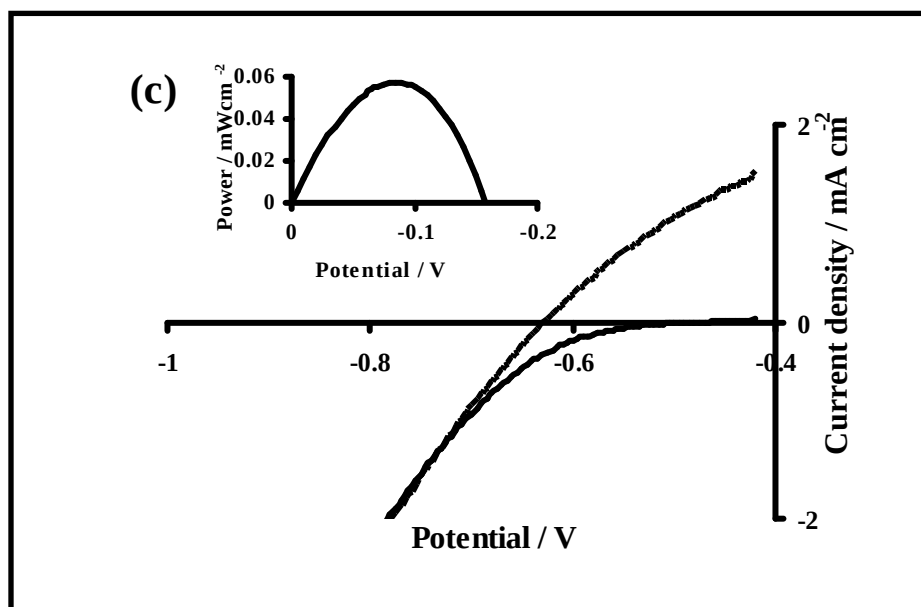


Figure 4.20: Photocurrent-voltage characteristics of nanocrystalline ZnO photoelectrochemical cell sensitized with ZnOCpC (a), AlOCpC (b) and SiOCpC (c). The black curve shows the dark current and dotted curves shows the AM 1.5 simulated sunlight curves. Inset: Power curves for the nanocrystalline ZnO photoelectrochemical cell sensitized with the respective MOCPcs.

absorbance of 0.32 (Table 4.7). This indicates a quantum efficiency of about a factor of ten higher than ZnO/SiOCpC electrode (3.95 %) at about the same absorbance (0.33) and about a factor of three higher than ZnO/AlOCpC which has a value of 10.5 % inspite of its higher absorbance of 0.53. The clear difference shows the influence of the central metal of the MOCPcs and the assumption of the strong chemical attachment of the complexes through the OH axial ligands to the ZnO surface. IPCE of 12.5 % has been reported for zinc tetrasulfonated phthalocyanine complex [349] on ZnO, our result of 31.1% therefore makes ZnOCpC the most efficient MPc so far to our knowledge. Considering the light absorption and scattering loss by the conducting glass, the

maximum efficiency for absorbed photon-to-current conversion efficiency (APCE) which serves as a measure of the internal quantum efficiency of conversion of excited states into current was 60 % (Table 4.7) for ZnO/ZnOCPc electrode which shows that above half of the light absorbed by the complex is converted to current.

The short-circuit photocurrent density (I_{sc}), open-circuit photovoltage (V_{oc}), and fill factor (ff , using Equation 4.13) of the ZnO/ZnOCPc electrode with a 0.5 M tetrabutylammonium iodide and 0.05 M iodine based electrolyte in a 1 : 4 by volume mixture of acetonitrile with ethylene carbonate under an irradiance of 100 mW cm^{-2} (AM 1.5), full sunlight are 2.09 mA cm^{-2} Figure 4.19, 280 mV Figure 4.18, and 45 %, respectively, yielding an overall conversion efficiency (η , using Equation 4.14) of 0.27 %.

$$ff = \frac{\text{Max.power}}{I_{sc} \times V_{oc}} \times 100 \quad (4.13)$$

where, I_{sc} is the short circuit photocurrent (mA cm^{-2}), V_{oc} , the open circuit photovoltage (V) and ff , fill factor

$$\eta(\%) = \frac{I_{sc} \times V_{oc} \times ff}{I_0} \times 100 \quad (4.14)$$

where I_0 is the light intensity (mW cm^{-2}).

ZnO/AlOCPc had an overall efficiency (η) of 0.09 % with a ff of 33.9 %, while ZnO/SiOCPc had an efficiency of 0.06 % with a ff of 28.6 %. Porphyrin Zn derivatives have also been found to exhibit superior efficiencies to other corresponding porphyrin metal derivatives [356]. The efficiencies of these electrodes are low which must have been a result of the poor fill factors. A technical ruthenium cell of efficiency of 10 % has been reported years ago [357].

Further optimization of the most efficient cell (ZnO/ZnOCPc) was carried out by varying the absorbance of the ZnOCPc on the nanocrystalline ZnO as shown in Table 4.8, but results were not as optimum as the electrode with 0.32 absorbance described above, though at a lower absorbance of 0.18, there was some improvement in the efficiency of the cell due to improved ff, but the IPCE and APCE were poor, however the study still leaves room for further optimization.

The stability of the cell was monitored by long time measurement of photocurrent transient under an irradiance of 500 mW cm^{-2} for 20 hours Figure 4.21 for ZnO/ZnOCPc and a very slow decrease of the anodic photocurrent was observed which can lead to the assumption that these cells can work well as long-term stable DSSCs.

Table 4.8: Spectral and photoelectrochemical data observed for ZnO/ZnOCPc complexes at an incident photon flux of $10^{16} \text{ s}^{-1} \text{ cm}^{-2}$ on varying the absorbance of ZnOCPc on ZnO film

Abs	λ_Q/nm (solid state)	IPCE (%)	APCE (%)	Fill factor (%)	Eff (%)
0.18	692	14.98	44.06	46.4	0.33
0.32	695	31.1	59.6	45.0	0.27
0.78	690	27.14	32.55	31.3	0.097
0.87	692	25.2	29.13	40.2	0.24

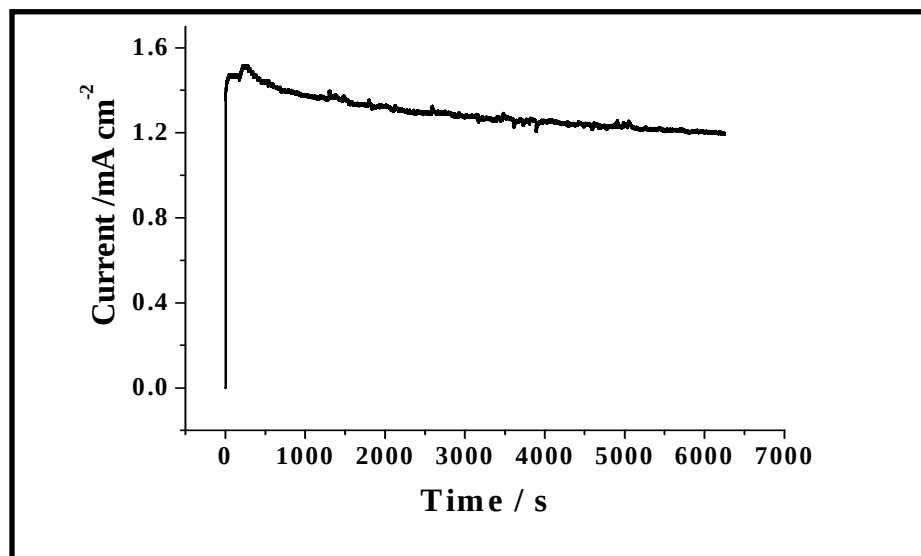


Figure 4.21: Time-resolved photocurrent transients of ZnO/ZnOCPc film at 500 mW cm^{-2} .

4.5 Conclusions

The photophysical and photochemical properties of synthesized MPcs were studied and found to be dependent on the central metal and solvents used. Addition of cremophore EL resulted in increased triplet quantum yields (Φ_T), lifetimes (τ_T) and singlet oxygen (Φ_Δ) compared with aqueous medium, suggesting an improved photosensitizing ability of these complexes in the presence of CEL. A difference in the nuclear configuration of the ground and excited states was observed in some of the complexes due to aggregation or the effect of the central metal with large atomic number leading to a displacement of the metal from the core of the phthalocyanine ring, hence a loss of symmetry, which is more pronounced on excitation. Photoreduction of AlPc and the SnPcs was observed during photolysis in the absence of oxygen due to ring reduction. Photodegradation was found to be dependent upon the singlet oxygen generating capabilities of the complexes. The

photophysical and photochemical parameters of the complexes reveal that the complexes would find use in applications requiring photosensitizers.

Fluorescence quenching of the carboxy-substituted MPc complexes by BQ was found to be diffusion-controlled. This was exploited to estimate the fluorescence lifetimes of the carboxy complexes which allowed for detailed photophysical studies of the complexes. The obtained fluorescence lifetime values were comparable to lifetimes obtained from PhotochemCAD software.

The photovoltaic properties for MPcs with carboxylic binding groups, revealed that the Zn containing diamagnetic MPc have the highest incident photon-to-current conversion (IPCE) efficiency obtained so far with phthalocyanine-type sensitizers on nanocrystalline ZnO films. Facile electron injection from the excited dye molecules to the ZnO conduction band was demonstrated by the different MOCPCs. These findings open up new avenues for improving the efficiency of nanocrystalline ZnO injection solar cells.

CHAPTER 5

INTERACTION OF METALLOPHTHALOCYANINES WITH NANOPARTICLES

5.1 Interaction of metallophthalocyanines with quantum dots

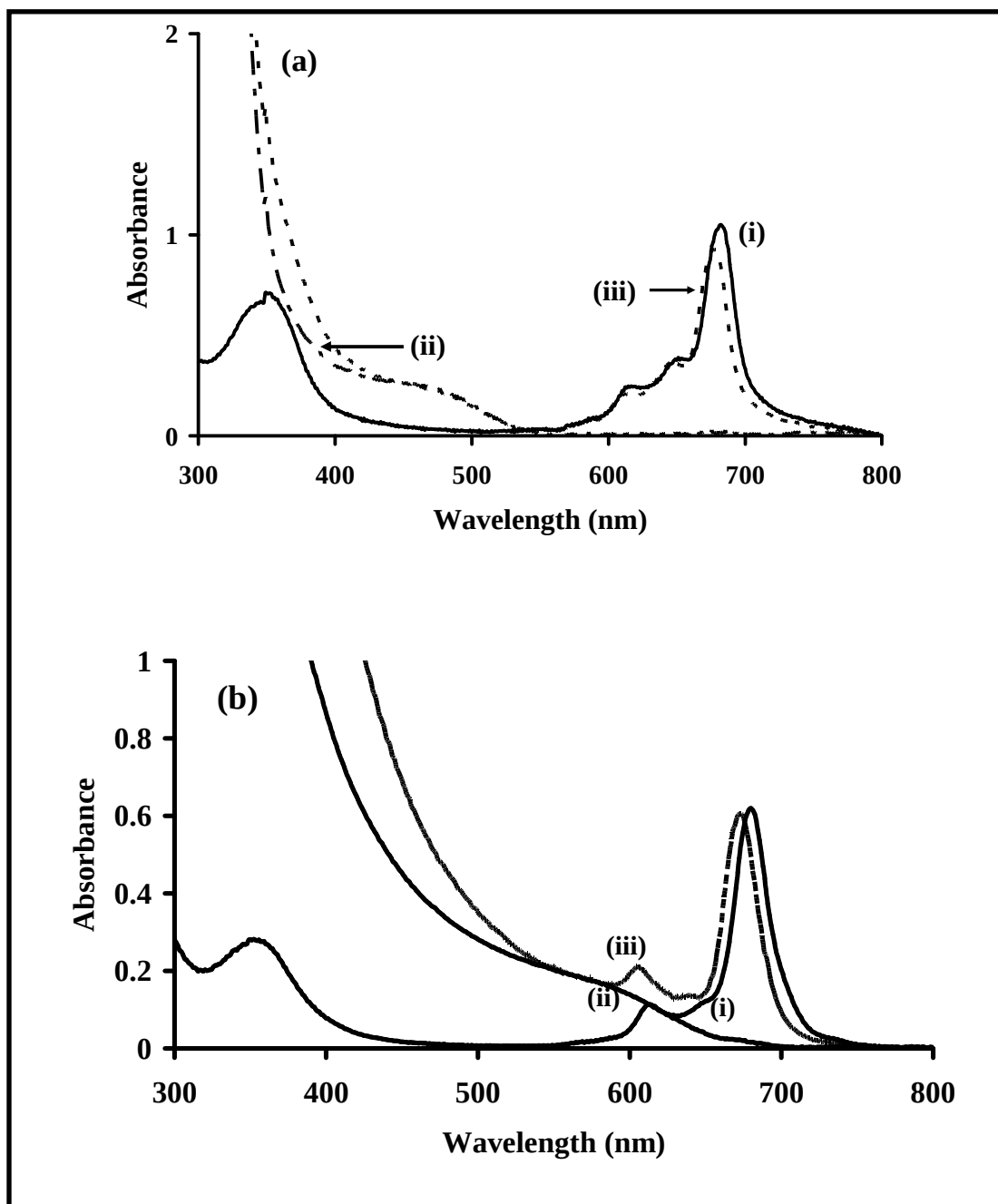
These studies were carried out with monomeric anionic water-soluble MPcs (AlPcS₄ (**34**), Zn, Al, Si and Ge octacarboxy MPcs (**41-44**)) in aqueous medium and anionic MPcS₄ (Zn, Si and Ge MPcS₄ complexes **33-36**) in water: methanol (1:1) solvent mixture, (w/m) since they are monomeric in this solvent mixture and monomerization is needed for high photochemical activity in processes involving these MPcs' excited states. The MPcS₄ complexes obeyed Beer's law for concentrations less than 1×10^{-5} M in this solvent mixture. Spectroscopic studies in 40:60 water: methanol solvent mixture were also carried out with the cationic water-soluble MPcs (α -TZnPcQ (**47b**), β -TZnPcQ (**48b**) and β -OZnPcQ **49b**).

5.1.1 Anionic MPcs and QDs

5.1.1.1 Spectral changes of MPcs in the presence of QDs

The electronic absorption spectrum of AlPcS₄ (**34**) in PBS pH 7.4 in the presence and absence of QD is shown in Figure 5.1a (similar spectral changes were observed for AlPcS₄ and the other MPcS₄ complexes in water : methanol solvent mixture (Figure 5.1b for ZnPcS₄ (**33**)). The spectrum is slightly blue-shifted by about 3 nm in the presence of QDs; this behaviour has been documented before for interaction of QDs with porphyrins [226]. For the MOCPCs, as seen in Figure 5.1c for GeOCPC (**44**) as a representative of MOCPCs, there was no significant shift in the absorption maximum in the presence of the QDs. The QD-MPc mixture gave an enhanced absorption in the 550 nm region (depending on the absorption maxima of the QD employed), a region where the MPc's absorption is negligible.

The shift in the absorption maxima of the MPcS₄ complexes in the presence of the QDs suggests that some sort of interaction is occurring probably due to surface plasma changes [226] as interaction occurs between the MPc and the surface of the QDs. It is however most likely that the QDs interact with the MPcS₄ and MOCPC complexes by adsorption since the substituent of these complexes and the cappings of the QDs



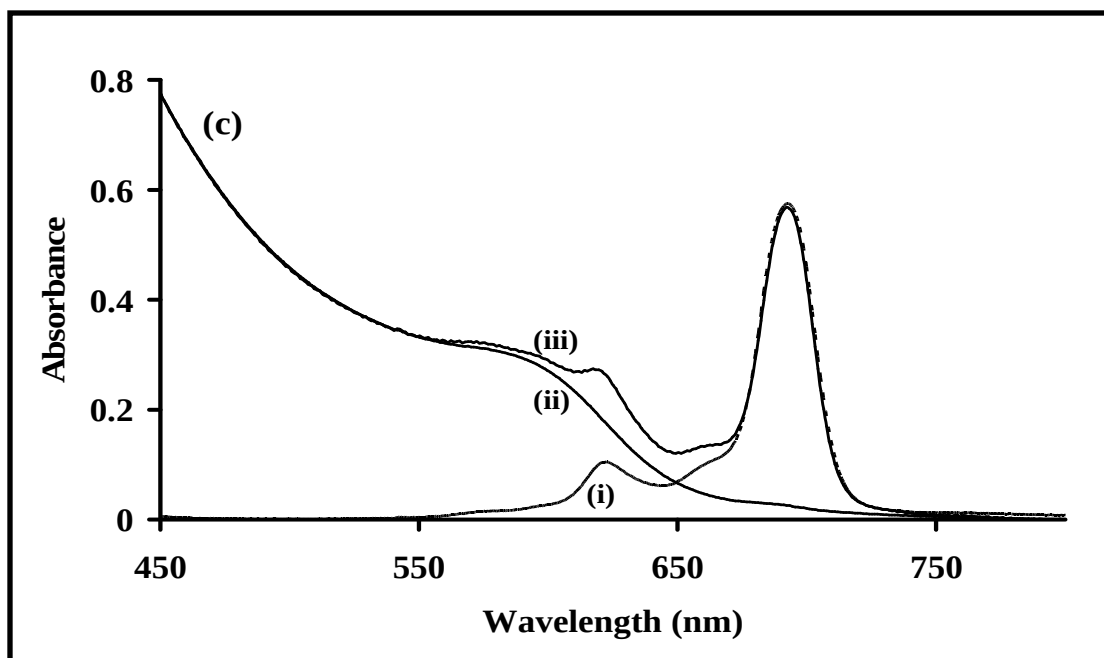


Figure 5.1: Absorption spectra of (i) MPc alone (ii) QD alone and (iii) mixture of MPc and QD. (a) AlPcS₄ (**34**) and MPA1 in PBS pH 7.4; (b) ZnPcS₄ (**33**) and MPA2 in 1:1 water: methanol mixture and (c) GeOCPC (**44**) and CYS3 in PBS pH 7.4. [MPc] = $\sim 6 \times 10^{-6}$ M, [QD] = $\sim 4 \times 10^{-6}$ M.

employed are both negatively charged.

Quenching studies were carried out in pH 7.4 buffer only with AlPcS₄ (**34**) to see the influence of the QDs on the excited state of **34** as a representative of all the monomeric water soluble MPcs studied in the absence of organic solvent (e.g. MOCPC). Respective QDs' fluorescence was found to decrease progressively with increasing concentration of **34**, Figure 5.2. This quenching in fluorescence was used to estimate the binding constants (K_b) and the stoichiometry (n) using Equation 5.1, same as Equation 1.28, with results obtained listed in Table 5.1.

$$\log\left[\frac{(F_0 - F)}{(F - F_\infty)}\right] = \log K_b + n \log[\text{MPc}] \quad (5.1)$$

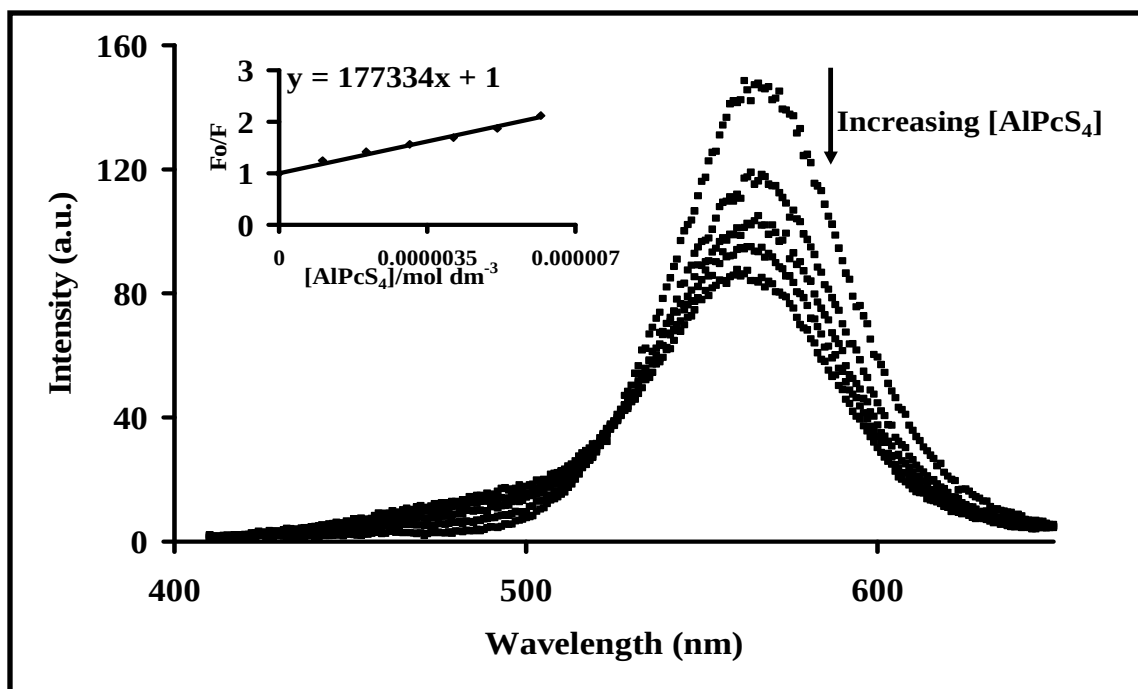


Figure 5.2: Fluorescence emission spectral changes of CYS1 with increasing $[AlPcS_4]$ in 0.01M PBS pH 7.4. Inset: Stern-Volmer (static) quenching plot for quenching of QD by **34**. $[QD] = 10^{-6} M$ $[34]$, = 0 to $6.18 \times 10^{-6} M$.

The high values for K_b in the $10^5 M^{-1}$ range indicate that there is a relative affinity for **34** by the QDs. The values of K_b for the MPA capped QD mixtures within each set of synthesized QDs were quite high compared to the others suggesting that a strong coupling may be occurring between MPA and **34**. CYS1 and CYS2 gave the lowest K_b values. The n was found to be ~ 1 . The quenching between QDs and **34** is likely static since there is a shift in the absorption maxima suggesting strong interaction.

The slopes of the plot of $\frac{F_0}{F}$ against $[AlPcS_4]$ gave the static quenching constant (K) [245] (Equation 1.17) for the fluorescence quenching of the QDs fluorescence by **34**, within investigated range of concentrations and an intercept of 1, (inset in Figure 5.2).

Table 5.1 lists the K values, which did not follow any particular pattern but it shows that

34 effectively quenches all the QDs.

Table 5.1: Binding and quenching data for AlPcS₄-QD interactions in PBS pH 7.4

QDs	^a K _b (x 10 ⁵ M ⁻¹)	n	^b K (x 10 ⁵ M ⁻¹)
CYS1	0.61	0.89	1.77
MPA1	1.62	1.07	0.62
TGA1	0.89	0.97	1.21
CYS2	0.34	0.94	0.68
MPA2	11.6	1.15	1.69
TGA2	6.43	1.09	1.80

^aK_b = binding constant and ^bK = static quenching constant for AlPcS₄-QD

5.1.1.2 Fluorescence quantum yields

AlPcS₄ (**34**) was studied in detail in PBS pH 7.4 since as stated above, it is not aggregated compared to the rest of the MPcS₄ complexes.

Fluorescence quantum yield (Φ_F) values for the CdTe QDs were calculated using Equation 1.14 and also shown as Equation 4.1 and are listed in Table 5.2 same as in Table 4.1. Fluorescence quantum yield (λ_{exc} , 400 nm) of the QDs ($\Phi_{F(QD)}^{Mix}$) in the mixture with **34** decreased, Table 5.2, compared to $\Phi_{F(QD)}$ of QDs alone, due to energy transfer from the QDs to **34**. Φ_F (λ_{exc} , 630 nm) of **34** ($\Phi_{F(AlPcS_4)}^{Mix}$) in the mixture of **34** and QDs compared to the former alone $\Phi_{F(AlPcS_4)} = 0.13$, remained almost unchanged with the

Table 5.2: Fluorescence quantum yields of QDs and photophysical parameters of AlPcS₄ (34) in the presence of QDs in pH 7.4 PBS.^a

^b QDs	^c $\Phi_{F(QD)}$	^d $\Phi_{T(AlPcS_4)}^{Mix}$	^e $\tau_{T(AlPcS_4)}^{Mix}$ (μs)	$\Phi_{F(QD)}^{Mix}$	$\Phi_{F(AlPcS_4)}^{Mix}$
MPA1	0.19	0.50	740	0.16	0.12
MPA2	0.59	0.42	570	0.25	0.07
TGA1	0.30	0.45	500	0.26	0.13
TGA2	0.62	0.42	320	0.40	0.09
CYS1	0.41	0.34	470	0.32	0.12
CYS2	0.09	0.45	530	0.003	0.10

^a legend:

$\Phi_{F(QD)}$ = Fluorescence quantum yield of QDs alone ($\lambda_{exc} = 400$ nm); $\Phi_{T(AlPcS_4)}^{Mix}$ = triplet quantum yield of 34 in the mixture with QDs; $\tau_{T(AlPcS_4)}^{Mix}$ = triplet lifetime of 34 in the mixture with QDs; $\Phi_{F(QD)}^{Mix}$ = fluorescence quantum yield of QDs in the mixture with 34 ($\lambda_{exc} = 400$ nm); $\Phi_{F(AlPcS_4)}^{Mix}$ = fluorescence quantum yield of 34 in a mixture with QDs ($\lambda_{exc} = 630$ nm); ^bMPA = 3-mercaptopropionic acid and TGA = thioglycolic acid, CYS = L-cysteine; ^c $\Phi_{F(AlPcS_4)} = 0.13$; ^d $\Phi_{T(AlPcS_4)} = 0.36$; ^e $\tau_{T(AlPcS_4)} (\mu s) = 470 \mu s$

exception of the larger QDs, TGA2 and MPA2, where there was a slight decrease.

With the MPcS₄ complexes in 1:1 water : methanol solvent mixture, L-cysteine capped QDs were not studied (Table 5.3) since the bigger ones, CYS2 behaved poorly with AlPcS₄ in PBS 7.4 as described above.

Φ_F values for the QDs also decreased in the presence of the respective MPcS₄ complexes in 1:1 water: methanol solvent mixture as shown in Table 5.3 ($\Phi_{F(QD)}^{Mix}$). This decrease in the fluorescence yield of the QDs in the presence of the MPcS₄ complexes is due to the transfer of energy from the QDs to the MPcS₄ complexes (as stated above) because as the

Table 5.3: Photophysical parameters of MPcS₄ complexes in the presence of QDs in 1:1 methanol: water mixture^a

MPc	^b QD	$\Phi_{T(MPcS_4)}^{Mix}$	$\tau_{T(MPcS_4)}^{Mix}$ (μs)	$\Phi_{F(QD)}^{Mix}$ λ_{exc} , 500 nm	$\Phi_{F(MPcS_4)}^{Mix}$ λ_{exc} , 620 nm
ZnPcS ₄ (33)	MPA1	0.51 (0.56)	240 (180)	0.17	0.16 (0.14)
	MPA2	0.42	220	0.33	0.16
	TGA1	0.49	250	0.12	0.16
	TGA2	0.45	290	0.45	0.17
AlPcS ₄ (34)	MPA1	0.46 (0.36)	600 (560)	0.17	0.20 (0.18)
	MPA2	0.43	610	0.45	0.22
	TGA1	0.41	610	0.27	0.19
	TGA2	0.46	560	0.49	0.26
SiPcS ₄ (35)	MPA1	0.45 (0.56)	140 (280)	0.18	0.05 (0.10)
	MPA2	0.55	310	0.25	0.09
	TGA1	0.53	340	0.09	0.05
	TGA2	0.54	340	0.32	0.07
GePcS ₄ (36)	MPA1	0.85 (0.81)	240 (250)	0.17	0.13 (0.12)
	MPA2	0.87	280	0.32	0.16
	TGA1	0.81	350	0.07	0.12
	TGA2	0.85	360	0.37	0.15

^a Number in brackets are the quantum yields ($\Phi_{F(MPcS_4)}$ or $\Phi_{T(MPcS_4)}$) or triplet lifetimes $\tau_{T(MPcS_4)}$ of MPcs alone. ^bMPA = 3-mercaptopropionic acid and TGA = thioglycolic acid. Fluorescence quantum yields of quantum dots alone are listed in Table 5.2

QD particles fluoresce; the MPc molecules (acceptor) absorb the energy, thus reducing the fluorescence intensity of the QDs (donor) in the QD-MPc mixture. Φ_F values for the MPcS₄ complexes in 1:1 water: methanol solvent mixture are listed in Table 5.3 (in brackets) (λ_{exc} 620 nm). Apart from the SiPcS₄, Φ_F values decreases with the size of the central metal in this solvent mixture, which is consistent with the strengths of spin-orbit coupling induced by the respective central metals based on their relative masses. There was a general slight increase in the Φ_F values of the MPcS₄ complexes, except for SiPcS₄ (all sizes of QDs) and GePcS₄ (TGA1 and MPA1) in the presence of the QDs (λ_{exc} 620 nm) compared to the values of the MPcS₄ complexes alone (in brackets, Table 5.3). The increase was more pronounced in the presence of the larger QDs; MPA2 and TGA2. For SiPcS₄, there was generally a small decrease in the Φ_F values. However, considering experimental errors, the changes in Φ_F values is insignificant in many cases. The slight decrease in Φ_F values (for SiPcS₄ or GePcS₄) could be due to the heavy atom effect of the QDs on these complexes, while the slight increase in Φ_F values (for the other MPcS₄ complexes) could be attributed to the possible shielding of the MPcS₄ complexes by the QDs, thus decreasing quenching of the former or due to energy transfer from the QDs to the MPcS₄ complexes with no significant loss in transit through collisions and other non radiative means. It is documented that energy transfer can be observed by monitoring quenching of donor fluorescence or the enhancement of acceptor fluorescence, but the latter is said to be complicated [227,358].

The MOCPcs were studied in the presence of L-cysteine capped QDs, (CYS3) since it is expected that the amino group on the L-cysteine capping of the QDs and the carboxylic group of the MOCPc will form an amide bond, resulting in a covalent attachment of the

MOCPc with the CdTe QDs. A decrease in the Φ_F values of the QDs was also observed in the presence of the respective MOCPcs ($\Phi_{F(QD)}^{Mix}$) as shown in Table 5.4 compared to $\Phi_{F(QD)}$ of QDs alone, which is expected as discussed above for MPcS₄. Φ_F values for the MOCPcs are listed in Table 5.4 (in brackets) (λ_{exc} 640 nm). There was a slight decrease in the Φ_F values of the MOCPcs in the presence of CYS3 (λ_{exc} 640 nm) compared to the values of the MOCPcs alone. It is expected that the heavy atom effect of the QDs on the MOCPcs would encourage intersystem crossing, which would result in the reduction of fluorescence.

Table 5.4: Photophysical parameters^a of MOCPcs in the presence of CYS3^b in PBS 7.4

MPc	$\Phi_{T(MOCPc)}^{Mix}$	$\tau_{T(MOCPc)}^{Mix}$ (μ s)	$\Phi_{F(QD)}^{Mix}$ λ_{exc} , 500 nm	$\Phi_{F(MOCPc)}^{Mix}$ λ_{exc} , 640 nm
ZnOCPc (41)	0.55 (0.50)	190 (160)	0.18	0.21 (0.23)
AlOCPc (42)	0.40 (0.32)	495 (450)	0.11	0.25 (0.27)
SiOCPc (43)	0.32 (0.34)	130 (90)	0.09	0.18 (0.24)
GeOCPc (44)	0.67(0.62)	270 (240)	0.08	0.12 (0.13)

^aNumber in brackets are the quantum yields ($\Phi_{F(MOCPc)}$ or $\Phi_{T(MOCPc)}$) or triplet lifetimes $\tau_{T(MOCPc)}$ of MOCPcs alone, ^bCYS = L-cysteine, $\Phi_{F(CYS3)} = 0.4$

5.1.1.3 Triplet quantum yields (Φ_T) and lifetimes (τ_T)

The variation of Φ_T values of AlPcS₄ (**34**) (which could be studied in pH 7.4 buffer since it is not aggregated compared to the rest of the MPcS₄ complexes) in the presence of the QDs is shown in Table 5.2. With the exception of CYS1, the values of Φ_T for **34** in the

presence of the QDs are higher than for **34** alone ($\Phi_T = 0.36$). This slight increase in Φ_T in the presence of QDs is attributed to the heavy atom effects of the QDs which contain heavy Cd and Te atoms. The increase in Φ_T may be advantageous since it means the combination of QDs with phthalocyanines will increase the triplet state population of the phthalocyanine, and so there will be higher photosensitizing ability when they are used together in photoactive reactions e.g. PDT. In general there is a decrease in Φ_T of **34** in the presence of QDs with increase in the size of the QDs (except for the L-cysteine capped QDs), suggesting that the size of the QDs influence the Φ_T for **34**. In most cases L-cysteine capped QDs behave differently from the others, this could be due to the fact that the nature of the thiol strongly influences the particle growth, which would in turn affect their interaction with the photosensitizers, in this case AlPcS₄ (**34**).

The variation of Φ_T amongst the MPcS₄ complexes in water: methanol solvent mixture in Table 5.3 depends on heavy atom effect which encourages intersystem crossing to the triplet state. The observed trend for Φ_T corresponds to the increase in atomic masses of the central metals except for SiPcS₄ (**35**) that has a triplet yield that is of the same value with ZnPcS₄ (**33**) even though there is a large difference in their relative atomic masses. A slight increase in the Φ_T was observed for AlPcS₄ (**34**) and GePcS₄ (**36**) in the presence of the QDs compared to the respective MPcS₄ complexes alone, Table 5.3. This slight increase in Φ_T in the presence of the QDs is attributed to the effect of heavy atoms of the QDs as discussed above. The Φ_T values for complexes **33** and **35** in the presence of QDs either decreased or remained the same, behaving contrary to what is expected on the basis of heavy atom effect.

The MOCPcs in the presence of CYS3 exhibited slightly increased Φ_T values compared

to the respective MOCPC alone (with the exception of SiOCPC (**43**)), Table 5.4.

Figure 5.3 shows the transient absorption spectra of AlOCPC (**42**) in the absence and presence of CYS3. AlOCPC, **42** maintained its monomeric state while in the presence of CYS3, with a slight broadening of the spectrum, which may be because some distortion is happening at the triplet state in the presence of the QD. The triplet decay curve of **42** in the presence of CYS3 is also shown in (Figure 5.3, inset) confirming a monoexponential decay.

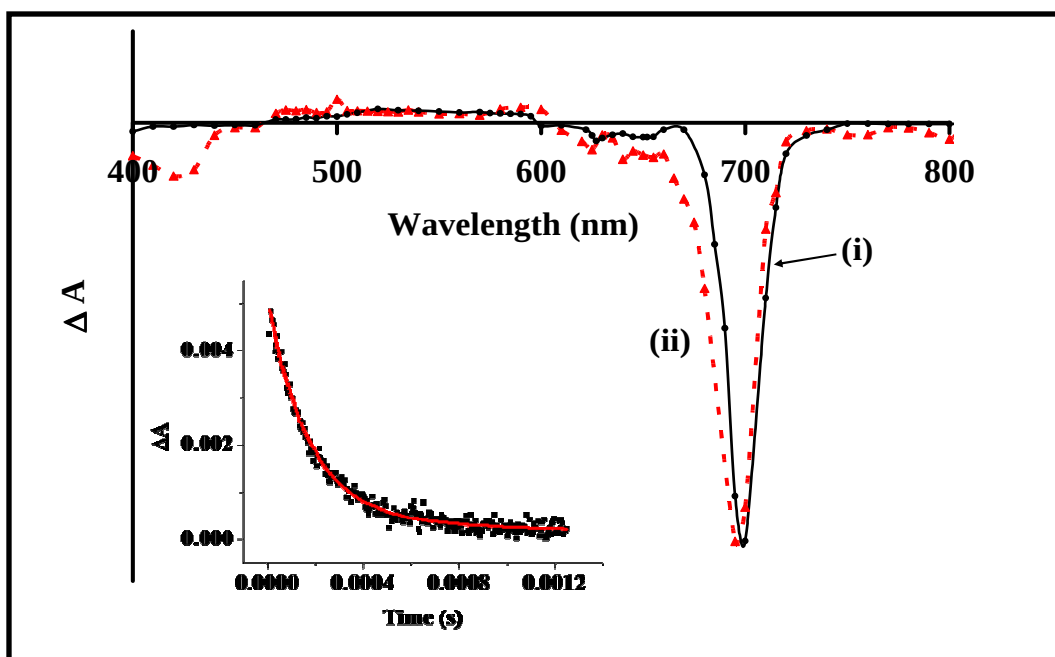


Figure 5.3: Normalized transient absorption spectrum of (i) AlOCPC (42**) and (ii) **42** in the presence of CYS3 in PBS pH 7.4 ($[42] \sim 8 \times 10^{-6}$ M $[CYS3] \sim 2 \times 10^{-6}$ M) $\lambda_{exc} = 690$ nm. Inset = the triplet decay curve for **42** in the presence of CYS3.**

Triplet state lifetimes (τ_T) of AlPcS₄ (**34**) in PBS pH 7.4 in the presence of the QDs were relatively high compared to τ_T value of 470 μ s for **34** alone, except for CYS1 and TGA2 QDs, where respectively the values were similar or lower, Table 5.2. It was observed that

the τ_T of **34** in the presence of QDs capped with 3- mercaptopropionic acid MPA1 and MPA2 had the longest triplet lifetime in the set, as seen in Table 5.2. This may be due to the fact that MPA being a strong coupling agent must have been firmly attached unto the surface of **34**, thereby reducing its exposure to the aqueous medium. With the exception of L- cysteine capped QDs, the τ_T values decreased with increase in the size of the QDs (comparing MPA1 with MPA2 and TGA1 with TGA2). The τ_T value increased with the size of QDs for the L- cysteine capped QDs.

In water: methanol solvent mixture, τ_T values of the MPcS₄ complexes alone ranged from 180-560 μ s, Table 5.3 while that of the MOCPCs in PBS 7.4 ranged from 90-450 μ s, Table 5.4. A general increase in the τ_T values in the presence of the various QDs as seen in Tables 5.3 and 5.4 was observed. This observation could be due to the fact that there is a reduction in the exposure of the MPcs to the aqueous medium because of the presence of the QDs since water is known to quench the triplet states of MPcs [234]. These increases in the τ_T of the MPcS₄ and MOCPC complexes in the presence of the QDs contradicts what is expected by the heavy atom effect, whereby when Φ_T increases as observed above for AlPcS₄ GePcS₄ and MOCPCs, the τ_T inevitably decreases but it is justified for the ZnPcS₄ and SiPcS₄ complexes where there is a general decrease in Φ_T in the presence of QDs. It is also justified for AlPcS₄ in PBS pH 7.4 in the presence of CYS1 or TGA2 where respectively the values were similar or lower. These long τ_T values however shows that the MPc complexes will likely spend more time at the triplet state allowing for increased diffusional interactions which will be an advantage in photosensitized reactions.

5.1.1.4 Singlet oxygen production

Photochemistry of the MOCPCs was studied due to the monomeric nature of all the complexes in this set in PBS 7.4.

The presence of molecular oxygen is a determinant in the phototoxicity of MPcs in photosensitized oxidation reactions. As stated in Chapter 4, an efficient production of Φ_{Δ} was observed with the efficiency of quenching of the triplet excited state by singlet oxygen, S_{Δ} , about unity (Table 5.5) for the MOCPCs in the absence of CYS3. Φ_{Δ} values for the MOCPCs were found to be higher in the presence of CYS3 corresponding to the

Table 5.5: Photochemical parameters for MOCPCs complexes in the presence of CYS3 in aqueous solution.

Sample	Φ_{Δ} (700 nm)	$\Phi_{Pd} (\times 10^{-5})$
ZnOCPc (41)	0.32	2.65
ZnOCPc-CYS3	0.60	2.23
AlOCPc (42)	0.12	0.26
AlOCPc-CYS3	0.31	0.17
SiOCPc (43)	0.22	86.3
SiOCPc –CYS3	0.21	1.26
GeOCPc (44)	0.31	2.12
GeOCPc –CYS3	0.66	1.98

higher Φ_T and τ_T values, Table 5.4. QDs have been reported to have the ability to produce singlet oxygen of about 5% in organic solvents [219]. It has also been implied that singlet oxygen should be produced during photooxidation of QDs since sodium azide, a physical

quencher for oxygen, can effectively inhibit QDs photooxidation in solution [359]. The increased Φ_{Δ} values in the presence of the MOCPCs can therefore be a small contribution from QDs combined with the increased production of singlet oxygen from MOCPCs, as a result of increased triplet yields and lifetimes. SiOCPC however behaved differently in that there was no significant change in the singlet oxygen value in the presence of the QDs, this may be due to the instability of this complex under irradiation (as reflected from its photodegradation value, discussed in Chapter 4, which may not allow for long time photosensitized reactions to occur.

5.1.1.5 Photodegradation

The stability of the molecules and possible oxidation by singlet oxygen can be studied by degradation under irradiation. Photodegradation quantum yields (Φ_p) of the MOCPC complexes decreased in the presence of CYS3 which can be attributed to the fact that QDs are photochemically stable [226] and this can improve on the photodegradation of the MPC they are interacting with. The decrease in Φ_p values is however contradictory to the Φ_{Δ} values obtained in this study since photodegradation process is believed to be singlet oxygen mediated [327]. Thus it is expected that an increase in Φ_{Δ} values should lead to an increase in Φ_p values. However, this is not observed probably due to the stabilization of the MOCPC complexes in the presence of QDs.

5.1.2 Cationic MPCs and QDs

These studies were carried out with cationic MPCs (α -TZnPcQ (**47b**), β -TZnPcQ (**48b**) and β -OZnPcQ **49b**) to exploit the possibilities of electrostatic interaction between the

MPcs and QDs that carry negative charges. The interaction may result in the formation of stable ion pair complexes in solution with unique properties that can allow their application in processes where mimicking of photosynthetic processes are useful. MPA2 and TGA2 with sizes 3.6 and 3.7 nm respectively were employed in this interaction. These sizes were chosen since they gave good spectral overlap with the cationic MPc complexes. Figure 5.4a shows the absorption and emission spectra of the QDs used in this study.

The studies were carried out in methanol/water (60:40 v/v) to allow for monomerization of the cationic MPc complexes (**47b**, **48b** and **49b**) since monomers are photoactive and also because the complexation of ion-pairs is known not to occur in solvents of high polarity [215].

5.1.2.1 Spectral changes of MPcs in the presence of QDs

The electronic absorption spectra of α -TZnPcQ (**47b**), β -TZnPcQ (**48b**) and β -OZnPcQ (**49b**) in methanol/water (60:40 v/v) are shown in Figure 5.4b. The complexes exhibit monomeric behaviour in methanol/water, (with Q band absorption maxima listed in Table 5.6) compared to aqueous medium alone (discussed in Chapter 3) since it is known that organic solvents tend to favour the monomeric nature of complexes [166].

Overlap exists between emission spectra of the CdTe QDs and the MPcs absorption spectra, as shown in Figure 5.5, and this is a good indication that energy transfer is possible from the CdTe QDs to the MPcs.

Titration of aliquots of the QDs [1×10^{-6} M] to a fixed concentration of MPc [1×10^{-5} M] in methanol/water mixture was carried out. Spectral changes observed on addition of

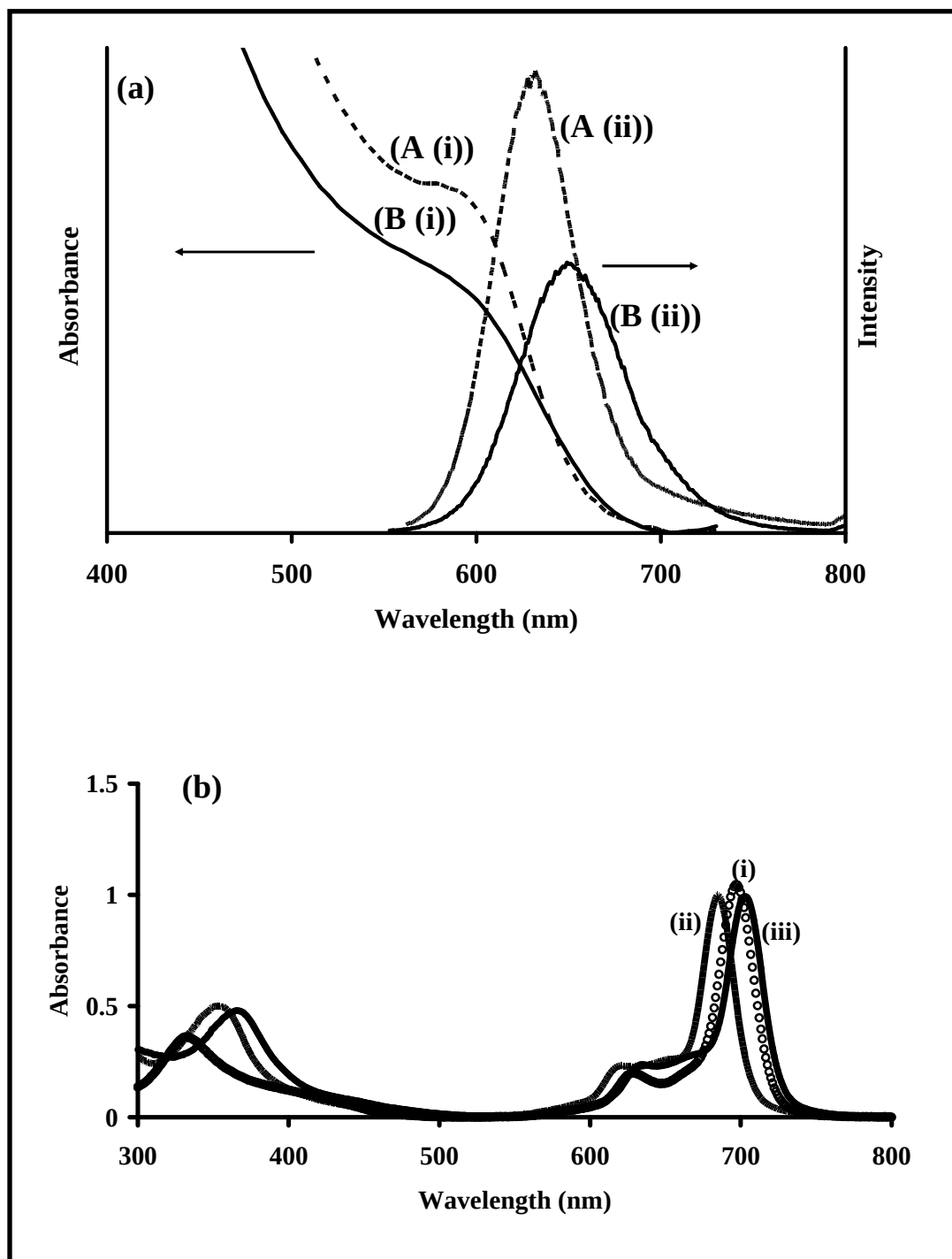


Figure 5.4: (a) Absorption (i) and emission (ii) spectra of TGA2 (A) (dotted line) and MPA2 (B) (solid line). $\lambda_{\text{exc}} = 500$ nm; (b) Ground state electronic absorption spectra of (i) α TZnPcQ (47b); (ii) β TZnPcQ (48b) and (iii) β OZnPcQ (49b) in methanol / water mixture (60: 40) (concentration $\sim 5 \times 10^{-6}$ M).

Table 5.6: Spectral and fluorescence data of cationic Zn phthalocyanine derivatives in aqueous and non-aqueous media.

Sample	^a Solvent	λ_Q (nm)	λ_F (nm)	Φ_F
α TZnPcQ	CH ₃ OH-H ₂ O	696	709	0.10
	H ₂ O	653,692	710	<0.01
β TZnPcQ	CH ₃ OH-H ₂ O	684	697	0.15
	H ₂ O	643,682	702	<0.01
β OZnPcQ	CH ₃ OH-H ₂ O	702	715	0.11
	H ₂ O	661,700	716	<0.01

^a CH₃OH-H₂O = methanol/water (60:40 (v/v))

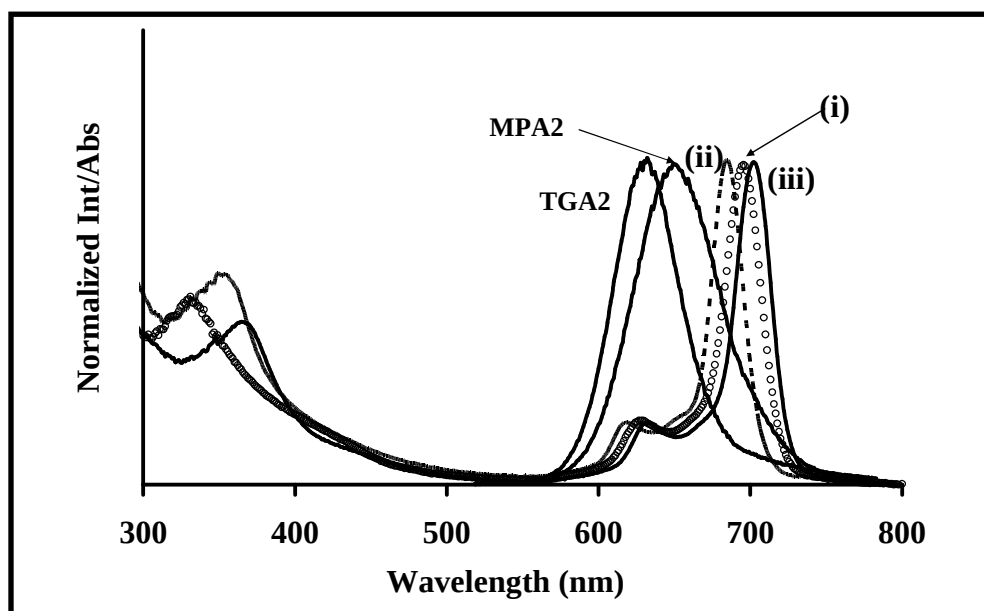
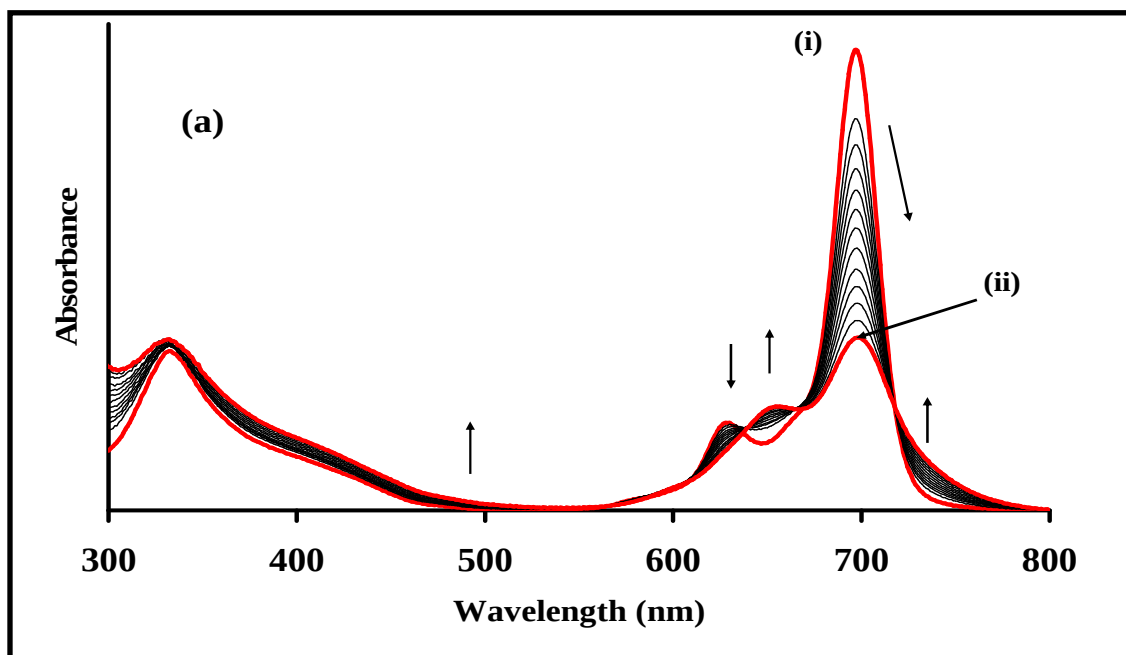


Figure 5.5: Normalized absorption spectra of MPcs and emission spectra of CdTe QD solutions showing overlap of the emission spectra of the CdTe QDs with the absorption spectra of MPcs in methanol / water (60:40 (v/v)). (i) α TZnPcQ (47b); (ii) β TZnPcQ (48b) and (iii) β OZnPcQ (49b).

MPA2 to α TZnPcQ (**47b**), or TGA2 to β TZnPcQ (**48b**) are shown in Figure 5.6a or Figure 5.6b, respectively. For **47b** Figure 5.6a, a reduction of intensity and broadening of the Q band of the MPc was observed; the intensity of the vibronic band at 630 nm also decreased with the formation of a new band at about 650 nm and increased intensity at around 730 nm region. There were isosbestic points at 717, 662, 636 and 608 nm. Similar spectral changes were observed on addition of TGA2 to **48b**, Figure 5.6b, (or to β OZnPcQ (**49b**)). Addition of MPA2 to any of the complexes also resulted in similar spectral changes. Further addition of the CdTe QDs solution did not change the spectra in Figures 5.6a and b any further. The spectral changes shown in Figures 5.6a and b occurred instantly, allowing time for the reaction to occur did not change the spectra. In the reverse titration, where ZnPcQ was added to QDs, the broadening of the Q band of the MPc was observed immediately on addition of the first aliquot of ZnPcQ to the CdTe QD solution. The typical spectral changes in these series are shown in Figure 5.6c for titration of MPA2 with α TZnPcQ (**47b**).



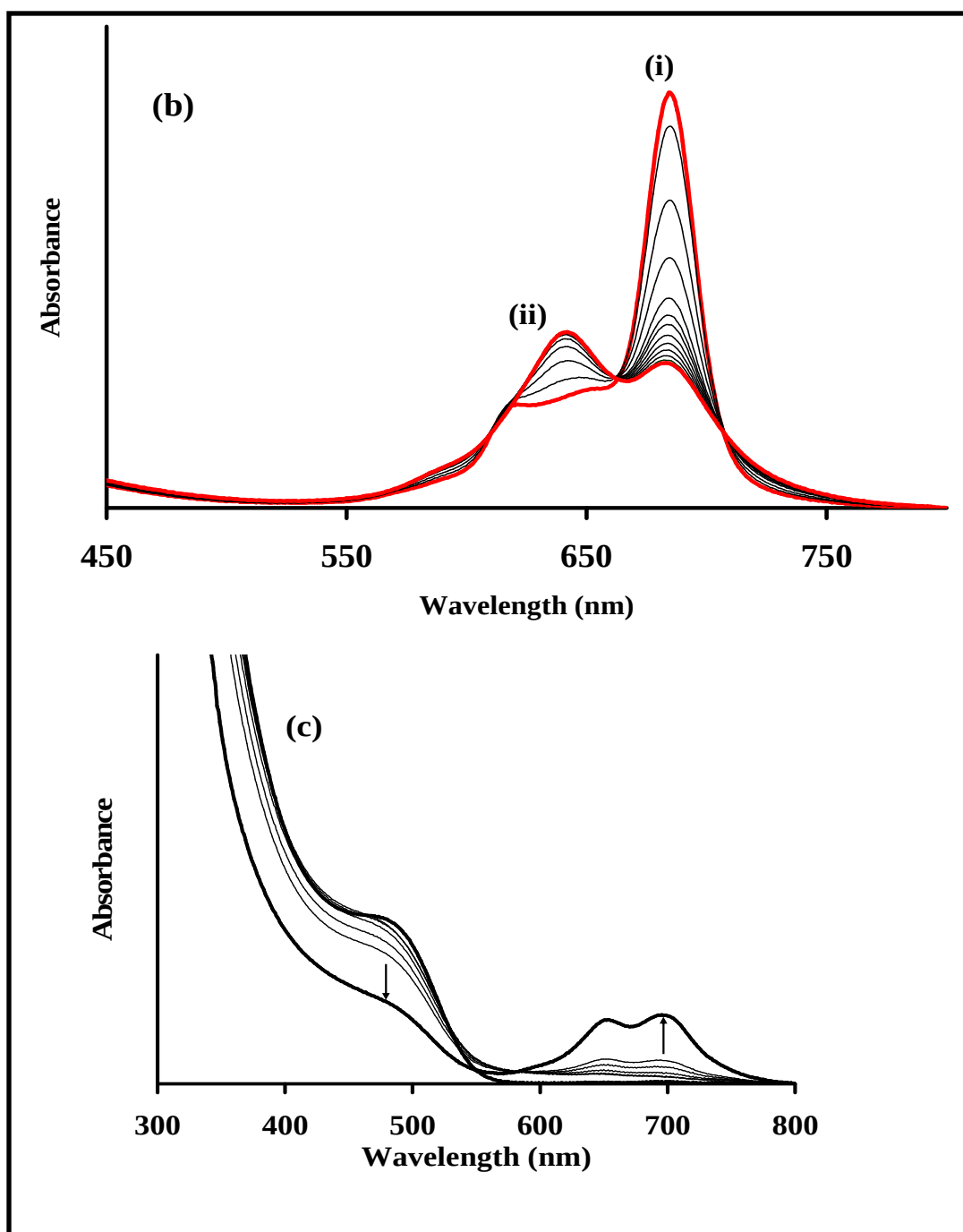


Figure 5.6: Gradual absorption spectral changes in (a) α TZnPcQ (47b) on addition of aliquots of MPA2, (b) β TZnPcQ (48b) on addition of aliquots of TGA2 and (c) on addition of aliquots of 47b to MPA2 in methanol / water (60:40 (v/v). (i) is before and (ii) is after addition of QDs (for a and b)

Aggregation in MPc complexes is due to a coplanar association of rings, resulting in splitting and broadening of spectra, with a blue shifted peak due to the aggregate. Spectral changes observed in Figure 5.6 suggest aggregation of the MPc complexes, with a broad blue-shifted band near 650 nm, typical of H aggregates. Adding excess methanol, hence increasing the ratio of methanol to water or addition of surfactants did not break the aggregates, suggesting these are not H aggregates. Dilution of the solution containing aggregates did not show evidence of monomerization, expected for H aggregates. Metal ion (e.g. Ag(I) or Pd(II)) binding to MPc complexes bearing thio functionality also shows spectral changes similar to those observed in Figure 5.6a and b [360]. The aggregates formed by metal binding are not easily monomerized. Thus, it can be inferred from the spectral changes in Figure 5.6a and b that an ion-pair complex which is aggregated in nature is formed as mixing of the MPc and QD occurs and that this aggregation in the MPcs is induced by the presence of the QDs. This type of aggregation may be similar to what was observed for positively charged porphyrazine complexes containing pyridine groups instead benzene rings [227].

The spectrophotometric titration experiments were analyzed by the continuous variation method [214,215], Equation 5.2 (same as Equation 1.12a). The titration data obtained from Figure 5.6 was used to construct the continuous variation plot using Equation 5.2 [214,215]:

$$F(x) = d(x) - (\epsilon_{QD} - \epsilon_{MPc})x - \epsilon_{MPc} \quad (5.2)$$

Figure 5.7 shows the continuous variation plots for the complexes in the presence of MPA2 ($\lambda = 684, 696$ and 702 nm for β TZnPcQ (**48b**), α TZnPcQ (**47b**) and β OZnPcQ (**49b**) respectively) with a stoichiometry of approximately 1:1 for **48b**, and **47b**, and

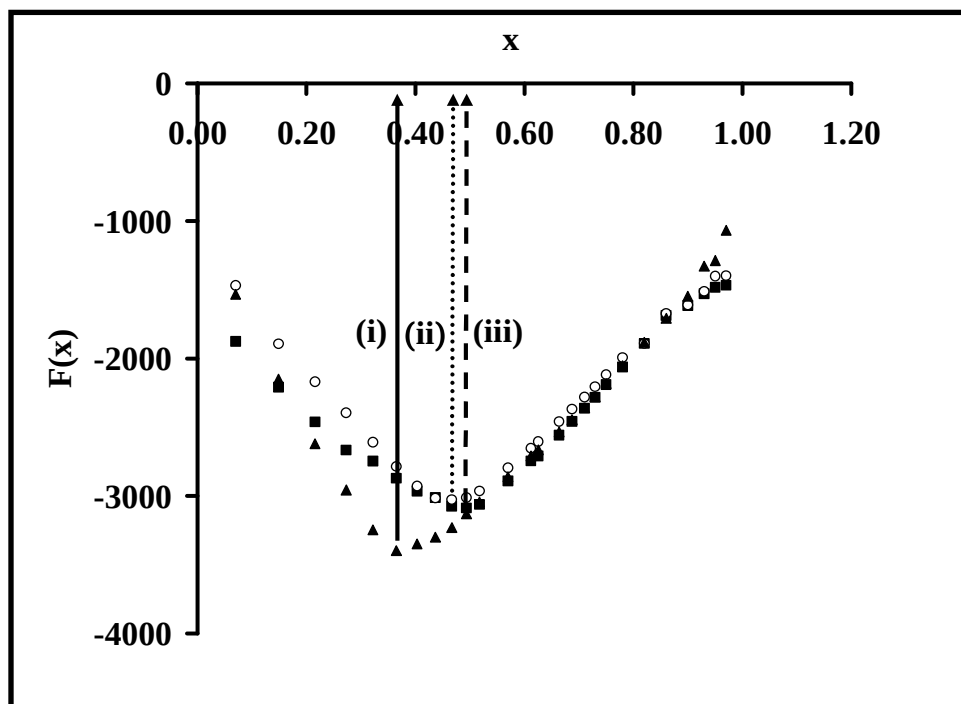


Figure 5.7: Continuous variation plots of (i) = β OZnPcQ 48b, (ii) = α TZnPcQ 47b and (iii) = β TZnPcQ 49b in the presence of MPA2 in methanol / water (60:40 (v/v)).

approximately 1:2 for **49b**. This is probably due to the presence of eight positive positions in **49b** for the electrostatic interaction to occur with QDs. This was also the trend for the MPc complexes with TGA2. It is assumed that the stoichiometry of 1:1; (QD..MPc) and 1:2 (MPc..QD..MPc) obtained is initial formation of dimers for **47b** and **48b** and trimers for **49b** and that there are subsequent formation of higher aggregates.

Association constants which are a measure of strength of interaction of the QDs with the MPcs were determined from the spectrophotometric titrations using Equation 5.3 (same as Equation 1.13) [218].

$$\frac{A_0}{\Delta A} = \frac{A_0}{\Delta A_{\max}} + \frac{A_0}{\Delta A_{\max}} \frac{1}{K_a} \frac{1}{C_t} \quad (5.3)$$

The association constant K_a was obtained from the ratio of $A_0/\Delta A_{\max}$ and the slope of the plot of $A_0/\Delta A$ versus $1/C_t$ as shown in Figures 5.8a and 5.8b. K_a obtained for these complexes in the presence of TGA2 and MPA2 were high and within the range expected for MPc complexes [361] as shown in Table 5.7. It was observed that K_a increased when the MPcs are in interaction with TGA2 compared to MPA2. This is probably due to stronger interaction occurring between the MPcs and TGA2.

In order to investigate the aggregation state of the MPcs solution in the presence of the CdTe QDs and to determine the equilibrium dimerization constant (K_D), the absorbance spectra of the MPc solutions were monitored with increasing QD concentrations in methanol-water medium. The absorbance data obtained with the estimated values of ϵ_M from the measurements in methanol-water solution within the concentration range at which the Beer- Lambert's law holds for each MPc were substituted in Equation 5.4 (same as Equation 1.11) and were fitted to obtain ϵ_D and K_D by a non- linear least square procedure using MATLAB 6.1 software.

$$\text{Abs} = \frac{[1 - \sqrt{(1 + 8K_D C)}][\epsilon_D/2 - \epsilon_M] + 2\epsilon_D K_D C}{4K_D} \quad (5.4)$$

The values of K_D are of the same order of magnitude for the complexes Table 5.7 and are within the range that have been observed for some MPc complexes [209] indicating a strong association between the aggregates. K_D for photosensitizers such as porphyrins and phthalocyanines ranges from 10^4 to 10^7 M^{-1} depending on solvent and temperature [194,209]. The values of the dimerization constants in this work will be affected by the possibility of higher aggregates. The values of ϵ_D (Table 5.7) are also within the range reported for some MPc complexes [207].

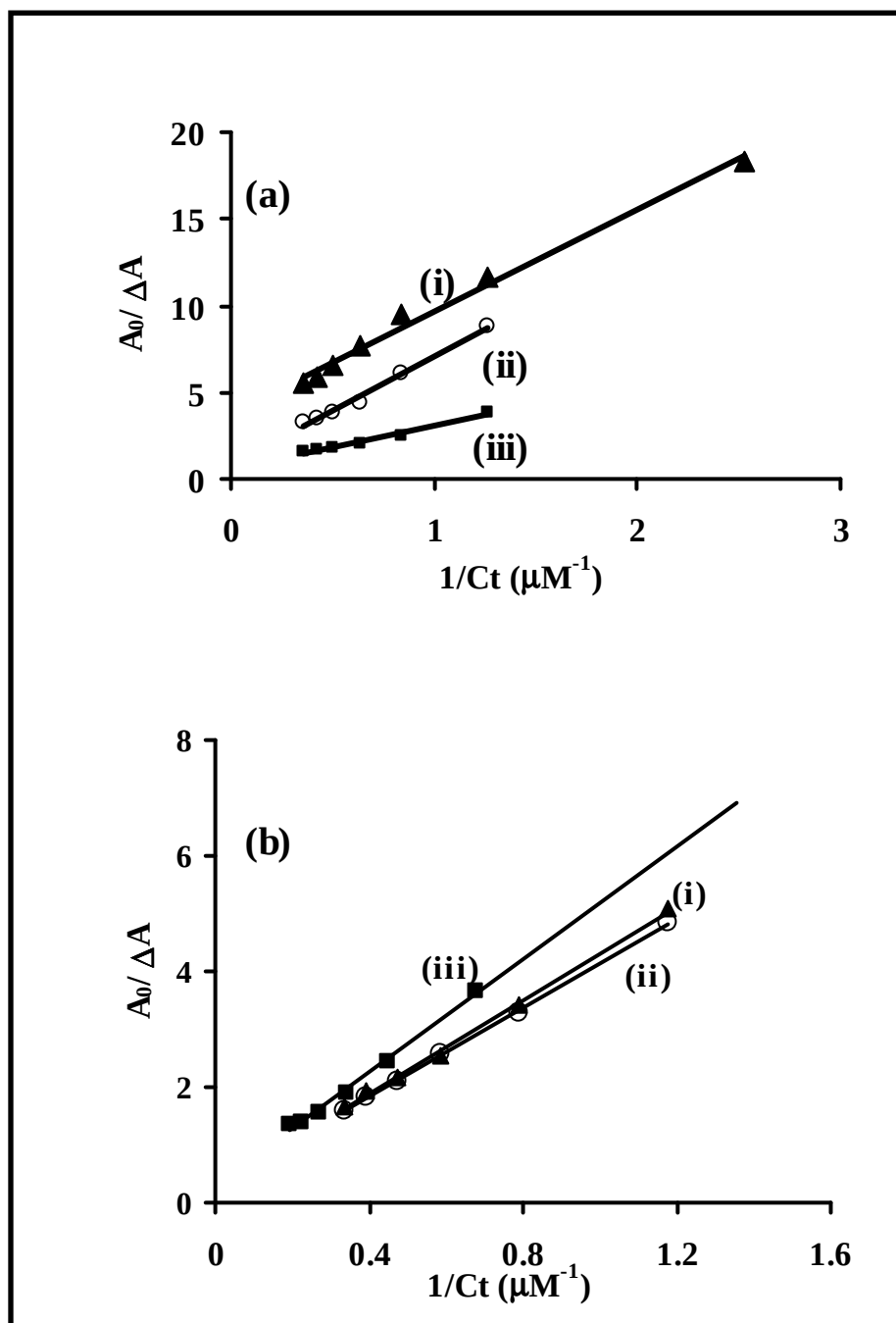


Figure 5.8: Plots for the determination of association constants in the interaction of MPc complexes ((i) = βOZnPc 49b, (ii) = αTZnPc 47b and (iii) = βTZnPc 48b) with (a) TGA2 and (b) MPA2 in methanol / water (60:40 (v/v)).

Table 5.7: Estimated association, equilibrium dimerization and quenching constants of the cationic ZnPc derivatives in association with CdTe QDs in (60:40) methanol-water medium.

Complex	^a K _a (x 10 ⁵ M ⁻¹)	^b K _D (x 10 ⁴ M ⁻¹)	^c Log ε _D (complex)	^d K _{SV} (x 10 ⁵ M ⁻¹)
αTZnPcQ (47b). MPA2	0.67	1.10	4.25	3.85
βTZnPcQ (48b). MPA2	0.61	1.41	4.99	2.56
βOZnPcQ (49b). MPA2	0.78	1.09	4.27	28.5
αTZnPcQ (47b). TGA2	1.20	1.05	4.14	5.48
βTZnPcQ (48b). TGA2	2.12	1.84	4.91	6.84
βOZnPcQ (49b). TGA2	6.43	1.79	4.08	15.6

^aK_a association constant; ^bK_D, equilibrium dimerization constant; ^cLog ε: αTZnPcQ (47b) , βTZnPc (48b) and βOZnPc (49b) = 5.29, 5.18 and 5.13 respectively in methanol / water (60:40 (v/v)); ^dK_{SV}, static quenching constant .

5.1.2.2 Fluorescence studies

The mixture of QDs and MPc complexes in a ratio of 1:1 mixture (or higher) had little or no emission both at the CdTe QDs and MPc excitation wavelengths (500 and 620 nm respectively) indicating that the emission of the complexes are simultaneously quenched. This is probably due to electronic coupling that occurs on mixing the two complexes. In the titration with small aliquots of CdTe QDs (resulting in less than 1:1 MPc:QDs), the emission spectrum of the solution of the MPc was gradually quenched, Figure 5.9 implying that the excited state of the MPc is quenched.

The quenching of the fluorescence intensity of the MPcs in the presence of the CdTe QDs Figure 5.9 were studied by analyzing plots of the relative intensity of the MPcs in the absence and presence of CdTe QDs against concentration of the CdTe QDs using Equation 1.17 (Stern-Volmer plot). Within investigated range of concentrations, linear Stern-Volmer plots were obtained as shown in inset of Figure 5.9. The Stern-Volmer constants obtained can be termed as that resulting from static quenching [362] though linear plots are obtained. This is because there is clear perturbation in the absorption spectrum of the MPcs in the presence of the CdTe QDs (Figure 5.6). Models have been

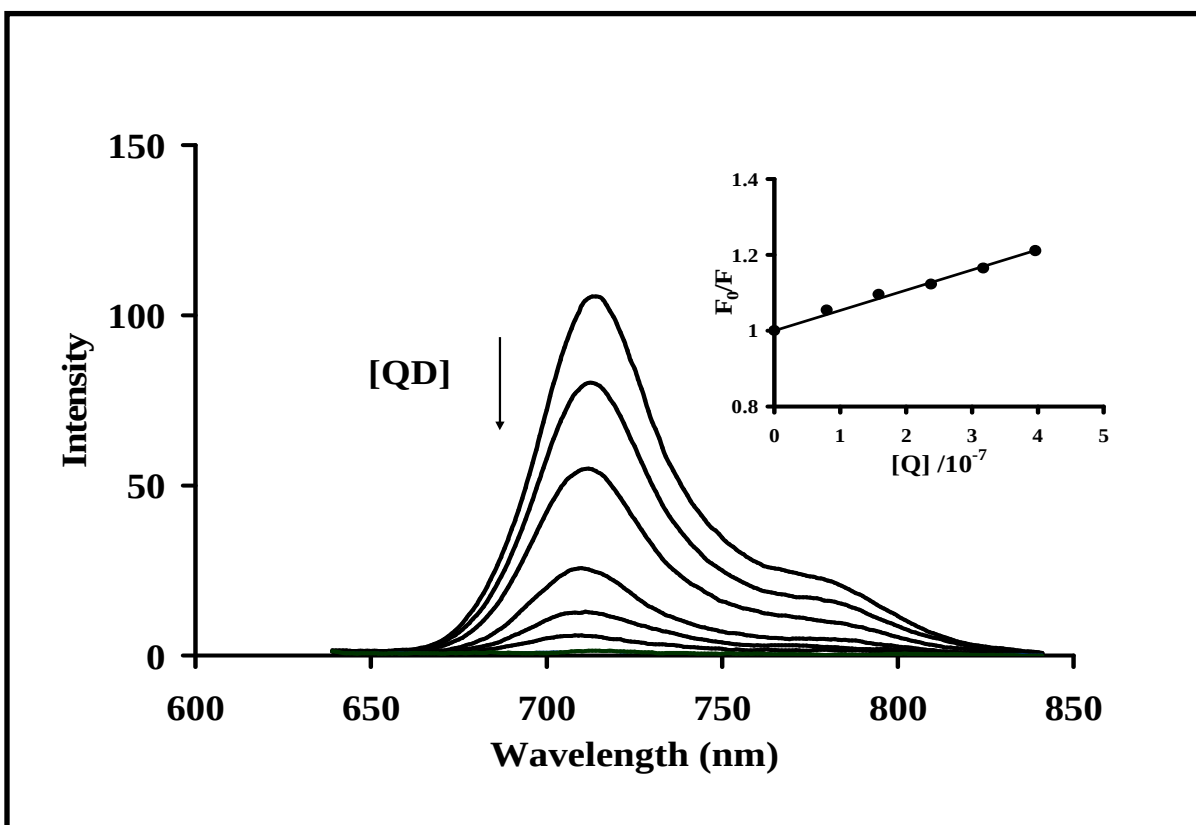


Figure 5.9: Fluorescence emission spectral changes of α TZnPcQ (47b) with increasing [MPA2] in methanol / water (60:40 (v/v)). Inset: Stern Volmer plot for quenching of 47b by MPA2.

derived for this type of quenching [245,362] where linear plots are obtained for static quenching of fluorescence intensity, and in such situations, K_{SV} is no more referred to as quenching constant but as the equilibrium constant for interaction. The values of K_{SV} were high Table 5.7 and within range that has been observed for MPcs that form ion-pair complexes. The highest K_{SV} values were observed for β OZnPcQ (**49b**) showing that the interaction in **49b** with the CdTe QDs is stronger than in the other MPcs.

5.2 Förster resonance energy transfer (FRET) studies between QDs and MPcs

Quantum dots can transfer energy to MPcs when they are in close proximity to each other. FRET studies were carried out between QDs and MPcs to assess the indirect activation of the MPcs by QDs. The energy transfer occurred with the MPcs at a molar ratio of 1.5:1 (MPcs : QD) or more.

5.2.1 MPcS₄ complexes

5.2.1.1 Monomeric AlPcS₄ (34**) complex in pH 7.4 PBS**

AlPcS₄ (**34**) is again studied in PBS pH 7.4 (not H₂O: methanol) with the QDs due to its monomeric behaviour in this solvent. An efficient overlap between the absorption spectrum of the AlPcS₄ (**34**) with the emission spectra of the QDs, (Figure 5.10), especially for the larger QDs (with more red shifted absorption) was observed. The shaded portion in Figure 5.10 shows the spectral overlap of fluorescence spectrum of each QD with the absorption spectrum of **34**. A decrease in the fluorescence emission (on exciting at 400 nm) of the QDs in the presence of **34** and an observation of **34**'s

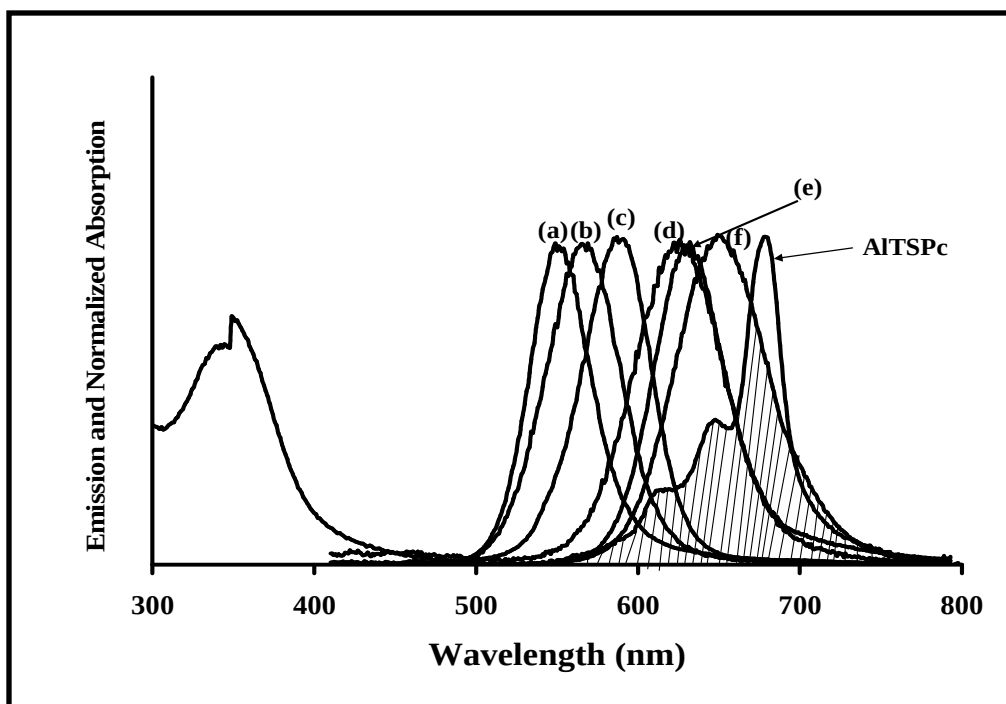


Figure 5.10: Normalized absorption spectra of AlPcS₄ (**34**) and emission spectra of the six CdTe thiol capped QD solutions showing overlap of the emission spectra of the QDs ($\lambda_{\text{exc}} = 400\text{nm}$) with the absorption spectra of **34** in PBS pH 7.4. (a) MPA1, (b) CYS1, (c) TGA1, (d) CYS2, (e) TGA2 and (f) MPA2.

fluorescence with a peak at 692 nm were observed in Figure 5.11, suggesting that the quenching of CdTe QDs by **34** involves energy transfer. The quenching is expected to be via energy transfer since **34** absorbs at a longer wavelength than the QDs. No significant fluorescence for **34** was observed on excitation at this wavelength (400 nm) in the absence of QDs. As stated above, fluorescence quantum yield of the QDs in the mixture of **34** and QDs ($\Phi_{\text{F(QD)}}^{\text{Mix}}$) decreased for all the conjugates compared to $\Phi_{\text{F(QD)}}$ of QDs alone, indicating quenching which results in energy transfer. The overlap integral (J) was estimated by integration of the spectra in Figure 5.10 from 400 nm to 800 nm where there is overlap using Equation 5.5 (same as Equation 1.32) and the J values are reported in

Table 5.8.

$$J = \int f_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (5.5)$$

Relatively high J values of the order of 10^{-13} were obtained, (with CYS2 having the highest value) compared to typical values of the order 10^{-14} obtained with porphyrins [270]. This could be as a result of the immense spectral overlap of the absorption spectra of the **34** and the fluorescence emission spectra of the QDs.

The Förster distance, R_0 (Å) which is the critical distance between the donor and the acceptor molecules for which efficiency of energy transfer is 50% [267] is also shown in Table 5.8. The center-to-center separation distance between donor and acceptor (r , Å), were calculated using Equation 5.6 same as Equation 1.30 and values are shown in Table

$$Eff = \frac{R_0^6}{R_0^6 + r^6} \quad (5.6)$$

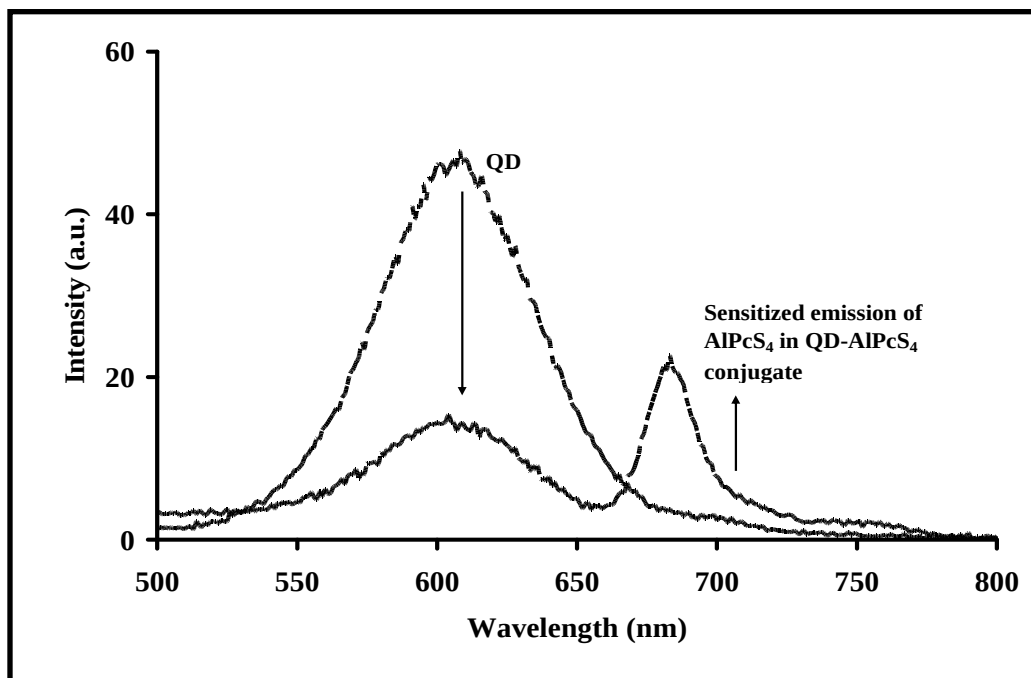


Figure 5.11: Indirect activation of AlPcS₄ (34) by CYS2 through FRET showing decrease in QD emission intensity and a sensitized emission of 34 in PBS pH 7.4. λ_{exc} = 400nm

Table 5.8: Energy transfer parameters for AlPcS₄-QD interactions in PBS pH 7.4

^a QD	J (x10 ⁻¹³ cm ⁶)	R ₀ (Å)	r (Å)	Eff
MPA1	1.08	39.39	52.06	0.16
MPA2	8.20	72.81	68.99	0.58
TGA1	1.73	46.09	62.38	0.14
TGA2	9.75	69.21	76.73	0.35
CYS1	1.37	46.57	57.52	0.22
CYS2	13.9	44.69	25.04	0.97

^aCYS= L-cysteine, MPA= mercaptopropionic acid, TGA= thioglycolic acid.

5.8 with CYS2 having the lowest values compared to the others. The distances are < 80 Å [363], which indicates that the energy transfer from the synthesized QDs to **34** occur with high probability. In the smaller first set of QDs; MPA1, CYS1 and TGA1, little FRET is expected since the average distance between the donor and the acceptor, r exceeds the critical distance R₀, this is also the case in TGA2.

Using Equation 5.7, same as Equation 1.29, the FRET efficiency was calculated with

$$Eff = 1 - \frac{\Phi_{F(DA)}}{\Phi_{F(D)}} \quad (5.7)$$

values stated in Table 5.8. FRET efficiency is a function of the inter-fluorophore distance and spectral properties of donor and acceptor (fluorescence quantum yields, molar absorptivities and relative orientation of transition moments). It is apparent from the results in Table 5.8, that the CdTe QDs capped with L-cysteine CYS1 and CYS2 had

the highest efficiency in each set of synthesized QDs (0.22 for CYS1 and 0.97 for CYS2) followed by the 3-mercaptopropionic acid capped CdTe QDs with the thioglycolic acid capped CdTe QDs having the lowest efficiency for each set. This brings up the possibility that the nature of the thiol used in capping the QDs may affect the efficiency of FRET to **34**. It is also evident that, the QDs with fluorescence emission at lower wavelengths, hence smaller QDs (MPA1, CYS1 and TGA1) were less efficient in FRET compared to the larger QDs (red shifted); this is probably due to their low spectral overlap with **34** as compared to the QDs at higher wavelengths of photoluminescence. The J values, Table 5.8 are directly related to Eff with each set of cappings of QDs showing a linear dependence of Eff on J according to Förster theory.

The high J value coupled with the small r value which is smaller than R_0 in CYS2 must have all contributed to the high efficiency experienced in CYS2 even though its fluorescence quantum yield is quite low. For the potential use in PDT application, MPA2 capped QD seems to be the suitable water-soluble conjugate with **34** since it possesses high energy transfer efficiency (0.58), and also, it maintains a relatively high fluorescence yield ($\Phi_{F(QD)}^{Mix} = 0.25$) in the mixture, that could favor detection. Although CYS2 mixed MPc had the highest efficiency (0.97), this compound resulted in QDs with low $\Phi_{F(QD)}^{Mix}$ (0.003) in the mixture. Thus, the MPA2 linked QD-MPc is a potential candidate for PDT studies in terms of imaging.

5.2.1.2 MPcS₄ complexes in water: methanol (w/m) solvent mixture

Efficient overlap occurs between the absorption spectra of the MPcS₄ complexes with the emission spectrum of QDs in water:methanol solvent mixture, Figure 5.12 for SiPcS₄

(35). Excitations of a mixture containing the respective QDs and respective MPcS₄ complex were carried out at 500 nm where the QDs absorb, but the MPcS₄ complexes have negligible absorbance, resulting in decreased fluorescence intensity of the QDs and an emergence of the respective MPcS₄ complex fluorescence, Figure 5.13 as shown for GePcS₄ (36) in the presence of TGA1 and TGA2. This suggests that energy transfer occurs from CdTe QDs to the MPcS₄ complexes. No significant fluorescence for the MPcS₄ complexes was observed on excitation at 500 nm in the absence of the QDs, so the fluorescence of the MPcS₄ complexes that emerged in this case must be due to the fluorescence induced by QDs unto the MPcS₄ complexes. The J values (Table 5.9) were about the same for all the complexes in the presence of the various QDs except for ZnPcS₄ in the presence of MPA1 where the value was low.

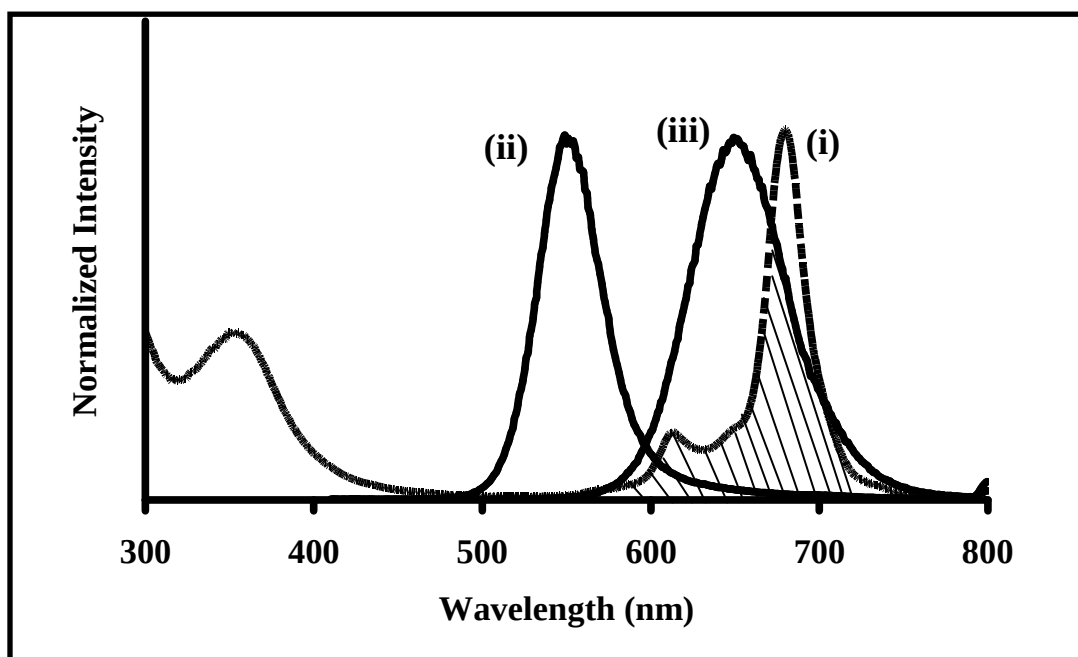


Figure 5.12: Normalized absorption spectra of SiPcS₄ (35) (i) and emission spectra of MPA1 (ii) and MPA2 (iii) in (1:1) methanol / water solvent mixture.

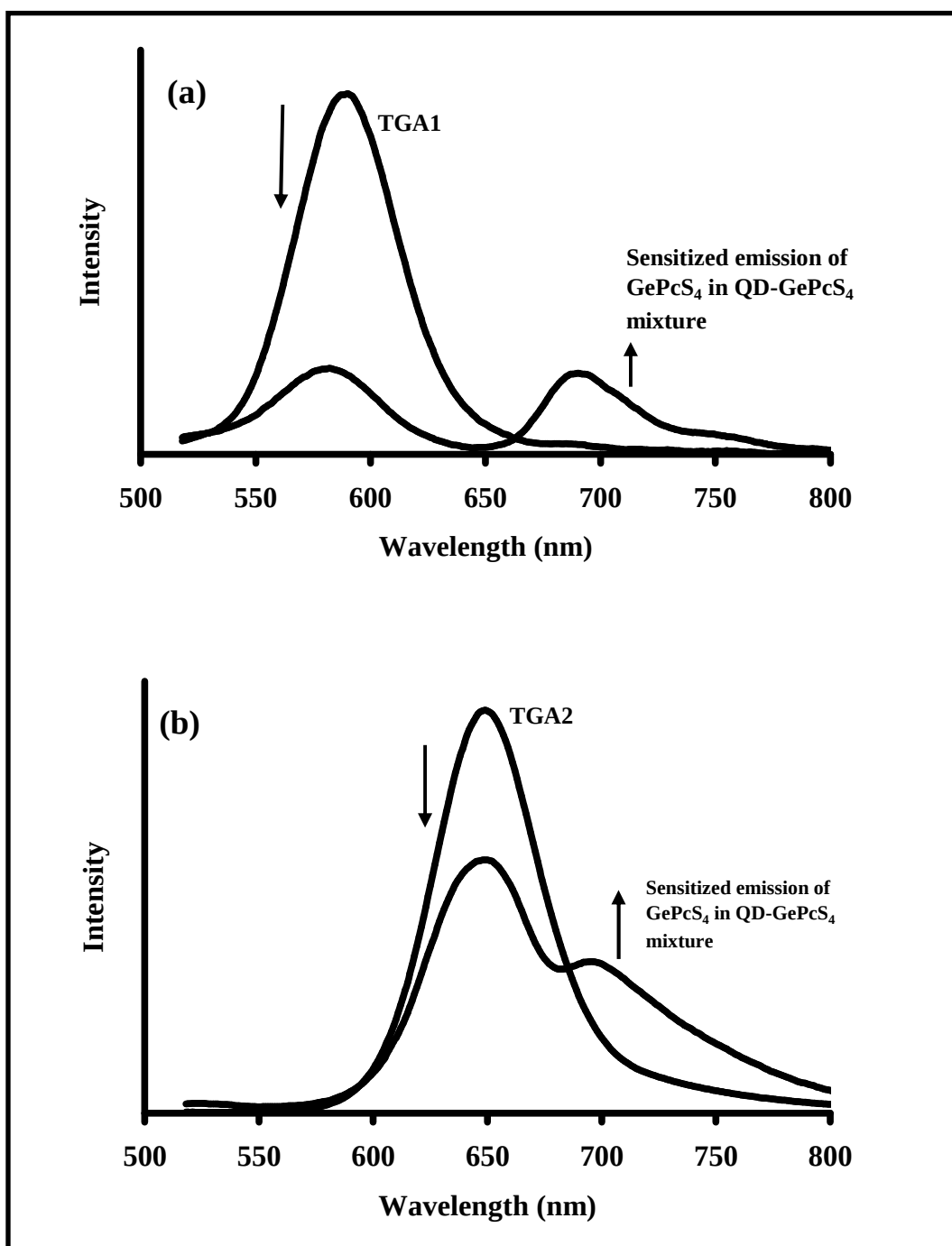


Figure 5.13: Indirect activation of GePcS₄ (36) by TGA1 (a) and TGA2 (b) through FRET showing decrease in QD emission intensity and a sensitized emission of 36 in water : methanol solvent mixture, $\lambda_{\text{exc}} = 500$ nm.

Table 5.9: Energy transfer parameters for MPcS₄-QD interactions in 1:1 water: methanol mixture

MPc	QD	J(x10⁻¹³cm⁶)	R₀ (Å)	r (Å)	Eff
ZnPcS₄	MPA1	0.68	30.71	43.51	0.11
	MPA2	7.44	55.21	57.47	0.44
	TGA1	1.73	38.70	36.17	0.60
	TGA2	7.33	55.54	65.55	0.27
AlPcS₄	MPA1	1.02	32.84	46.53	0.11
	MPA2	1.31	60.71	73.57	0.24
	TGA1	2.38	40.68	58.67	0.10
	TGA2	1.18	59.58	72.20	0.24
SiPcS₄	MPA1	1.13	33.39	54.54	0.05
	MPA2	1.13	59.19	56.09	0.58
	TGA1	2.61	41.52	36.05	0.70
	TGA2	1.01	58.50	59.29	0.48
GePcS₄	MPA1	0.44	28.57	40.48	0.11
	MPA2	5.73	52.87	54.30	0.46
	TGA1	1.11	35.90	29.35	0.77
	TGA2	4.83	51.81	55.43	0.40

Most of the calculated r values were above the critical distance (R_0) at which energy transfer is 50% except for the complexes in the presence of TGA1 (with exception of AlPcS₄). SiPcS₄ in the presence of MPA2 also gave r less than R_0 . This gives an indication that the energy transfer in most of the combinations may not be optimum in general, since for efficient energy transfer to occur r should be lower than R_0 .

It is reasonable to assume that the QD-MPc mixture having the highest J value will also have the highest Eff from the QD to the MPc since according to Förster theory; Eff has a linear dependence on J . However, this was not observed in all cases with each set of QDs, with these MPcS₄ complexes in water: methanol, showing that there are other factors contributing to Eff apart from the spectral overlap in this case. It was recently reported that a non - Förster type energy transfer behaviour can occur in QD-MPc donor-acceptor systems and this was explained to be due to the fact that there is an involvement of the QD surface states in the energy transfer process [225]. The obtained values of Eff , listed in Table 5.9 were highest in each set for the MPcS₄ complexes in the presence of TGA1 except with AlPcS₄, as already predicted from the r values obtained. AlPcS₄ maintained the same trend it had in PBS pH 7.4 only. The values of Eff obtained for the MPcS₄ complexes in the presence of TGA2 and MPA2 were also very reasonable. However, bringing all the results together, TGA1 though exhibited high Eff , resulted in low fluorescence yield ($\Phi_{F(QD)}^{Mix}$) in the presence of the MPcS₄ complexes (Table 5.3) while TGA2 and MPA2, though with a lower Eff , maintained slightly higher fluorescence values ($\Phi_{F(QD)}^{Mix}$) in the presence of the individual MPcS₄ complexes (Table 5.3). TGA2 and MPA2 QDs in the presence of MPcS₄ complexes may therefore be of better value in

photosensitization reactions where detections will be needed since their fluorescence intensities will still be high enough to help in visualization.

5.2.2 MOCPC complexes

Efficient overlap occurs between the absorption spectra of the MOCPCs with the emission spectrum of CYS3, (Figure 5.14). Excitations of a mixture containing CYS3 and the respective MOCPC were carried out at 500 nm and an emergence of peak at ~ 701 nm was observed like in the MPCs₄ complexes studied as shown for GeOCPC (**44**) in Figure 5.15, (similar to other MOCPC complexes) following decreased fluorescence of the QDs suggesting energy transfer occurs from CYS3 to **44**. The energy transfer occurred with all

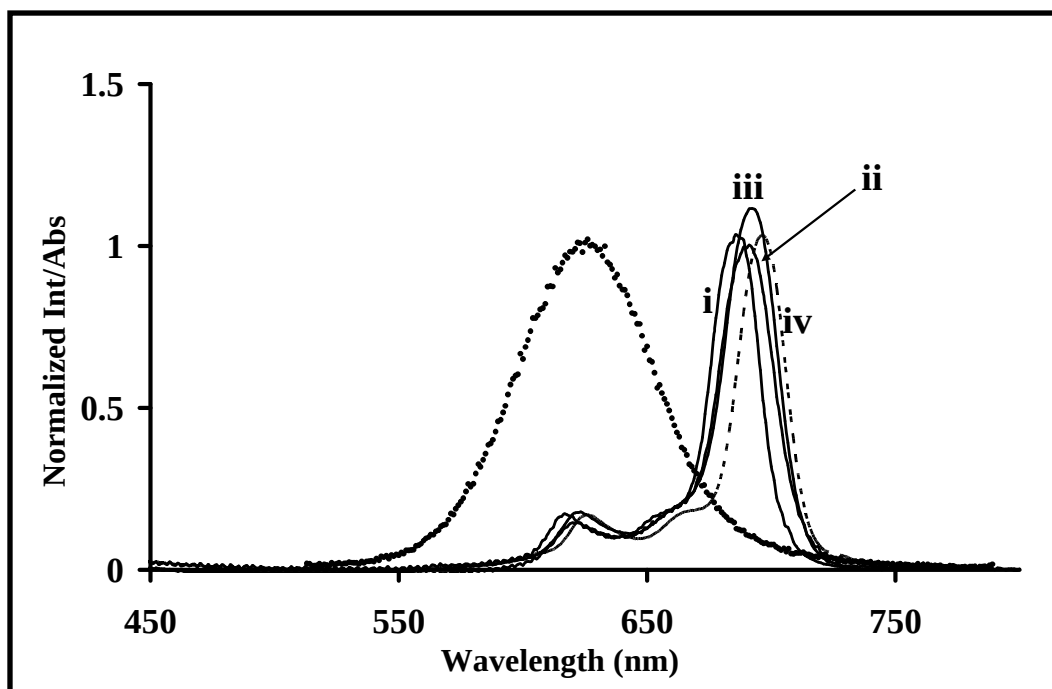


Figure 5.14: Absorption spectra of the MOCPCs and emission spectrum of CYS3 (dotted lines) showing overlap of the emission spectrum of CYS3 ($\lambda_{\text{exc}} = 500$ nm) with the absorption spectra of the MOCPCs in PBS pH 7.4. (i) ALOPC (**42**), (ii) SiOCPC (**43**), (iii) ZnOCPC (**41**) and (iv) GeOCPC (**44**).

the MOCPcs at a molar ratio of 1.5:1 (MPcs : QD) or higher. No significant fluorescence for the MOCPcs was observed on excitation at 500 nm in the absence of CYS3, so the fluorescence of the MOCPcs that emerged in this case must be due to the fluorescence induced by CYS3 unto the MOCPcs.

The overlap integral (J) values obtained are shown in Table 5.10 and are relatively high. An increase in overlap integral (J) in the order, GeOCPc (**44**) < SiOCPc (**43**) < AlOCPc (**42**) $\cong$ ZnOCPc (**41**) was observed.

The center-to-center separation distance between donor and acceptor (r, Å) values are shown in Table 5.10. All r values were below the critical distance (R_0) at which energy transfer is 50% which will allow good interaction of the donor and acceptor thereby allowing energy transfer to occur readily at a high efficiency. SiOCPc (**43**) exhibits the lowest value of r indicating a very close proximity of this complex to the donor, CYS3

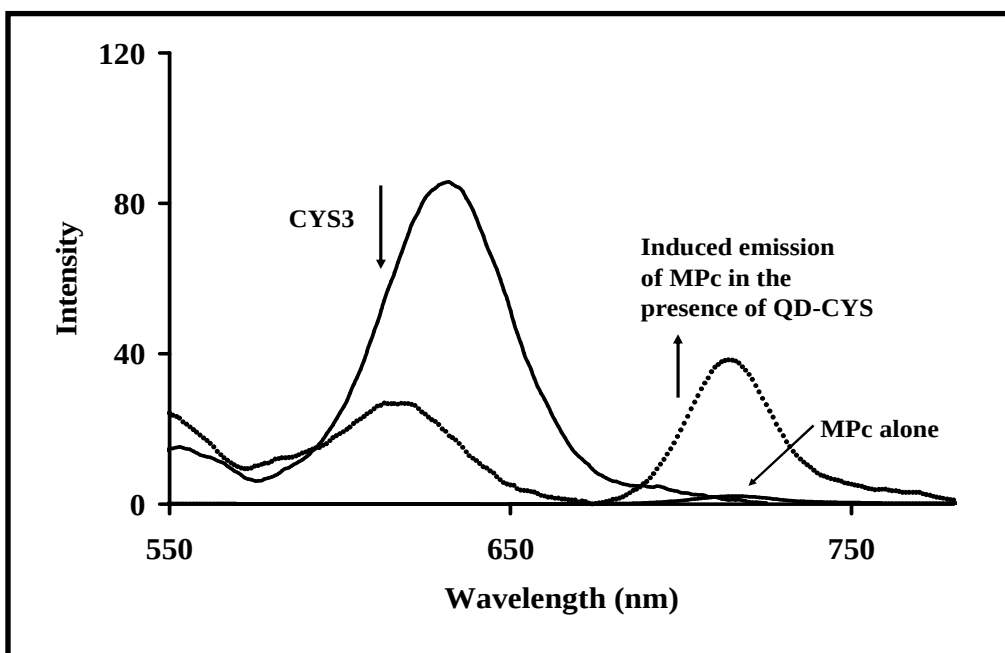


Figure 5.15: Indirect activation of GeOCPc (44**) by CYS3 through energy Transfer in PBS pH 7.4. ($\lambda_{exc} = 500nm$)**

Table 5.10: Energy transfer data for the interaction of MOCPCs with CYS3 in PBS pH 7.4.

Complex	^a J (x10 ⁻¹³ cm ⁶)	^b R ₀ (Å)	^c r (Å)	<i>Eff</i>
ZnOCPc (41)-CYS3	7.97	62.56	60.91	0.54
AlOCPc (42)-CYS3	7.95	62.54	52.99	0.73
SiOCPc (43)-CYS3	5.79	59.31	47.07	0.80
GeOCPc (44)-CYS3	5.13	58.14	47.98	0.76

^aJ, overlap integral; ^bR₀, critical distance at which energy transfer efficiency is 50 %; ^cr, centre to centre separation of donor and acceptor.

and thus encouraging an ease of energy transfer.

Eff (Table 5.10) followed the trend SiOCPc (43) > GeOCPc (44) > AlOCPc (42) > ZnOCPc (41). The values were relatively high, with SiOCPc (43) which had the smallest *r* having the highest *Eff* due to its close proximity to the donor. The MOCPCs had the highest *Eff* values amongst all the MPCs studied, (compare Tables 5.8 to 5.10). AlPcS₄ (34) also exhibited high *Eff* in PBS pH 7.4 in the presence of CYS2 (Table 5.8), probably due to the more monomeric nature of these complexes in aqueous medium. As stated above, the *r* values obtained for the MOCPCs were below the critical distance (R₀), which allows for good interaction of the donor and acceptor, but they were still relatively high if covalent attachment of MOCPC to the QDs is assumed, suggesting that the MOCPCs may not be covalently attached to QDs which would have been assumed on the basis that amide bonds form between amino (of QDs) and carboxylic (of MOCPC) groups.

Eff has a non-linear dependence on *J* as was the case for MPCs₄ complexes in water: methanol mixture reflecting involvement of the QD surface states in the energy transfer

process [225]. Considering the structure of the MOCPCs in this study and the trend of Eff , it is reasonable to assume that Eff is related to the existence of axial ligands on the molecules. ZnOCPC with no axial ligand has the lowest Eff while SiOCPC and GeOCPC with two axial ligands experienced highest Eff . There may be increased adsorption due to the presence of the axial positions.

5.2.3 Production of singlet oxygen through energy transfer

Figures 5.1a and c shows enhanced absorption in the 550 nm region of the MPCs in the presence of the QDs, a region where the MPC's absorption is negligible. This enhanced absorption in this region could lead to high production of singlet oxygen, $^1O_2$ via FRET route for biological applications. Irradiation of the QD-MPC mixture in this study (employing the monomeric MPCs (**34,41-44**) in water only) under the 532 nm (a wavelength where there is negligible absorption of the MPCs) laser light produced singlet oxygen in the presence of the $^1O_2$ chemical quencher, ADMA of concentration $\sim 6 \times 10^{-5}$ M. As shown in Figure 5.16, ADMA was photodegraded in QD solution while ADMA alone was not affected by the 532 nm laser irradiation, indicating production of singlet oxygen by the QDs. The photodegradation of ADMA in the presence of the QD-MPC mixture was monitored since there is a linear dependence of degradation of ADMA to production of singlet oxygen [289] using Eosin Y with quantum yield of 0.6 as reference [311]. The production of $^1O_2$ at 532 nm wavelength in the MPCs alone was poor with just about 1 to 2% production since absorption of the MPCs at this wavelength is negligible, even that of CYS3 was <1% in aqueous medium. However, Samia et al has reported $\sim 5\%$ yield of singlet oxygen from CdSe QDs in organic solvent [219]. The production of $^1O_2$

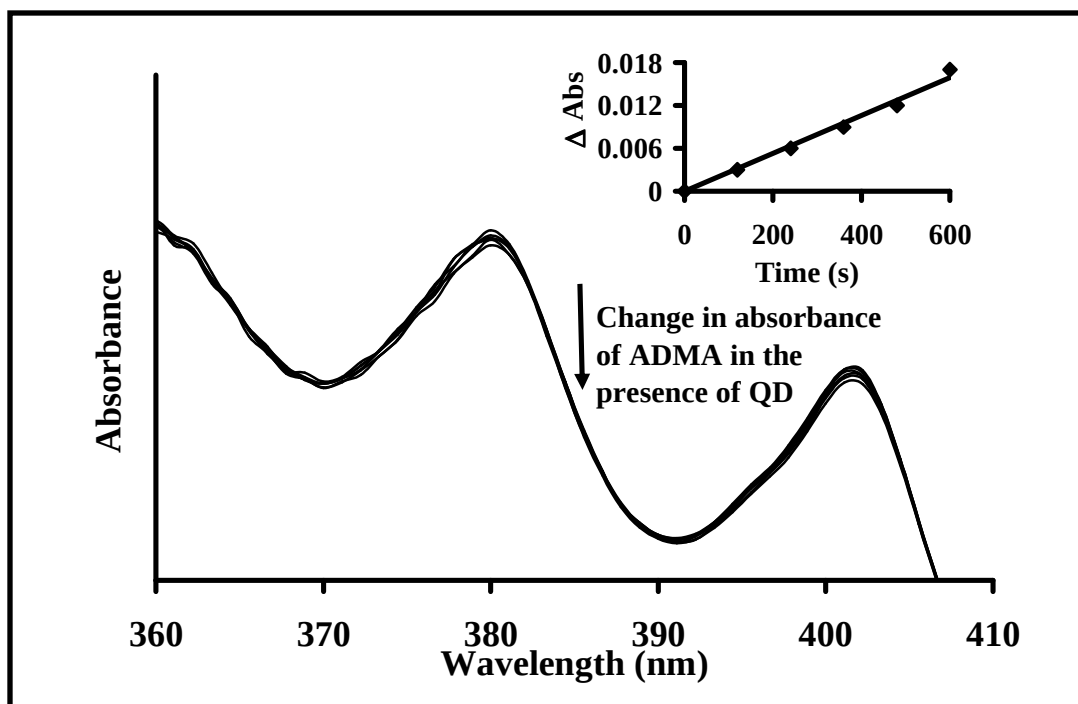


Figure 5.16: The photodegradation of ADMA in QD solution ($1.2 \times 10^{-6} \text{M}$) under 532 nm laser irradiation in PBS pH 7.4. Typical absorption band (379 nm) of ADMA gradually decreased with irradiation time.

by the MPcs through FRET ($\Phi_{\Delta(\text{ET})}$) was enhanced in the presence of the QD as shown in Table 5.11. It has been documented that singlet oxygen can be produced via excitation of the QD followed by a FRET mechanism in QD- porphyrin composite systems [226]. AlPcS₄ (**34**) was also studied in the presence of MPA2, since as stated above, the interaction of **34** in the presence of MPA2 was found to be the best. The Φ_{Δ} of MPA2 was calculated as $1.2 \pm 0.1\%$ and that of AlPcS₄-MPA2 was found to be $9.5 \pm 1\%$ confirming the considerable $^1\text{O}_2$ production of QD-MPc mixtures due to energy transfer. The values of $\Phi_{\Delta(\text{ET})}$ obtained are however lower than the Φ_{Δ} values obtained for the MOCPCs alone (Table 5.11) and 0.34 for AlPcS₄ (**34**), which is actually monitored at the maximum absorption of the MPcs. Though values of $\Phi_{\Delta(\text{ET})}$ for the QD-MPc mixture are

lower compared to Φ_{Δ} of MPcs alone, it is necessary to bear in mind that QDs can be repetitively exposed for a prolonged time to UV-vis irradiation without photobleaching which occurs in photosensitizers, therefore, it can be speculated that this can ensure a steady level of $\Phi_{\Delta(ET)}$ in the mixture.

Table 5.11: Indirect singlet oxygen for MOCPcs-CYS3 in PBS pH 7.4.

Sample	$^a\Phi_{\Delta(ET)}$ (532 nm)	Φ_{Δ} (700 nm)
ZnOCPc (41)	0.011	0.32
ZnOCPc-CYS3	0.12	0.60
AlOCPc (42)	0.006	0.12
AlOCPc-CYS3	0.05	0.31
SiOCPc (43)	0.012	0.22
SiOCPc –CYS3	0.095	0.21
GeOCPc (44)	0.018	0.31
GeOCPc –CYS3	0.14	0.66

$^a\Phi_{\Delta(ET)}$ = Singlet oxygen production through energy transfer mechanism. Φ_{Δ} (QD-CYS3) = 0.007

5.3 Interaction of metallophthalocyanines with magnetic fluid

Unsubstituted MPcs (31,32) and anionic water-soluble MPcs (MPcS₄ (33-36) and MOCPcs (41-44)) were employed in this study. Further anchorage was also carried out with the anionic water-soluble zinc and aluminium tetracarboxy metallophthalocyanines

(37 and 38). These studies are carried out to exploit the possibilities of combination of PDT with HT.

5.3.1 MPcs in the presence of magnetic fluid

5.3.1.1 Spectral changes of MPcs in the presence of MNH (2a)

Figure 5.17 shows the transmission electron microscopy (TEM) pictures of MNH, **2a** and MNH in the presence of AlPc (**31**). There was a slight change in the morphology of MNH in the presence of **31** showing slight aggregation, probably due to the less hydrophilic phthalocyanine molecules adsorbed onto MNH (**2a**), though the crystallinity of the nanoparticles was maintained.

The electronic absorption spectrum of AlPc (**31**) (similar to ZnPc (**32**)) in the presence and absence of MNH, **2a** is shown in Figure 5.18a. The Q band maxima of the MPc derivatives did not shift in the presence of MNH, showing that MNH does not affect the absorbance properties of the MPc derivatives, hence can be used in conjunction with them for medical applications. This is an important point in the development of

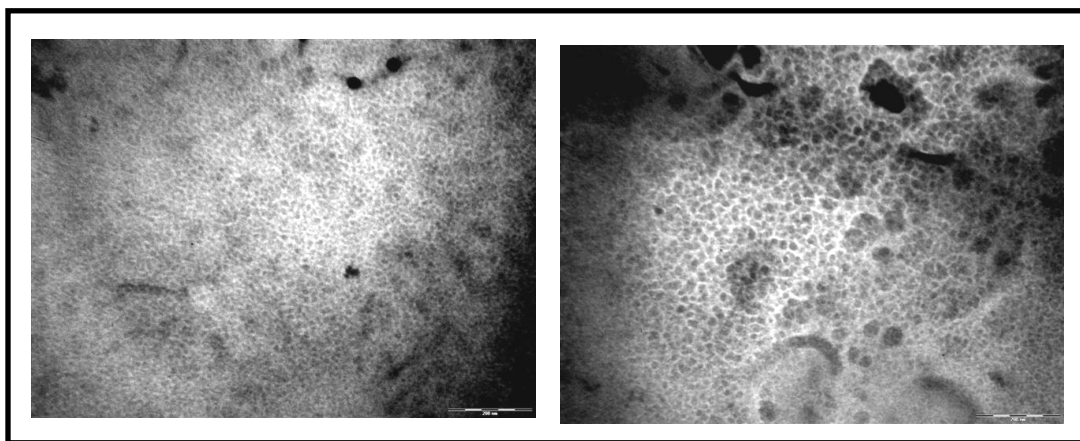


Figure 5.17: Scanning electron microscopic images of (a) MNH (2a) alone and (b) 2a plus AlPc (31). Magnification = 100 000. Burnt in scale bar = 200 nm

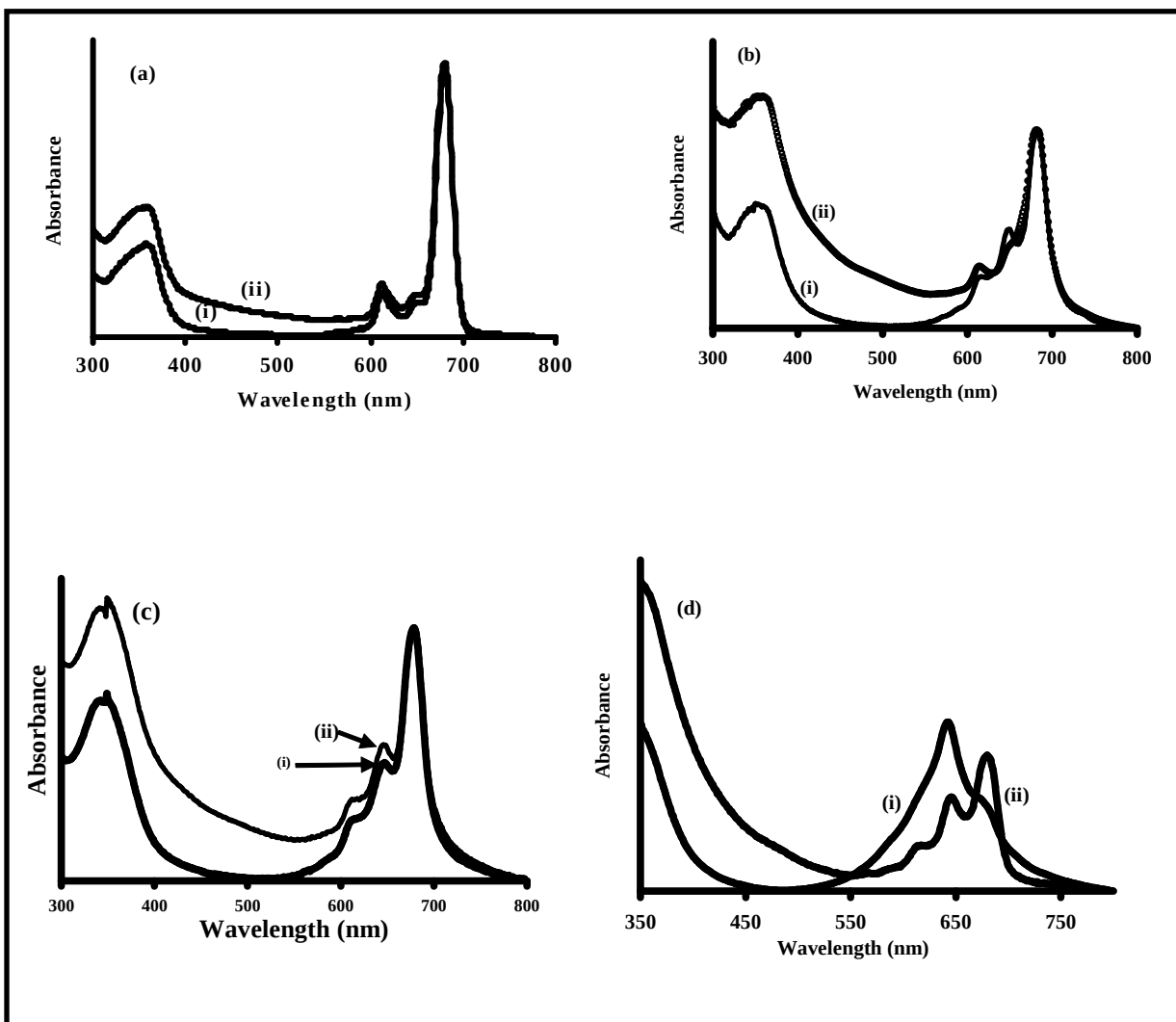
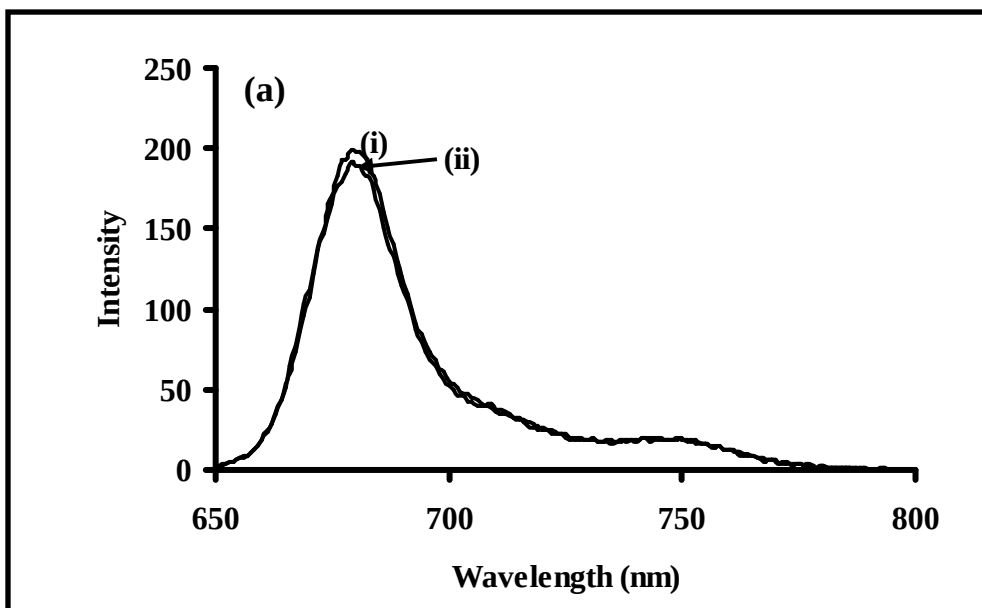


Figure 5.18: Spectral changes of (a) AlPc (31) and (b) GePcS₄ (36) (i) alone and (ii) in the presence of MNH (2a) in DMSO; (c) AlPcS₄ (34) and (d) GePcS₄ (36) in PBS pH 7.4 (i) alone and (ii) in the presence of MNH (2a).

MPcs/MN systems that can be used for combinatorial therapy of PDT and HT. Enhanced absorption in the 300-550 nm region of the MPcs in the presence of the MNH was observed, a region where the MPc's absorption is negligible. This enhanced absorption in this region could lead to increased photoactive reactions in the UV region e.g. in photodynamic inactivation of viruses. For all complexes in DMSO, no aggregation was

observed for concentrations less than 1×10^{-5} M in the presence or absence of MNH. In PBS pH 7.4, there was also no shift in the Q band on addition of MNH, only an increase in background. It is also important to note that there was no induced aggregation of the MPcs by MNH. For GePcS₄ (**36**), reduced aggregation was observed in the presence of MNH both in DMSO Figure 5.18b and in PBS pH 7.4 Figure 5.18d which may suggest that MNH has the ability to break aggregates in some of these complexes.

The lack of shift in the Q band maxima was also observed in the fluorescence spectra of the complexes both in DMSO and in PBS pH 7.4 (Figure 5.19a for AlPc in DMSO in the presence and absence of MNH, **2a**) as has been reported before [281] for ZnPc in ethanol in the presence of MNH. Also, the emission spectra were mirror images of the excitation spectra of the MPcs in the presence of **2a** as shown in Figure 5.19b for GePcS₄ (**36**) in PBS pH 7.4 showing that MNH does not affect the excited state configuration of the MPcs.



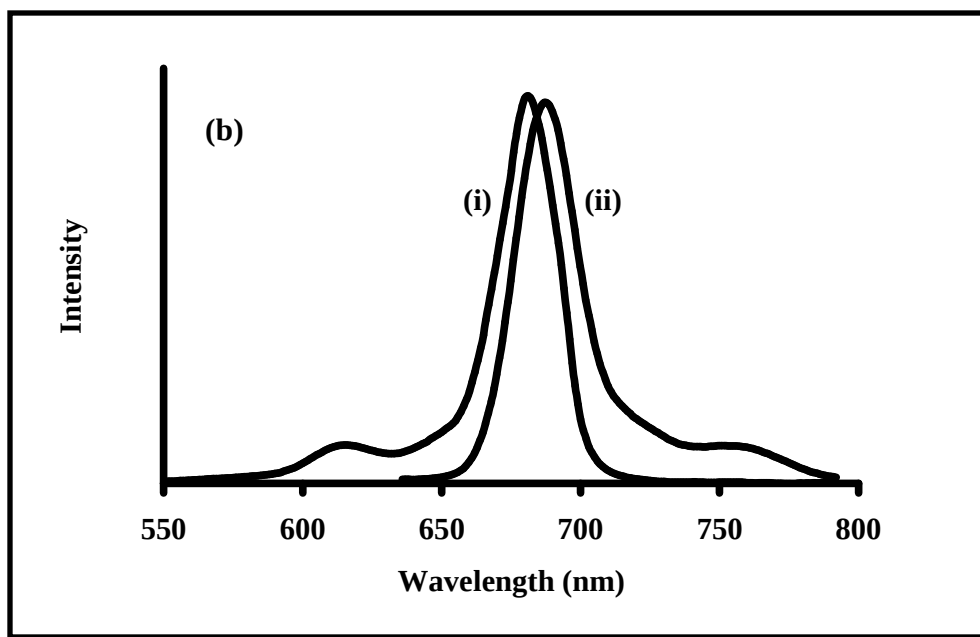


Figure 5.19: Fluorescence emission of AlPc (31) (a) in the absence (i) and presence (ii) of MNH, 2a and (b) fluorescence excitation (i) and emission (ii) spectra of GePcS₄ (36) in the presence of 2a in PBS pH 7.4.

5.3.1.2 Effect of MNH (2a) on the photophysical behaviour of MPcs

On addition of MNH, **2a** to the MPcs, the Φ_F values (Table 5.12) for the complexes decreased in PBS 7.4 or DMSO due to the heavy atom effect and the paramagnetic nature of the MNH except for ZnPcS₄ (**33**) and GePcS₄ (**36**) where there was slight increase which may be related to the disaggregation of **36** in the presence of MNH; dimers are known to be non-photoactive [165,166], so the increased monomer concentration could have led to increased Φ_F yield.

Figure 5.20 shows the triplet decay curve for AlPc in the presence of MNH in DMSO which is similar to the curve in the absence of MNH. Plots of $\ln A$ versus time (inset) are linear, confirming that only the observed decay is due to the depopulation of the triplet state and not quenching by triplet state quenchers such as oxygen. This was also observed

Table 5.12: Photophysical and photochemical results obtained for MPc complexes in the presence of MNH, 2a in PBS pH 7.4 and DMSO.

Complexes ^a	Solvent	Φ_F	Φ_T	Φ_{IC}	Φ_{Δ}	S_{Δ}	Φ_P ($\times 10^{-5}$)	$\tau_T(\mu s)$
AlPc - MNH	DMSO	0.27 (0.34)	0.28 (0.20)	0.45 (0.46)	0.24 (0.29)	0.86 (1.45)	0.14 (0.12)	750 (720)
ZnPc - MNH		0.16 (0.20) ^b	0.70 (0.65) ^c	0.14 (0.17)	0.50 (0.67) ^e	0.71 (1.03)	4.02 (4.53)	310 (350)
AlPcS ₄ - MNH		0.15 (0.30)	0.41 (0.38)	0.44 (0.32)	0.28 (0.38)	0.68 (1.00)	0.29 (0.32)	1295 (1335)
ZnOCPc - MNH	PBS	0.19 (0.23)	0.56 (0.50)	0.25 (0.27)	0.61 (0.32)	1.09 (0.64)	2.93 (2.65)	140 (150)
AlOCPc - MNH		0.22 (0.27)	0.36 (0.32)	0.42 (0.41)	0.12 (0.12)	0.33 (0.38)	0.27 (0.26)	370 (450)
SiOCPc - MNH		0.21 (0.24)	0.45 (0.34)	0.34 (0.42)	0.21 (0.22)	0.47 (0.65)	81.1 (86.3)	90 (90)
GeOCPc - MNH		0.12 (0.13)	0.68 (0.62)	0.20 (0.25)	0.36 (0.31)	0.53 (0.51)	2.04 (2.12)	170 (240)
ZnPcS ₄ - MNH		0.03 (0.02)	0.61 (0.56) ^d	0.36 (0.42)	0.13 (0.23)	0.21 (0.41)	2.05 (2.21)	160 (180)
AlPcS ₄ - MNH		0.10 (0.13)	0.38 (0.36)	0.52 (0.51)	0.32 (0.34)	0.84 (0.94)	0.11 (0.24)	500 (560) ^f
SiPcS ₄ - MNH		0.001 (0.01)	0.51 (0.49)	0.49 (0.50)	0.24 (0.50)	0.47 (1.02)	4.42 (4.48)	160 (200)
GePcS ₄ - MNH		0.09 (0.05)	0.62 (0.61)	0.29 (0.34)	0.34 (0.64)	0.55 (1.05)	3.24 (3.66)	160 (180)

^a values in bracket are for the MPcs alone ^b [234], ^c [307], ^d [308], ^e [310], ^f [325]

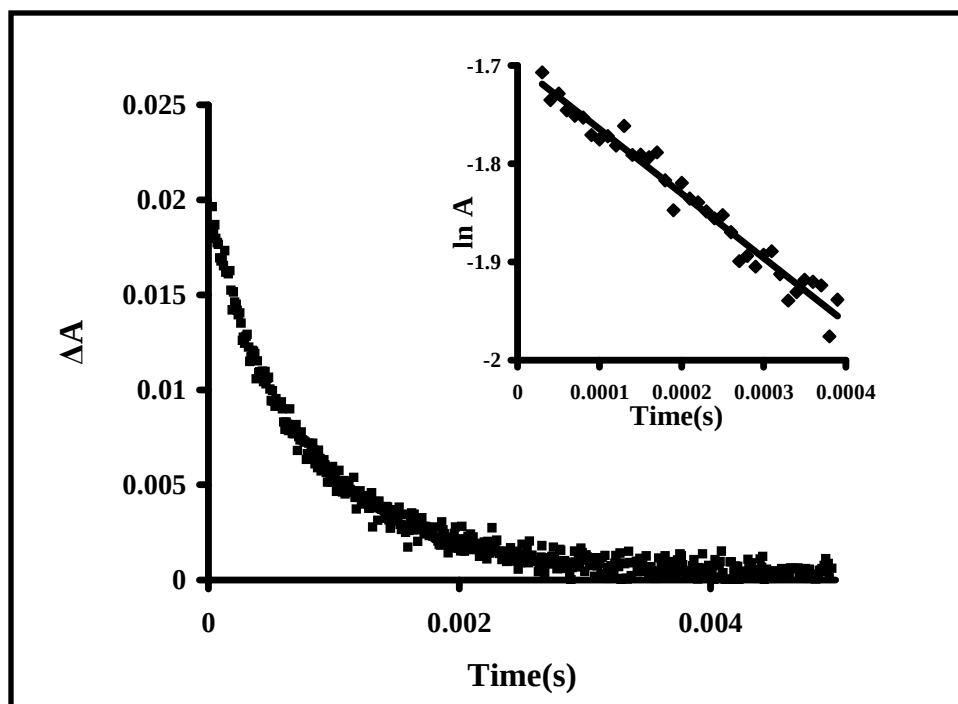


Figure 5.20: Triplet decay curve of AlPc (31) in the presence of MNH (2a), solvent: DMSO. Inset: plot of $\ln$ of absorbance versus time.

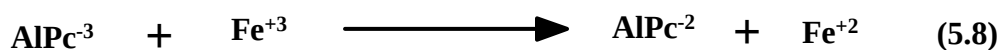
for the other complexes in PBS pH 7.4. Changes in the shape of the triplet curves have been reported before for ZnPc in the presence of MNH in ethanol [281]. This confirms that solvents do affect the photophysical behaviour of the complexes. The presence of oxygen in the solvent may also affect the triplet decay behaviour.

The curve in Figure 5.20 was employed in calculating triplet lifetimes (τ_T) and quantum yields (Φ_T) of the complexes in the presence and absence of MNH. On addition of MNH, Φ_T values increased for all complexes (Table 5.12) as expected by the heavy atom effect and the presence of paramagnetic species enhancing ISC to the triplet state. The increase in Φ_T is only marginal for the MPcS₄ complexes in PBS pH 7.4, Table 5.12.

τ_T values generally (except for AlPc and SiOCPC) decreased in the presence of MNH as expected by the heavy atom effect both in water and DMSO. The lack of decrease in τ_T

for AlPc might be due to the phototransformation behaviour in AlPc discussed earlier. The laser energy was kept the same for studies in the presence and absence of MNH, hence the lack of decrease in τ_T values is not due to the changes in laser energy. Triplet lifetime remained the same for SiOCPC both in the presence and absence of MNH. The triplet lifetimes observed for ZnPc in ethanol [281] were much lower than reported here in DMSO. It is important to note that τ_T values are affected by oxygen so it is essential to remove oxygen efficiently in order to obtain good results. This was done in this work as explained in the experimental section.

As discussed in Chapter 4, Figure 4.9, phototransformation occurred in AlPc upon irradiation with laser light. On addition of MNH, the phototransformation of AlPc derivatives decreased. For example the Q band intensity of AlPc decreased by 11% in the absence of MNH, but only by 3% in the presence of MNH. These observations suggest that the MNH results in the recovery of the Q band absorption by oxidizing the Pc^{-3} back to the Pc^{-2} as shown by Equation 5.8. Thus in the presence of MNH, the effects of Pc^{-3} on the photophysical properties will be minimal.



Φ_{IC} values were generally high and followed the trend of the Φ_T .

5.3.1.3 Photochemical Studies

The singlet oxygen quantum yields (Φ_Δ) for AlPc and ZnPc in DMSO decreased in the presence of MNH, suggesting quenching of singlet oxygen by MNH (Table 5.12). In PBS pH 7.4, decrease in Φ_Δ was also observed with the MPcS₄ complexes, while with the MOCPcs, Φ_Δ either increased or there was no significant change Table 5.12. $S_\Delta (\Phi_\Delta/\Phi_T)$

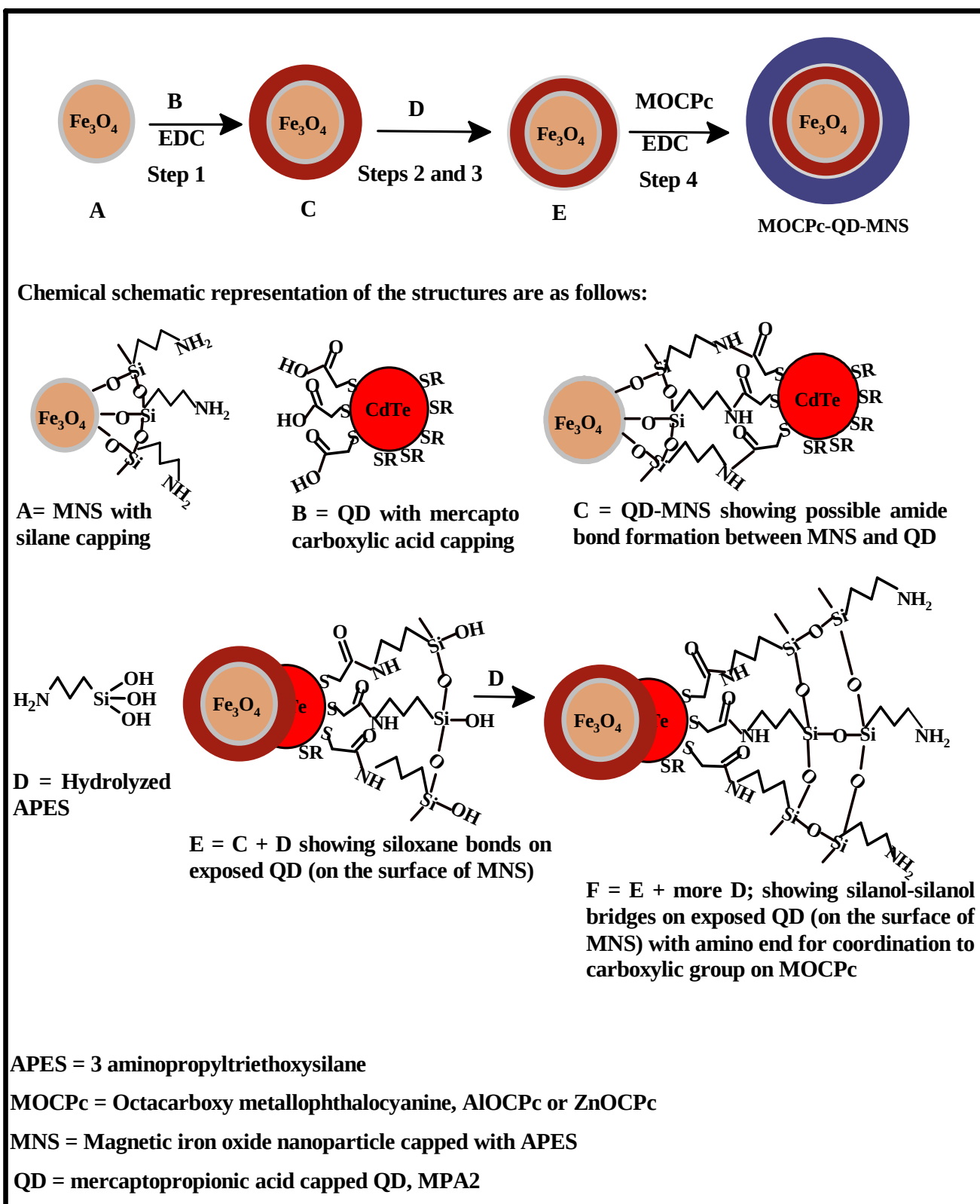
values decreased following addition of MNH except in ZnOCPc and GeOCPc showing a less efficient quenching by oxygen. However, these values are still sufficiently enough for photosensitized reactions to occur.

Photodegradation quantum yields (Φ_P) for the complexes are shown in Table 5.12. There was a general decrease in the Φ_P values in the presence of MNH. Again a deviation from the trend is observed in AlPc, ZnOCPc and AlOCPc. It is believed that photodegradation is a singlet oxygen mediated process, hence its efficiency should depend on the value of Φ_Δ . Thus since Φ_Δ generally decreases in the presence of MNH, Φ_P should decrease also.

5.3.2 Attempted synthesis of MOCPCs-QD-MNS, a 3-in-one photosensitizer conjugate

Poor water solubility and aggregation tendencies of MPcs in aqueous solutions results in loss of photochemical activity and this can affect their cell-penetrating properties [166,364,365]. In resolving this, nanoparticles can be used as potential delivery systems for PDT photosensitizers [364,365] illustrating the potential of nanoparticle based PDT for cancer therapy applications.

Combination of PDT and HT, with quantum dots which are highly photoluminescent can lead to excellent energy transfer from the quantum dots to the MPc and help in localization within the cancer cells with the help of magnetic fluid, thereby combining magnetic and fluorescent properties. In this thesis the synthesis of a hydrophilic three-component nanocomposite (metallophthalocyanine /quantum dot /magnetic iron oxide nanoparticle) that will enhance the effectiveness of PDT through a dual function of visualization and simultaneous treatment of tumor cells was attempted according to Scheme 5.1, same as Scheme 2.1 employing MOCPC complexes of zinc (ZnOCPc (**41**))



Scheme 5.1: Schematic representation of synthesis of MOCPC-QD-MNS

or aluminium (AlOCPC (**42**)) with iron oxide nanoparticles coated with 3-aminopropyl triethoxysilane (APES) (MNS (compound **A** in Scheme 5.1)) and QDs coated with mercaptopropionic acid, MPA2 (compound **B** in Scheme 5.1). This is mainly a preliminary study.

5.3.2.1 Spectroscopic studies

Firstly, the interaction between QDs and MNS occurs in that the amino end of APES used in capping the iron oxide nanoparticles, MNS is expected to form an attachment with the carboxylic functional groups on QDs resulting in an amide bond between MNS (**A**) and QD (**B**) to give QD-MNS (**C**), Scheme 5.1, Step 1. Now QDs surrounds MNS but are expected to have some exposed carboxylic groups on the outside. Further coverage of QD-MNS with hydrolysed APES (**D** in Scheme 1) will slow down the corrosion of the QDs (**B**) and help its attachment to the MOCPCs, since the exposed carboxylic groups of the QDs surrounding MNS gets coordinated to the amino end of the hydrolysed APES exposing the silanol (Si-OH) groups, **E** in Scheme 5.1, Step 2. The excess hydrolysed APES added helps to tailor the nanocrystal surface functionality since it leads to formation of silanol-silanol bridges with the exposed silanol groups (Si-OH) on the QDs [35,39] and exposes the NH₂ groups (**F** in Scheme 5.1, Step 3) for functionalization with the carboxylic group of the MOCPCs.

Scanning electron microscope (SEM) image, shows dispersion of the MOCPC-QD-MNS samples with an average diameter of ~100 nm, Figure 5.21. This is consistent with what has been observed for silica coated Fe₃O₄-QD in literature [366]. Though the diameter is large; it can still work well for cell studies; it is documented that biomedical applications

require nanoparticles of size ≤ 100 nm [48] and a narrow particle size distribution so that the particles have uniform physical and chemical properties.

Figure 5.22 shows the photos of AlOCPc-QD-MNS in PBS pH 7.4 under daylight (i) and UV light (ii). The composite look brown and non-fluorescent under daylight compared to the bright red QDs (middle) or green MPc (left), but under UV light its fluorescent property was evident, by its glowing red colour. The photos show the stabilized dispersion of the composite even after several weeks of storage, retaining its strong emission intensity. Characterization of the MOCPc-QD-MNS composites was performed with IR measurements. The IR spectra were similar to that of the MOCPcs alone though a lot of overlap must have occurred from the functional groups of the individual compounds involved in the composite; hence creating weakness of some bands. The characteristic O-H bands were still observed in both composites (AlOCPc-QD-MNS and

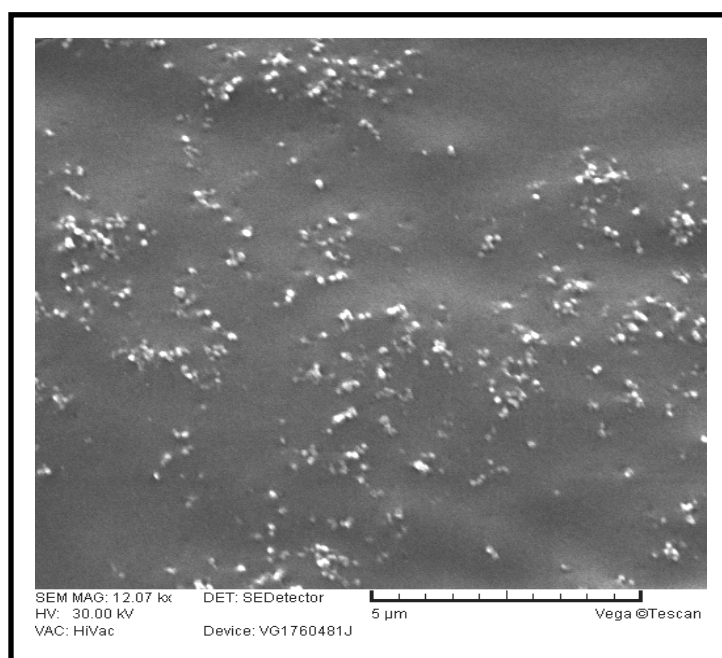


Figure 5.21: Scanning electron microscopic image of AlOCPc-QD-MNS Magnification 12.07 kx.

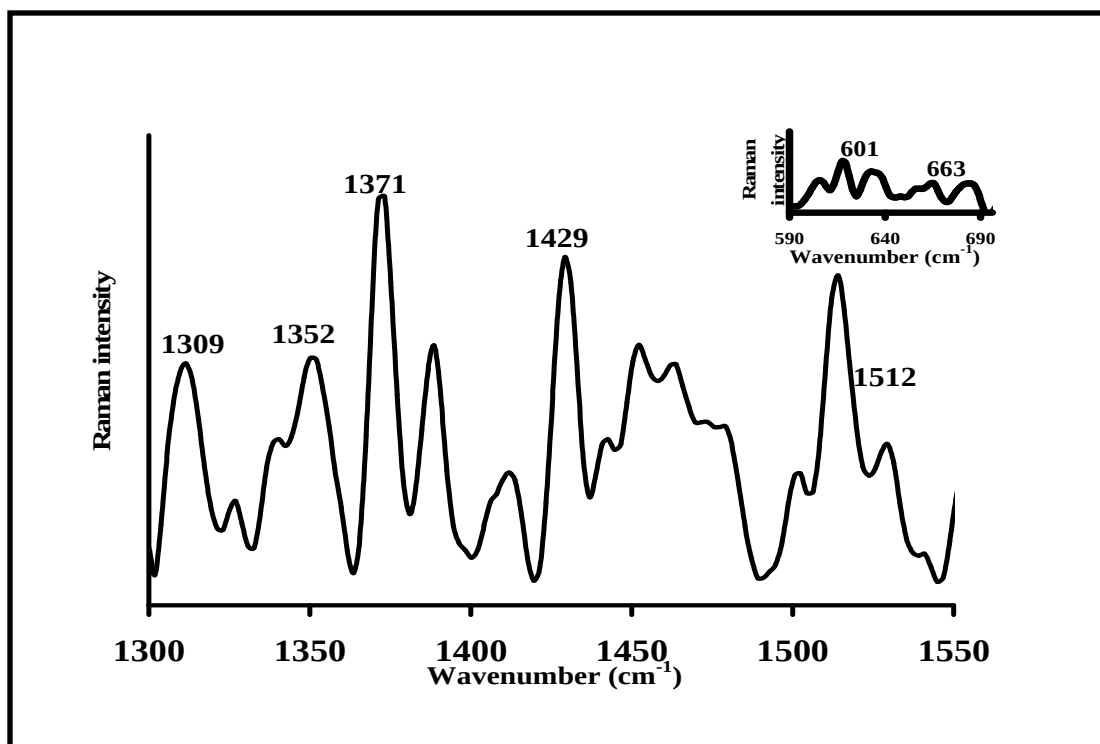


Figure 5.23: Raman spectra for AlOCPc-QD-MNS. Inset shows 400-800 cm^{-1} region of the composite. Inserted numbers are in cm^{-1}

respectively. Raman spectra is known to be highly sensitive to the metal ion present in a complex [368]. Peaks observed at 601 and 663 cm^{-1} can be assigned to characteristic Fe-O band, which is consistent to what was observed in literature [296], this peak was observed in the zinc composite at $\sim 688 \text{ cm}^{-1}$.

Figure 5.24a shows the electronic absorption spectra of linked AlOCPc-QD-MNS (i), mixed AlOCPc-QD-MNS (ii), free AlOCPc (iii), QDs (iv) and MNS (v) (Figure 5.24b is for the zinc complex) with an enhanced absorption in the 550 nm region, a region where the MPC's absorption is negligible. The increase is indicative of the presence of MNS and QDs absorption. The enhancement was also observed in the mixed AlOCPc-QD-MNS. This enhanced absorption in this region could lead to high production of singlet oxygen

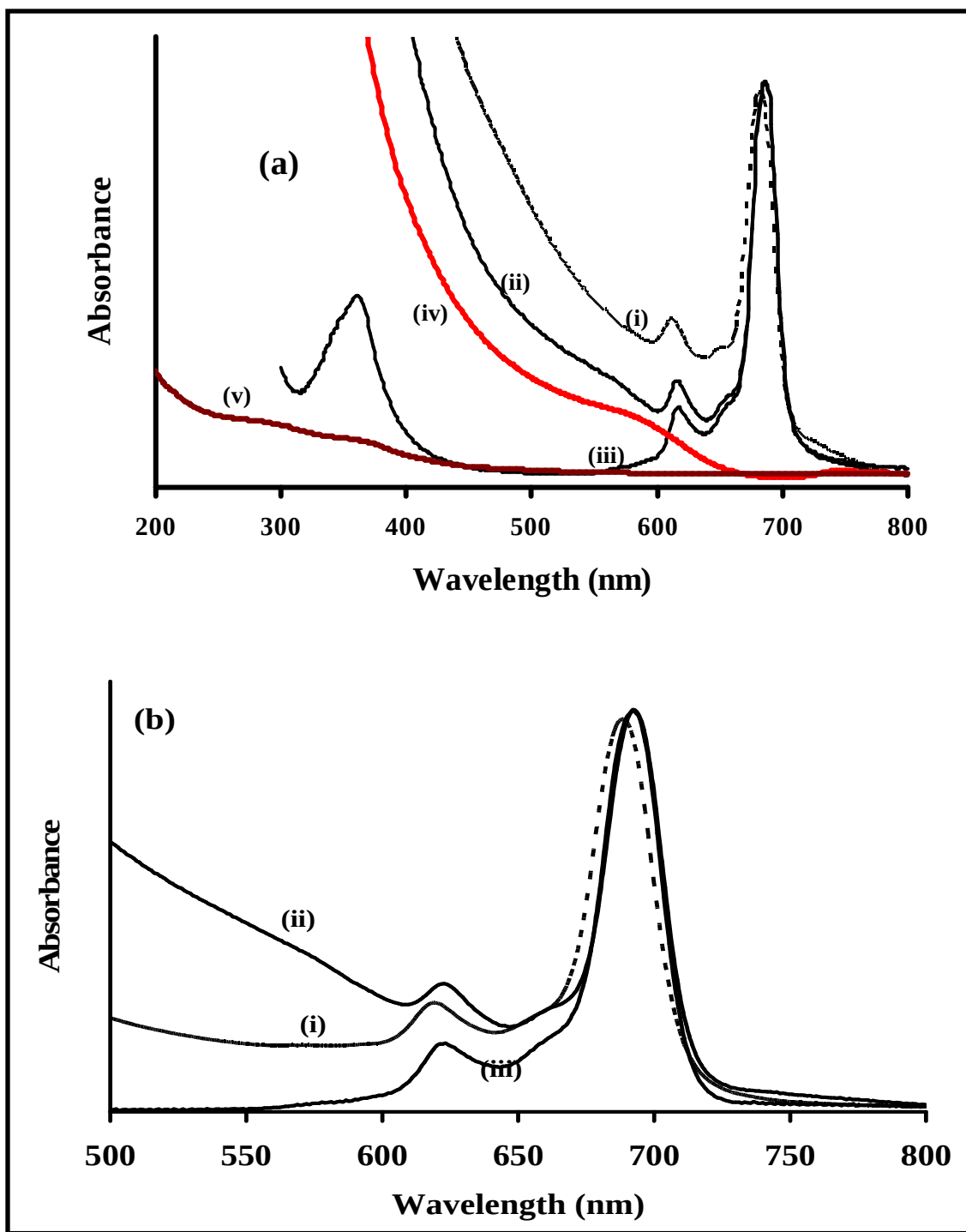


Figure 5.24: Electronic absorption spectra of (a) AlOCPc-QD-MNS linked (i), AlOCPc-QD-MNS mixed (ii), AlOCPc alone (iii), QD alone (iv) and MNS alone (v); (b) ZnOCPc-QD-MNS linked (i), ZnOCPc-QD-MNS mixed (ii) and ZnOCPc alone (iii) in PBS pH 7.4.

$^1\text{O}_2$ via FRET route for biological applications. The Q-band maximum was at 683 nm for ALOCPc-QD-MNS linked. This value is blue shifted by 6 nm as compared to the free ALOCPc, suggesting that indeed there is an attachment within the components of the composite. A similar spectral change was obtained for ZnOCPc-QD-MNS, Figure 5.24b. In the mixture of the three components without linking (mixed MOCPc-QD-MNS, Figure 5.24 (ii)), no shift in Q band maxima was observed, further confirming an attachment. Figure 5.25 shows the emission peaks of the QDs alone (i), when it was combined with the magnetic nanoparticles (QD-MNS) (ii) and that of ALOCPc-QD-MNS linked (iii). Slight red shift of the fluorescence emission peak (~ 3 nm) of QDs in the presence of MNS was observed and we base this on the strong interactions between the QDs on the

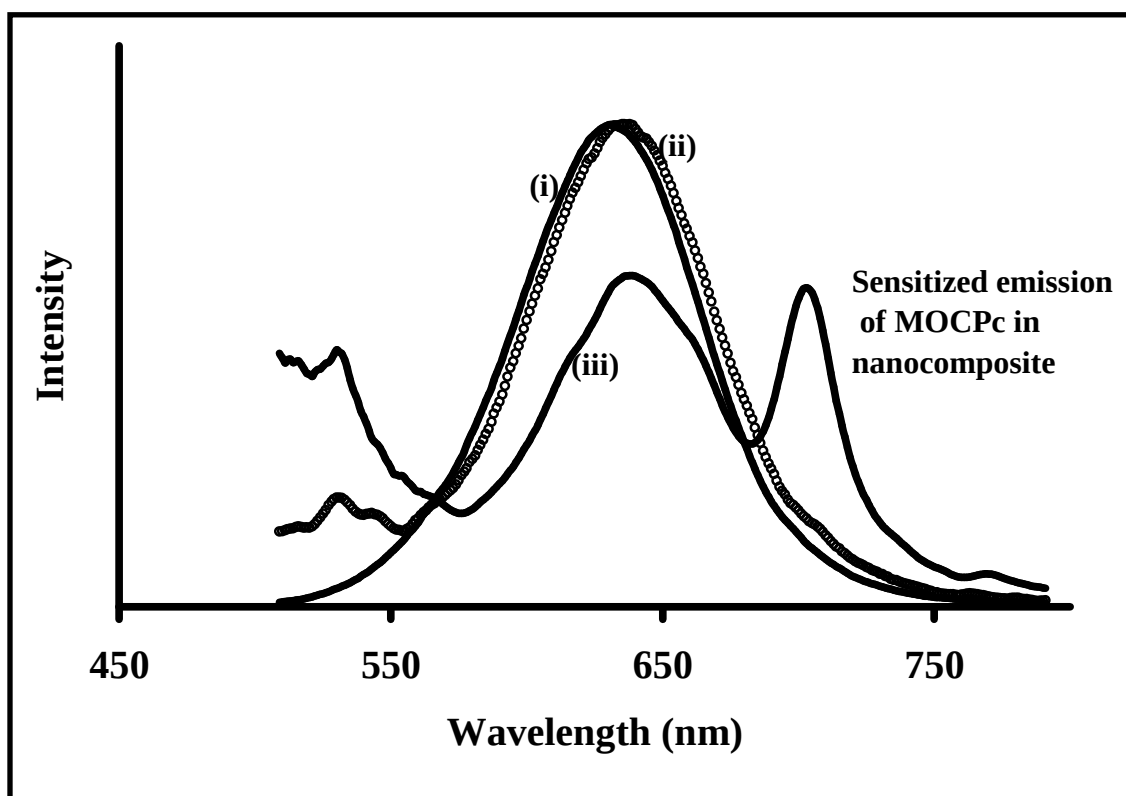


Figure 5.25: Fluorescence emission spectra of (i) QDs, (ii) QD-MNS and (iii) ALOCPc-QD-MNS showing sensitized emission of ALOCPc in PBS pH 7.4.

surfaces of the magnetic iron oxide particles. Similar shift in absorption spectra has been observed before in QD-MN system capped with silica [366]. The full width at half maximum (FWHM) of the emission spectrum of QD-MNS was not affected.

Two emission peaks were observed when the composite was excited at 500 nm (a wavelength where the MOCPcs have negligible absorbance, but the QDs absorb appreciably), one which can be attributed to the QDs emission (at ~ 654 nm) and the other to the MOCPc (~ 705 nm), (MNS have very poor emission). This suggests that energy transfer occurs from the QDs to the MOCPcs within the composite. This was observed with both complexes. No significant fluorescence for the free MOCPcs was observed on excitation at 500 nm so the fluorescence of the MOCPcs that emerged in this case must be due to the fluorescence induced by the QDs onto the MOCPcs in the composite (all samples prepared for fluorescence were adjusted to absorbance of ~ 0.05 at the λ_{exc} since fluorescence is dependent on absorbance). The fluorescence intensity of the QDs in the linked complex was observed to be lower than that in QD-MNS or QDs alone, supporting the idea that energy transfer occurs within this system.

A strong emission peak was observed for the MOCPc-QD-MNS complexes like in their free MOCPcs counterpart when emission was monitored at λ_{exc} of the MOCPc (640 nm) as seen in Figure 5.26 for ALOCPc-QD-MNS. There is a slight shift to the red by about 4 nm in both composites compared to the free MOCPcs, (Figure 5.26 and Table 5.13) this is an opposite trend to what was observed in their absorption spectra, however, this results in a larger Stokes' shift which may be an advantage since it will enable fluorescent signals from the composite to be easily separated from scattered excited light. This shift was however not observed when the mixture of the three components that make up the

composite was excited at the λ_{exc} of the MOCPC, further confirming the attachment.

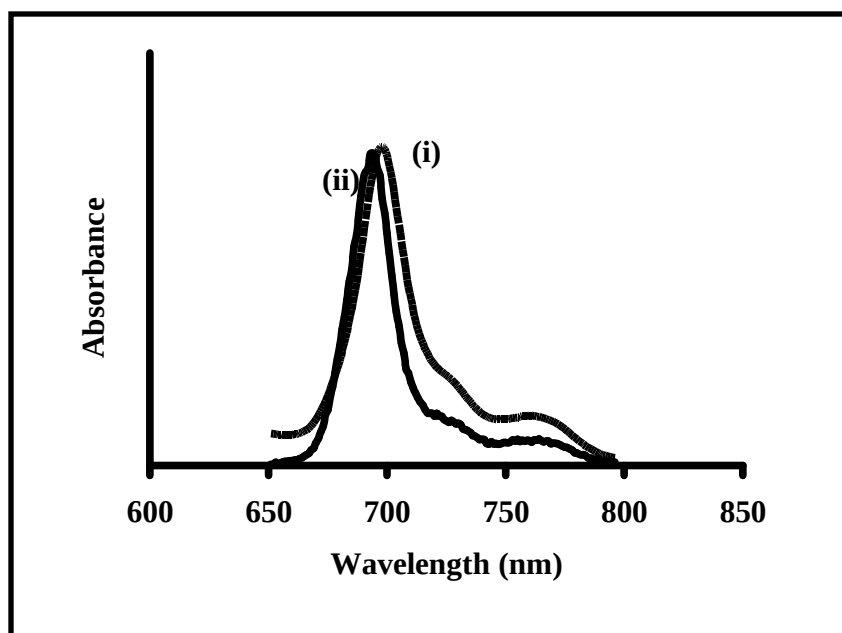


Figure 5.26: Fluorescence emission spectra of (i) AlOCPC-QD-MNS and (ii) AlOCPC in PBS pH 7.4.

5.3.2.2 Photophysical studies

Fluorescence quantum yield (Φ_F) values for the composites were determined and shown in Table 5.13. A decrease in Φ_F values of MOCPC, $\Phi_{F(\text{MOCPC})}$ was observed in both composites and was more pronounced with the zinc complex. The values obtained are however still comparable to values for MPCs [236]. This decrease in value may be due to the heavy atom effect (from QDs and MNS) and the paramagnetic nature of the MNS in the composite encouraging ISC. The Φ_F values for QD in the linked complexes, $\Phi_{F(\text{QD})}$ are lower than the Φ_F value for QDs alone (0.59, Table 5.13).

In the mixture of the three components (without linking), Φ_F values further decreased both at excitation of 640 nm $\Phi_{F(\text{MOCPc})}$ and 500 nm $\Phi_{F(\text{QD})}$, Table 5.13, probably due to the absence of a spacer between the magnetic nanoparticles and the QDs or MOCPcs,

Table 5.13: Photophysical properties of MOCPc-QD-MNS in PBS pH 7.4.

^a Complexes	λ_Q	λ_F	Φ_T	$\tau_T(\mu s)$	^b $\Phi_{F(\text{MOCPc})}$	^c $\Phi_{F(\text{QD})}$
AlOCPc	689	694	0.32	450	0.27	-
AlOCPc-QD-MNS mixed	689	694	0.41	495	0.14	0.20
AlOCPc-QD-MNS linked	683	699	0.43	480	0.18	0.36
ZnOCPc	693	702	0.50	160	0.23	-
ZnOCPc-QD-MNS mixed	693	702	0.58	130	0.098	0.21
ZnOCPc-QD-MNS linked	688	706	0.61	120	0.10	0.24

^a $\Phi_{F(\text{QD})}$; fluorescence quantum yield of QD alone = 0.59; ^b $\Phi_{F(\text{MOCPc})}$ λ_{exc} , 640 nm

^c $\Phi_{F(\text{QD})}$ λ_{exc} , 500 nm.

thereby allowing strong surface interactions because of the QD contact with the metal oxide particle surface, resulting in a non-radiative energy transfer process [286].

The values of Φ_T obtained were high for the linked complexes (Table 5.13) and higher than for the respective free MOCPcs which is a result of the combination of heavy atom effect of QDs and the paramagnetic nature of the MNS in the composite encouraging ISC. The zinc complex have a higher value than its aluminium counterpart, since Zn has a higher relative atomic mass compared to Al; and this will result in spin-orbit coupling encouraging ISC to the triplet state. For the mixed components, Φ_T values were slightly

lower than in the linked Table 5.13, but still high, since the heavy atoms of the QDs and MNS are still present in solution even though they are not linked to one another.

Long τ_T values comparable to MPcs in general [236] were obtained for the complexes. Aluminium complexes are known for their long lifetimes [165]; hence their longer τ_T than those of their zinc counterparts is not surprising, Table 5.13. Values of the τ_T are longer in the linked ALOCPc-QD-MNS compared to its free ALOCPc; the trend was opposite with the zinc complex. It is expected that paramagnetic species will increase Φ_T with a corresponding decrease in τ_T due to quenching of the triplet state; however ALOCPc-QD-MNS behaves differently. The long τ_T in the aluminium complex will allow for high level of energy transfer from its triplet state to molecular oxygen for the production of cytotoxic singlet oxygen species thereby increasing the rate of photosensitized reactions. For the mixed complexes, τ_T were higher than for the linked for both ALOCPc and ZnOCPC.

It is evident that the MOCPC-QD-MNS can generate high yields of triplet state species which will lead to enhanced singlet oxygen production as compared to free MOCPC. These results show that this composite is a useful vehicle for the delivery of MPcs as agents in PDT, and MNS as agents in HT, leading to increased tumor damage. These however are preliminary studies.

5.4 Conclusions

The results obtained clearly demonstrated that the interaction of nanoparticles with MPcs lead to improved photophysical and photochemical properties reinforcing the idea of

excellent photodynamic activity of MPc-QD or MPc-MNH systems for PDT and local HT. Rules of photophysics were contradicted in that the MPcs in the presence of nanoparticles showed high triplet state quantum yields with corresponding long lifetimes. Increased photostability of the MPcs was observed in the presence of the nanoparticles.

Interaction between CdTe QDs and MPc complexes was shown to be highly dependent on the substituents of the MPcs; ion-pair complexes resulting in aggregates were formed with cationic MPcs, whereas interaction with anionic MPc complexes led to FRET. With the complexes that experienced FRET, non-radiative energy transfer was evident from QDs to MPcs, leading to quenching of the excited state of the QDs coupled with emergence of emission for the MPcs. A non-Förster type energy transfer behaviour occurred with the MOCPcs in QD-MPc donor-acceptor systems due to the involvement of the QD surface states in the energy transfer process since efficient energy transfer process was established in this case even with small spectral overlap.

Singlet oxygen was produced through excitation of the QD via a FRET mechanism. Lower values of singlet oxygen via FRET mechanism were obtained compared to direct singlet oxygen generation, but are speculated to produce a steady level of singlet oxygen since QDs are photostable and can be repetitively exposed for a prolonged time to UV-vis irradiation.

Preliminary studies on the preparation of fluorescent-magnetic nanocomposites (MOCPc-QD-MNS) have shown that they possess excellent photophysical properties which can be exploited for combined therapy (PDT and HT plus imaging) since their cell destructive abilities are enhanced.

CHAPTER 6

**INTERACTION OF BOVINE SERUM
ALBUMIN (BSA) WITH
METALLOPHTHALOCYANINES
(MPcs) OR QUANTUM DOTS (QDs)**

6.1 Interaction between BSA and MPcs

The water-soluble MPc complexes (MPcS₄, **33-36**; MOCPCs, **41-44**; α -TZnPcQ **47b**, β -TZnPcQ **48b** and β -OZnPcQ **49b**) employed in the study of the interaction of MPcs with BSA were soluble in PBS 7.4 which is a physiological pH for biological studies. The aggregates in MTCPCs (**37-40**) could not be broken for use in these studies. The association of the MPc complexes with BSA is studied since hydrophilic dyes such as are synthesized in this thesis bind preferentially to serum proteins, such as BSA [206] and serum albumin is one of the key components in the body that influences drug delivery [255].

6.1.1 Binding constants and fluorescence quenching

The progressive quenching of BSA fluorescence by respective MPcs as shown in Figure 6.1 for β -TZnPcQ (**48b**) (similar to other MPcs) was used to estimate the binding constants (K_b) (from the intercept) and the binding stoichiometry (n) (from the slope) of plot in Figure 6.2 using Equation 6.1 same as Equation 5.1.

$$\log\left[\frac{(F_0 - F)}{(F - F_\infty)}\right] = \log K_b + n \log[\text{MPc}] \quad (6.1)$$

The values of K_b and n are shown in Table 6.1. High K_b values were obtained for the MPcS₄ complexes with the exception of the monomeric AlPcS₄ (**34**) which is in contrast to what has been observed before with MPcS_{mix} where the non aggregated molecules (e.g. AlPcS_{mix}) had the largest binding constant [259], but the behaviour is similar to that which is reported for SnPcS₄ [207]. This shows that aggregation plays an important role in the binding and confirms the high affinity of BSA for negatively charged molecules

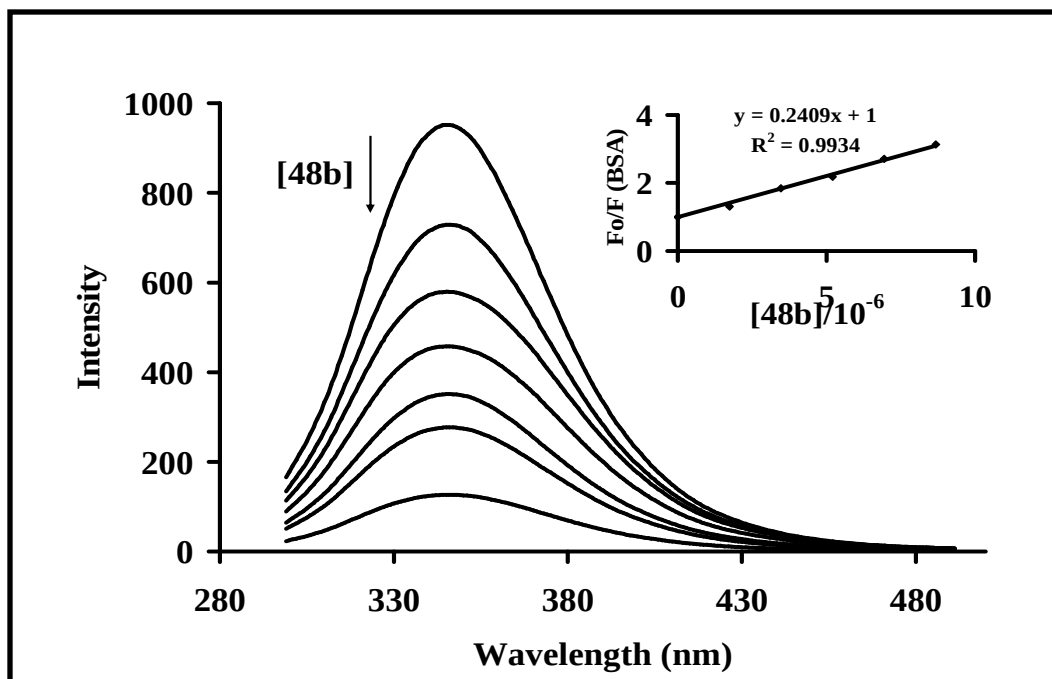


Figure 6.1: Spectral changes of BSA (3 x 10⁻⁵ M) on addition of β-TZnPcQ (48b) (0 to 8.68 x 10⁻⁶ M) in PBS pH 7.4. Inset is the Stern-Volmer's plot.

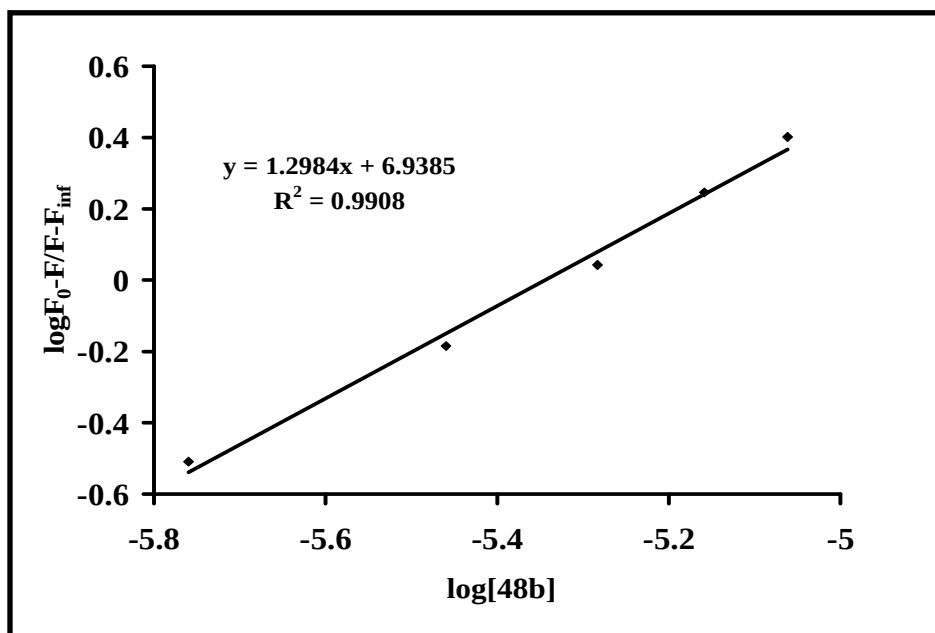


Figure 6.2: Binding plot of BSA to β-TZnPcQ (48b) in PBS pH 7.4 for the determination of binding constant.

Table 6.1: Quenching and binding data for the interaction of MPcs with BSA in PBS
7.4

Complex	^a K_{SV}^{BSA} ($\times 10^5 M^{-1}$)	^b k_q ($\times 10^{13} M^{-1} s^{-1}$)	^c K_b ($\times 10^6 dm^3 mol^{-1}$)	n
ZnPcS₄ (33)	3.32	3.32	29.4	1.54
AlPcS₄ (34)	4.00	4.00	5.24	1.21
SiPcS₄ (35)	2.51	2.51	30.2	1.38
GePcS₄ (36)	2.21	2.21	23.8	1.38
ZnOCPc (41)	1.75	1.75	8.52	1.30
AlOCPc (42)	1.78	1.78	2.24	1.20
SiOCPc (43)	1.42	1.42	0.27	1.05
GeOCPc (44)	1.62	1.62	0.57	1.10
αTZnPcQ (47b)	1.44	1.44	1.90	1.21
βTZnPcQ (48b)	2.41	2.41	8.68	1.29
βOZnPcQ (49b)	3.19	3.19	12.3	1.30

^a K_{SV}^{BSA} = Stern-Volmer constant of fluorescence quenching of BSA in the presence of MPc; ^b k_q = bimolecular quenching constant; ^c K_b = binding constant.

[369]. The value of K_b was highest in SiPcS₄ (35) in the set suggesting that (35) binds most strongly to BSA amongst the MPcS₄ complexes studied which may be due to the fact that (35) disaggregates easily.

The K_b values for the cationic complexes (α -TZnPcQ (**47b**), β -TZnPcQ (**48b**) and β -OZnPcQ (**49b**)) were not as high as observed for the MPcS₄ complexes (**33**, **35** and **36**) which may be because their aggregates do not break easily as discussed in Chapter 4. The K_b values increased in the order **47b** < **48b** < **49b**. This suggests that the peripherally substituted derivatives **48b** and **49b** bind more strongly to BSA than the non-peripherally substituted derivative, **47b**, probably due to steric hindrance that the substituents of **47b** may be experiencing in binding to BSA. It is also evident that the K_b value for **49b** is the highest in the set, which may be due to the presence of eight substituents on the periphery that are available for binding compared to four in the other derivatives.

The K_b values for the monomeric MOCPCs, Table 6.1, are lower than values obtained for the MPcS₄ complexes, suggesting that MOCPCs bind to BSA less efficiently when compared to the tetrasulfonated (MPcS₄) derivatives. The K_b values for the SiOCPC (**43**) and GeOCPC (**44**) complexes are lower than those of ZnOCPC (**41**) and AlOCPC (**42**) complexes which may be due to the steric hindrance of axial ligands which does not allow the full exposure of the MPcs to the protein environment. Axial ligands are also present in SiPcS₄ and GePcS₄ but the effect of aggregation may surpass steric hindrance in these complexes.

The binding stoichiometry in these experiments is ~ 1 suggesting a 1:1 stoichiometry or a single binding site for the MPcs which is characteristic for MPc-BSA interactions in aqueous medium [209].

The inset in Figure 6.1 shows the Stern-Volmer plot which indicates that within the investigated range of concentrations, S-V equation (Equation 1.17, now Equation 6.2) is

$$\frac{F_0}{F} = 1 + K_{SV} [\text{MOCPC}] \quad (6.2)$$

obeyed. The K_{SV}^{BSA} values were determined from the slopes of the S-V plots, e.g. Figure 6.1 (inset) for **48b**. The K_{SV}^{BSA} values determined are static quenching constants since there is a formation of a ground state complex between the MPcs and BSA as shown from their ground state absorption spectra in Figure 6.3 for GeOCPc (**44**) with the slight shift in the absorption maxima and decrease in absorption. Table 6.1 shows that AlPcS₄ has the highest K_{SV} value amongst the MPcS₄ complexes suggesting that the BSA fluorescence quenching is most effective in this complex probably due to its monomeric

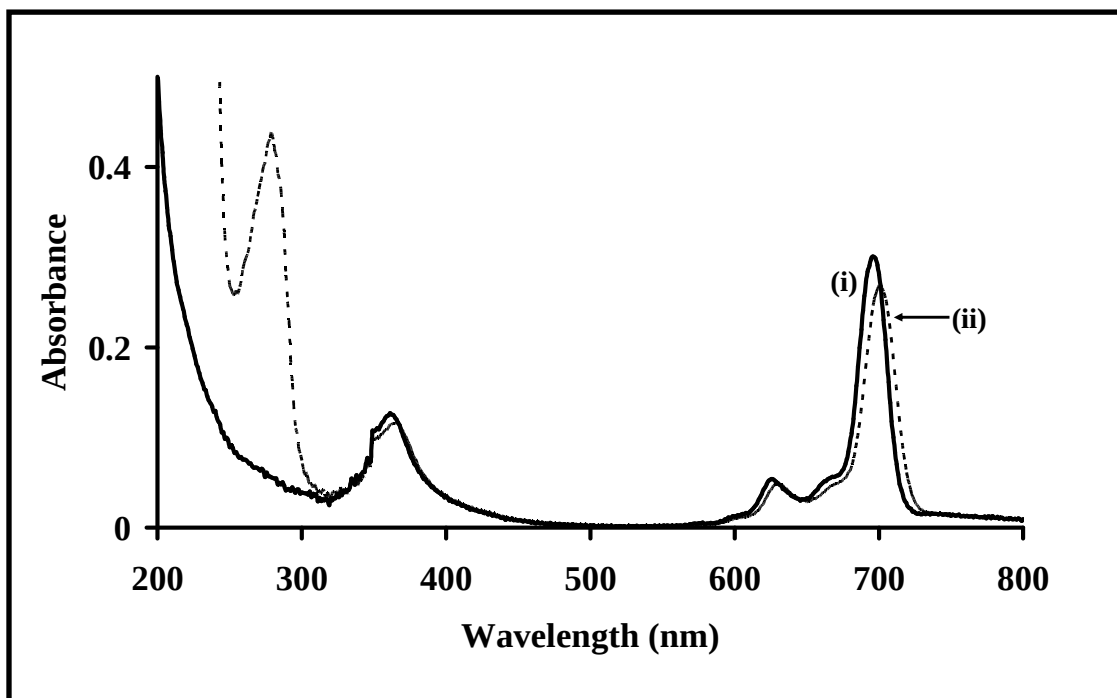


Figure 6.3: Absorption spectra of GeOCPc (**44**) alone (i) and in the presence of BSA (ii) showing a shift on addition of BSA in PBS pH 7.4 ($[44] = 4.1 \times 10^{-6}$ M, $[BSA] = 3 \times 10^{-5}$ M).

state; in that all the absorbed molecules also fluoresce and are able to participate in the quenching, unlike the aggregated ones where not all the absorbed molecules fluoresce.

There was some agreement between K_b and K_{SV} values with the cationic complexes **47b**, **48b** and **49b**; in that the one with the highest K_b also exhibited the highest K_{SV} (all molecules here are aggregated, so they are expected to behave in the same manner). The K_{SV}^{BSA} value was highest in **49b** suggesting that the BSA fluorescence quenching is most effective in this complex in this particular set. K_{SV}^{BSA} values for SiOCPC (**43**) and GeOCPC (**44**) are smaller than those of ZnOCPC (**41**) and AlOCPC (**42**) complexes, suggesting that the BSA fluorescence quenching with **43** and **44** may not be as effective as that of **41** and **42** due to steric hindrance that may result from the axial ligands of the former complexes. **42** however also has an axial ligand, but it shows higher K_{SV} value compared to **41**.

Using Equation 1.18, now Equation 6.3 and the approximate values of fluorescence lifetime of BSA (10ns) [256], the bimolecular quenching constants (k_q) were determined for the individual MPcs.

$$K_{SV} = k_Q \cdot \tau_F \quad (6.3)$$

As shown in Table 6.1, the k_q values are higher (being in the order of $10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) than the proposed value for dynamic quenching ($10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [246] indicating that quenching mechanism in this case is static as already observed from the ground state spectra of the MPcs in the presence of BSA (e.g. Figure 6.3).

6.1.2 Photophysical and photochemical properties of MPcs in the presence of BSA

These studies were only done for MOCPcs since they are monomeric in PBS pH 7.4.

Fluorescence spectra of the MOCPcs (Figure 6.4 for AlOCPC (**42**)) indicate that the

fluorescence of these species are slightly quenched in the presence of BSA. This resulted in slight decreases in the Φ_F values of all the MOCPCs in the presence of BSA, Table 6.2. Such quenching of fluorescence have been observed before for non-aggregated sulfonated MPcs in the presence of BSA [259] and aluminium sulfonated phthalocyanine (AlPcS_I) in the presence of human serum albumin [325]. This suggests that the interaction with BSA at the singlet excited state involves some dissipation of the electronic energy of the excited singlet state, thereby lowering fluorescence.

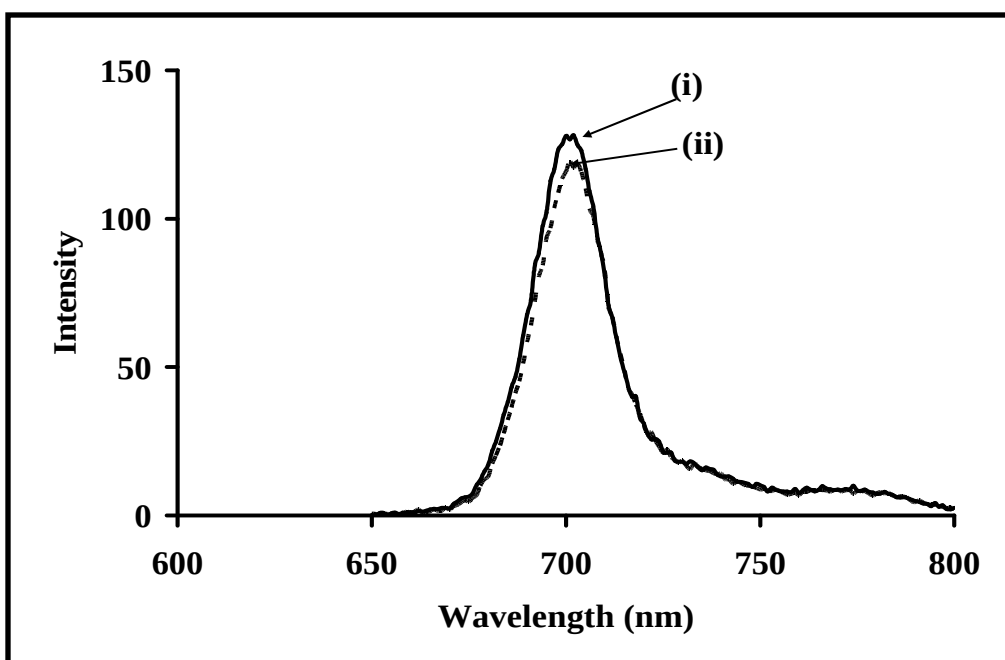


Figure 6.4: Fluorescence emission spectra of AlOCPc (42) in the absence (i) and presence (ii) of BSA in PBS pH 7.4 ([42] = 1.1×10^{-6} M (ii) [BSA] = 3×10^{-5} M) (λ_{exc} = 640nm).

The Φ_T values in the presence of BSA in Table 6.2 suggest that the BSA binding slightly reduces the Φ_T of the species, though not significantly, except for SiOCPc (43) where there was a slight increase. The triplet decay curves, Figure 6.5 of the MOCPCs obtained in the presence and absence of BSA are similar and obeyed second order kinetics.

Table 6.2: Spectral and photophysicochemical parameters for MOCPC complexes in the presence of BSA in PBS pH 7.4. BSA: MOCPC (10:1)

Complex	λ_Q (nm)	λ_F (nm)	Φ_F	Φ_T	Φ_Δ	$^a S_\Delta$	Φ_P ($\times 10^5$)	τ_T (μs)
ZnOCPc (41)	693	702	0.23	0.50	0.32	0.64	2.65	160
ZnOCPc + BSA	695	709	0.21	0.43	0.40	0.93	7.01	280
AlOCPc (42)	689	694	0.27	0.32	0.12	0.38	0.26	450
AlOCPc + BSA	688	706	0.25	0.28	0.29	1.04	3.01	580
SiOCPc (43)	691	703	0.24	0.34	0.22	0.65	86.3	90
SiOCPc + BSA	689	705	0.21	0.36	0.26	0.72	93.2	110
GeOCPc (44)	697	704	0.13	0.62	0.31	0.51	2.12	240
GeOCPc + BSA	700	708	0.12	0.58	0.40	0.69	5.21	300

$$^a S_\Delta = \Phi_\Delta / \Phi_T$$

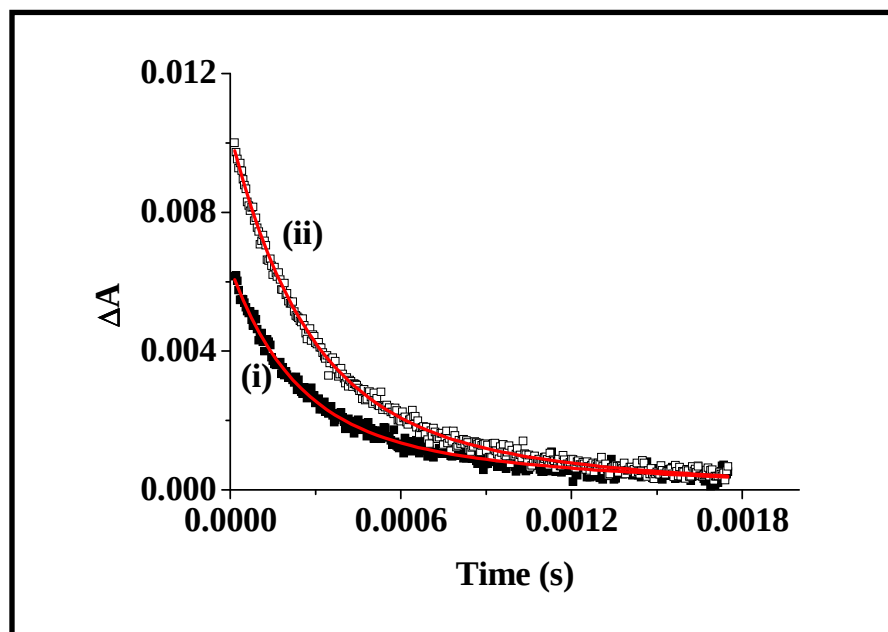
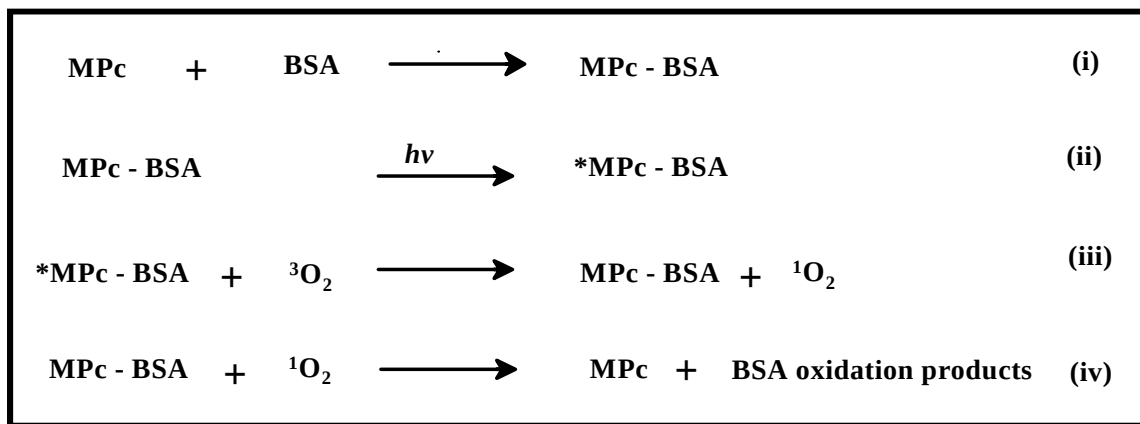


Figure 6.5: Triplet decay curve for ZnOCPc (41) (i) and (ii) 41 in the presence of BSA in PBS pH 7.4.

Triplet state lifetimes (τ_T) of the MOCPCs in the presence of BSA were observed to be longer than those of the MOCPC complexes in the absence of BSA. This observation could be due to the fact that there is a reduction in the exposure of the phthalocyanine to the aqueous medium because of the presence of the serum proteins.

Φ_Δ values were found to be higher in the presence of BSA, corresponding to higher τ_T . The efficiency of singlet oxygen generation should depend on the triplet state quantum yield and lifetime and the efficiency of energy transfer from the excited triplet state. The fact that higher Φ_Δ values were observed in the presence of BSA may be due to an efficient quenching of the triplet state by oxygen in the presence of BSA, as a result of the increased lifetime of the triplet state of the MOCPCs in the presence of BSA, Table 6.2.

Photodegradation quantum yields (Φ_p) of the MPc complexes increased in the presence of BSA, and this can be attributed to the fact that there may be formation of active oxidative albumin species, Scheme 6.1 (step iv) and the fact that Φ_Δ values increase in the presence of BSA and these oxidative species can additionally react with



Scheme 6.1: Photosensitized oxidation of BSA in the presence of MPc

the MOCPCs and increase the photodegradation of the MPc complexes in the presence of BSA. Figure 6.6 shows the photodegradation spectra of **42** in the presence of BSA with an increase in the 280 nm and 350 nm (UV) region, buttressing the fact that there are photo-oxidation products of BSA formed.

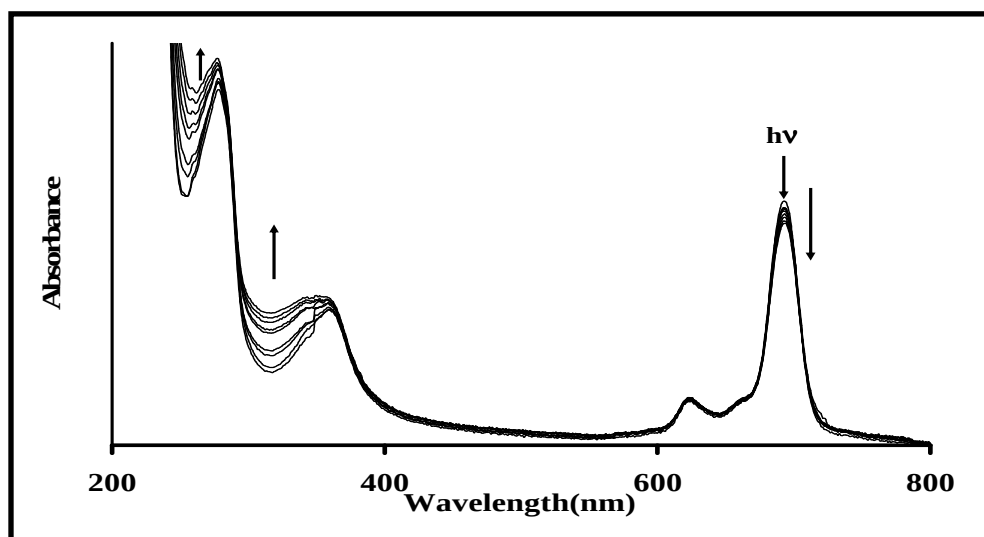


Figure 6.6: Photolysis of AlOCPC (42) in the presence of BSA showing the spectral changes observed at irradiation time interval of 5 mins in PBS pH 7.4. Light intensity = $3.12 \times 10^{16} \text{ photons s}^{-1} \text{ cm}^{-1}$ ($[42] = 5.5 \times 10^{-6} \text{ M}$ and $\text{BSA} = 3 \times 10^{-5} \text{ M}$).

6.2 Interaction between BSA and QDs

The smaller QDs that absorb between 500 and 550 nm (TGA1, MPA1 and CYS1) (Figure 6.7); a position at which good spectral overlap can occur with the emission spectra of BSA, were employed in the study of the interaction of QDs with BSA in PBS 7.4. Studying the interaction of CdTe QDs with BSA in aqueous medium, will give a representative model of the effect of CdTe QDs on cells in *in vivo* studies. A crosslinker (ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, EDC) was used between BSA and CdTe QDs as a coupling agent for the coordination of CdTe QDs (through

carboxylic acid groups) to the amino group of BSA, to give an understanding of the capabilities of biomolecules–QDs coupling (these were termed ‘linked’ complexes in this thesis). A control experiment without EDC was also studied (‘mixed’ complexes).

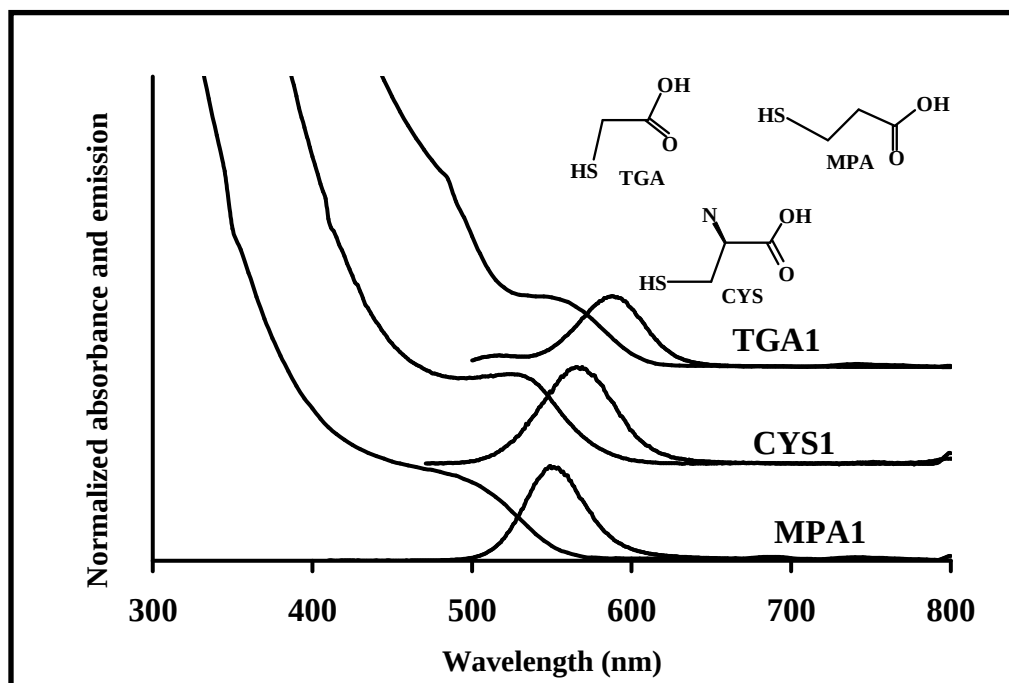
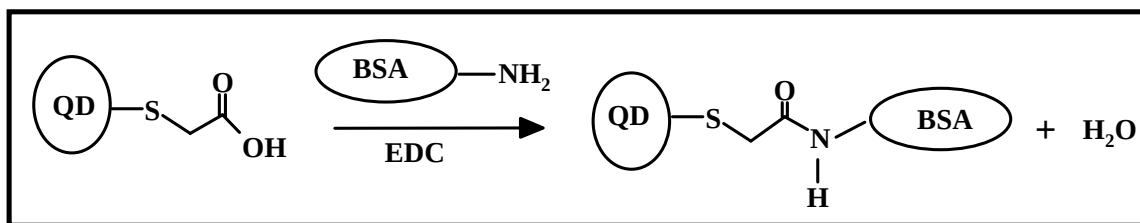


Figure 6.7: Absorption and emission spectra of CYS1, MPA1 and TGA1 in PBS pH 7.4. Inset shows molecular structures of carboxylic thiol-ligands used in capping the QDs.

6.2.1 Conjugation of CdTe QDs to BSA

The thiol groups (thioglycolic acid, mercaptopropionic acid and L-cysteine) located on the surface of CdTe QDs were linked to BSA by coordination of the carboxylic group of the thiol with the amine group on BSA. EDC was used to activate the carboxylic acid group of the thiol capping the QDs to facilitate linkage with the amine group of BSA, Scheme 6.2 for the formation of an amide bond. The intensity of QDs emission peaks (excitation 280 nm) during the EDC activated coupling of CdTe QDs to BSA was



Scheme 6.2: BSA and QD linking process.

monitored at fixed time intervals of 10 minutes each. The intensity of emission peaks of the QDs increased with time with all the QDs and then slowed or decreased slightly after 120 minutes, Figure 6.8. Thus all the data reported in this work was for QDs-BSA conjugates with a reaction time of 120 minutes. This time is a compromise between optimum formation of the conjugate and length of synthesis.

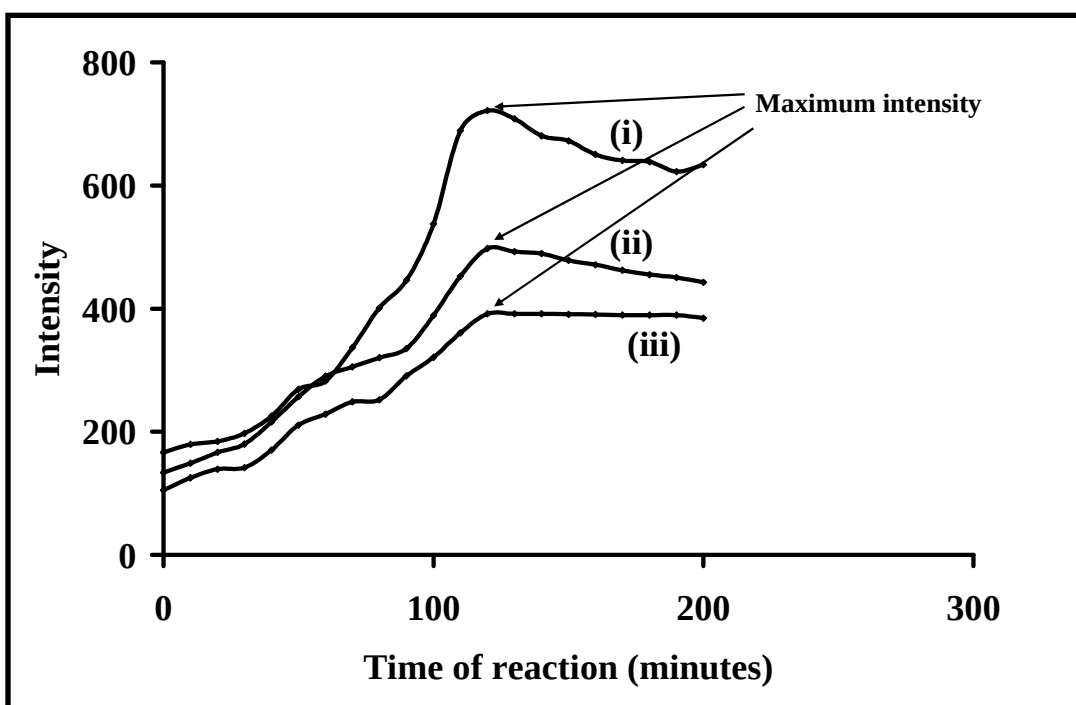


Figure 6.8: Effect of time on conjugate formation: (i) TGA1, (ii) MPA1 and (iii) CYS1 in the presence of BSA in PBS pH 7.4, $\lambda_{\text{exc}} = 280\text{nm}$.

The increase in emission intensity of QDs observed in Figure 6.8 may be due to the fact that the interaction of QDs with BSA passivates the surface of QDs and inhibits the radiationless recombination at the surface vacancies [370]. This kind of interaction is very useful in enhancing fluorescence intensity.

To establish the assumption of the formation of a link (amide bond), between the QDs and BSA, IR spectroscopy was carried out. In the linked QD-BSA form, there was an indication of an amide bond with the band at 3400 cm^{-1} (ν_{NH} (CONH)), while the mixed form showed a broad band around 3300 cm^{-1} . Characteristic amide band was also observed at 1654 cm^{-1} in the linked, but this was not observed in the mixed where there is no amide bond.

6.2.2 Spectral changes in the interaction between CdTe QDs and BSA

Figure 6.9 compares the absorption spectra of the BSA-QDs conjugates (linked or mixed) with that of QDs or BSA alone. There was a small decrease in the intensity of the QDs absorption on linking to BSA which was not observed in the mixed. In the emission spectra, a shift occurred in the wavelength of the QDs both in the mixture of CdTe QDs with BSA (Figure 6.10, curves iii) and CdTe QDs linked to BSA (Figure 6.10, curves iv) with excitation at 280 or 450 nm (inset in Figure 6.10a). Excitation at 280 nm, excites both BSA and QDs, however, this does not affect BSA emission since QDs emission is observed at much longer wavelengths. Figure 6.10 shows that the shift in emission of QDs in the presence of BSA was to shorter wavelength while for the linked; there was a shift to longer wavelength. The blue shift in the emission maximum of QDs has been documented before in the interaction of QDs with silica cappings on its surface [371] and

was explained to be due to the corrosion of the QDs during deposition on its surface. The blue shift in spectra was also reported when denatured BSA was used to modify the

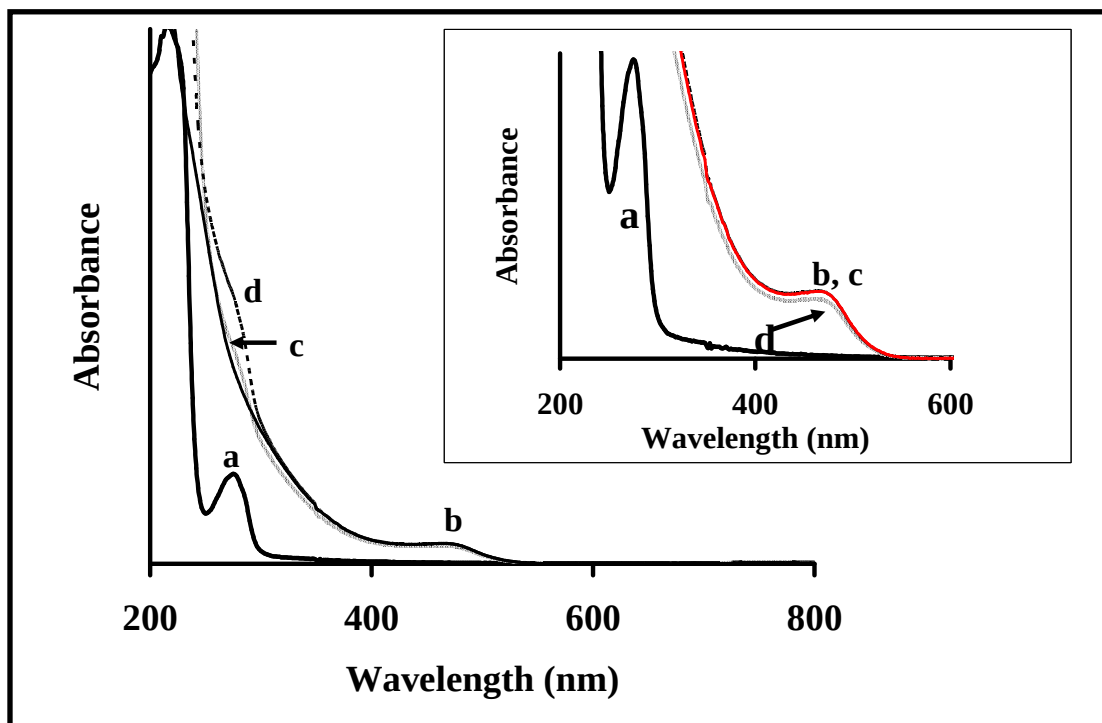
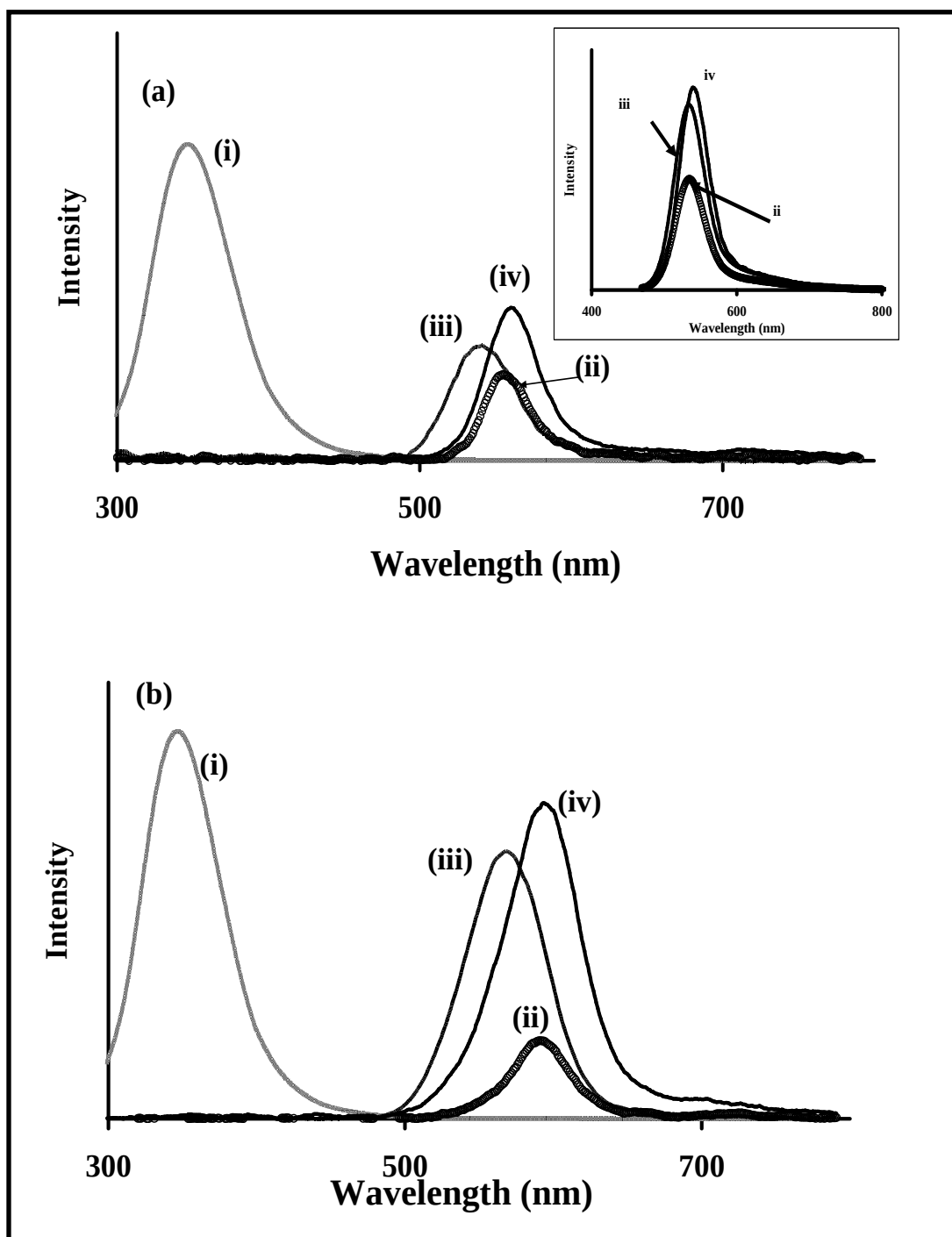


Figure 6.9: UV-Vis absorption spectra of (a) BSA alone, (b) MPA1 alone, (c) MPA1 and BSA mixed and (d) MPA1 and BSA (linked) in PBS pH 7.4. ([MPA1] = 3×10^{-7} M, [BSA] = 3×10^{-6} M). Inset shows absorbance spectra in the 500 nm region enlarged.

surface of CdTe QDs [263] and was explained in terms of possible formation of capping of CdTe-BSA which leads to decrease in the CdTe inner core. The blue shift was also observed on excitation at 450 nm, Figure 6.10a (inset). On the other hand, the red shift observed for the linked may be a result of amide bond formation as against corrosion (removal of QDs surface ligands) in the mixture of QDs and BSA. An increase in the emission intensity of QDs in the mixture (or linked) compared to equimolar concentration

of QDs alone was observed in Figure 6.10 on excitation at 280 nm (where both BSA and QDs absorb). However, this increase was also observed on excitation of the mixture (or linked complex) at the QDs wavelength only, i.e. at 450 nm excitation, Figure 6.10a (inset), suggesting that the increase is not due to energy transfer from BSA to QDs. The



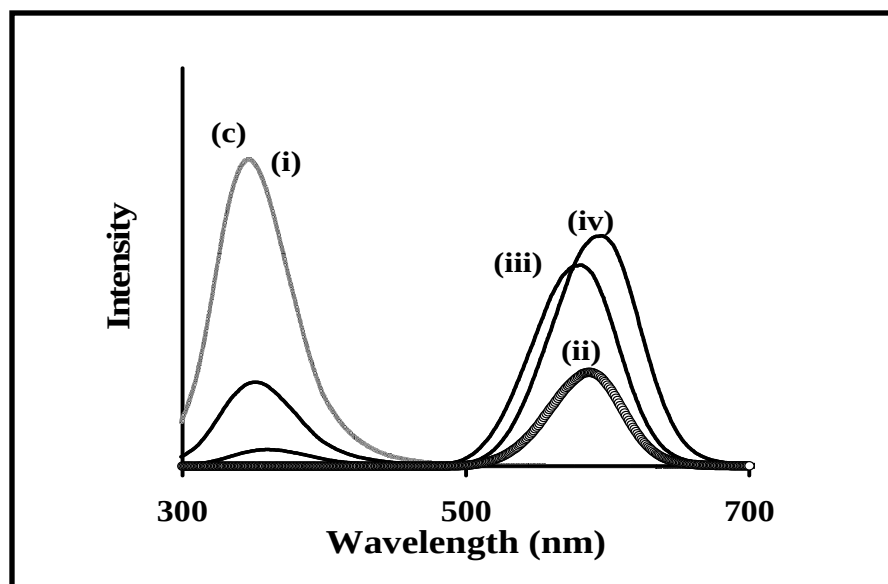


Figure 6.10: Fluorescence spectra of (i) BSA, (ii) QD, (iii) BSA + QD and (iv) BSA + QD + EDC in PBS pH 7.4. $\lambda_{\text{exc}} = 280 \text{ nm}$. $[\text{QD}] = 3 \times 10^{-7} \text{ M}$ $[\text{BSA}] = 3 \times 10^{-6} \text{ M}$ kept constant for all experiments. (a) MPA1, (b) TGA1 and (c) CYS1. Inset in (a) shows (ii), (iii), and (iv) MPA1, $\lambda_{\text{exc}} = 450 \text{ nm}$.

enhancement in the photoluminescence of QDs in the presence of BSA has also been reported before [372] and used in the quantification of BSA. The concentration of BSA-QDs conjugate was kept the same as that of BSA alone or BSA in a mixture. The increase in intensity of the QDs emission in the presence of BSA could be due to passivation of the surface of QDs by BSA which increases fluorescence intensity as discussed above.

There was a complete collapse of the emission intensity of BSA in the presence of QDs on exciting at 280 nm (hence exciting both BSA and QDs, for MPA1 and TGA1 and a large reduction in intensity for CYS1, Figure 6.10c. The decrease (or complete disappearance) in BSA emission in the presence of QDs could be due to radiationless quenching of BSA fluorescence by QDs.

6.2.3 Quenching of BSA fluorescence by QDs

An efficient overlap between the absorption spectrum of the QDs with the emission spectra of BSA, (Figure 6.11), was observed. This would normally be associated with a good energy transfer between the donor (BSA) and the acceptor (QDs). However as stated above, there was no evidence that the increase in intensity of the emission of QDs in the presence of BSA is due to energy transfer.

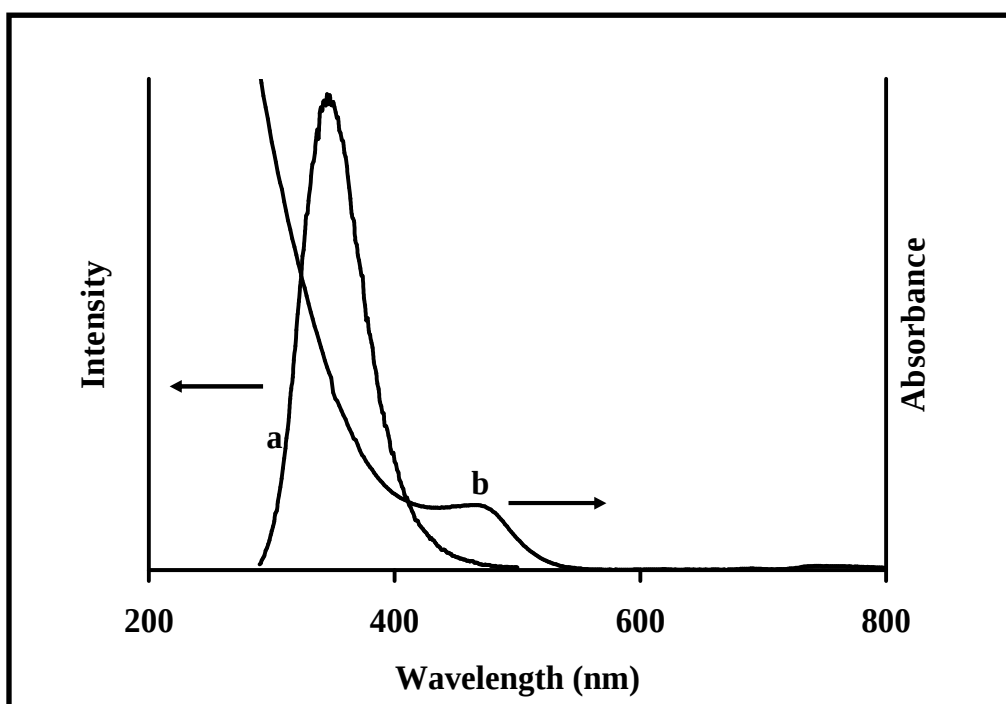


Figure 6.11: Spectral overlap of (a) BSA fluorescence emission with (b) MPA1 absorption in PBS pH 7.4.

Fluorescence quantum yield (Φ_F) values for the CdTe QDs alone are listed in Table 6.3 (discussed in Chapter 4, Table 4.1). Φ_F values of the QDs and BSA ($\Phi_{F(QD)}^{Mix}$ and $\Phi_{F(BSA)}^{Mix}$) in the mixture and the linked form ($\Phi_{F(QD)}^{Linked}$ and $\Phi_{F(BSA)}^{Linked}$) were calculated using the determined fluorescence quantum yield values of QDs and BSA. This was done by using a modified form of Equation 1.14 (also Equation 4.1) as shown by Equations 6.4a and b:

$$\Phi_{F(QD)}^{Mix} = \Phi_{F(QD)} \cdot \frac{F_{QD-BSA}}{F_{QD}} \quad (6.4a)$$

where $\Phi_{F(QD)}$ is the fluorescence quantum yield of the QDs alone, and was used as standard, F_{QD-BSA} is the fluorescence intensity of the QD in the mixture and F_{QD} is the fluorescence intensity of the QD alone. Excitations were done at 450 nm for equation 6.4a.

$$\Phi_{F(BSA)}^{Mix} = \Phi_{F(BSA)} \cdot \frac{F_{BSA-QD}}{F_{BSA}} \quad (6.4b)$$

where $\Phi_{F(BSA)}$ is the fluorescence quantum yield of the BSA alone, and was used as standard, F_{BSA-QD} is the fluorescence intensity of the BSA in the mixture and F_{BSA} is the fluorescence intensity of the BSA alone. Excitations were done at 280 nm for equation 6.4b.

The $\Phi_{F(BSA)}^{Linked}$ and $\Phi_{F(QD)}^{Linked}$ were determined in the same manner except the mixed forms, ($\Phi_{F(BSA)}^{Mix}$ and $\Phi_{F(QD)}^{Mix}$) were replaced by the linked forms ($\Phi_{F(BSA)}^{Linked}$ and $\Phi_{F(QD)}^{Linked}$) in Equations 6.4.

Excitation at 280 nm, excites both BSA and QDs, however, BSA and QDs emit at different wavelengths. Hence, the Φ_F determined in the mixture and linked for BSA are not affected by QDs emission. Table 6.3 shows that there is a decrease in $\Phi_{F(BSA)}^{Mix}$ and $\Phi_{F(BSA)}^{Linked}$ for all the conjugates compared to $\Phi_{F(BSA)}$ of BSA alone (0.118 [256]), indicating the interaction occurring between the QDs and BSA results in quenching of the fluorescence of the latter. There was an increase in $\Phi_{F(QD)}^{Mix}$ and $\Phi_{F(QD)}^{Linked}$ (Table 6.3) compared to $\Phi_{F(QD)}$ of the respective QDs. The error in Φ_F values shown in Table 6.3 is $\pm$

10%.

Table 6.3: Fluorescence quantum yields of QDs^a in the presence and absence of BSA, PBS pH 7.4.

QD	^b $\Phi_{F(QD)}$	$\Phi_{F(QD)}^{Mix}$	$\Phi_{F(QD)}^{Linked}$	$\Phi_{F(BSA)}^{Mix}$	$\Phi_{F(BSA)}^{Linked}$
MPA1	0.19	0.20	0.22	0.009	0.0015
CYS1	0.41	0.58	0.64	0.032	0.0064
TGA1	0.30	0.69	0.82	0.007	0.0012

^a legend:

$\Phi_{F(QD)}$ = Fluorescence quantum yield of QDs alone; $\Phi_{F(QD)}^{Mix}$ = fluorescence quantum yield of QD in the mixture with BSA, $\lambda_{exc} = 450 \text{ nm}$; $\Phi_{F(QD)}^{Linked}$ = fluorescence quantum yield of QD when linked with BSA, $\lambda_{exc} = 450 \text{ nm}$; $\Phi_{F(BSA)}^{Mix}$ = fluorescence quantum yield of BSA in the mixture with QD ($\lambda_{exc} = 280 \text{ nm}$); $\Phi_{F(BSA)}^{Linked}$ = fluorescence quantum yield of BSA when linked with QD ($\lambda_{exc} = 280 \text{ nm}$)

^b $\Phi_{F(BSA)} = 0.118$ [256]

Figure 6.12 shows the fluorescence emission spectra of BSA ($3.0 \times 10^{-6} \text{ M}$) in the presence of varying concentrations (0 to $9.7 \times 10^{-7} \text{ M}$) of MPA1. BSA's fluorescence was found to decrease progressively with increasing concentration of QDs. This was also observed for all the other QDs. A positive deviation (with a concave towards the y axis Figure 6.12 inset) from the Stern-Volmer's relationship was observed from the plot of $\frac{F_0}{F}$ against [QD] for the quenching of BSA's fluorescence with QDs, within investigated range of concentration, suggesting that static and dynamic quenching may be occurring together. In order to accommodate both types of quenching, a modified Stern-Volmer's equation, Equation 1.22 now Equation 6.5 [245,373], which has been derived before is

introduced. The deviation allows for an additional term to be introduced into the S-V's equation.

$$\frac{F_0}{F} = (1 + K_{SV}[QD])(1 + K_a[QD]) \quad (6.5)$$

The first term is the original S-V's equation, Equation 6.2, which accounts for the dynamic quenching, the second term accounts for the upward curvature (static quenching). The quenching constant for the second term (K_a) is termed association constant. To solve for K_a , apparent values of K_{SV} (K_{app}) were calculated at each quencher

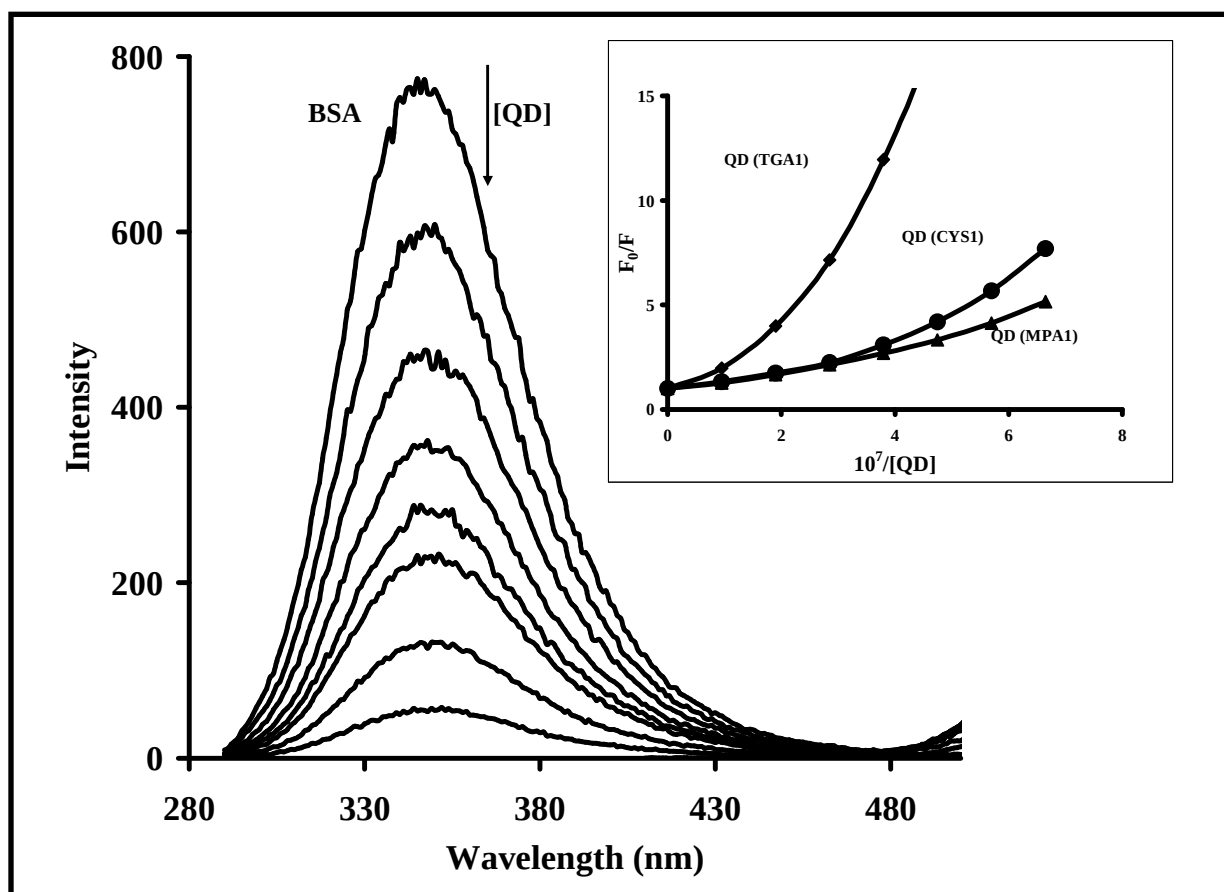


Figure 6.12: Change in fluorescence intensity of BSA with MPA1 in PBS pH 7.4. $[MPA1] = 0$ to 9.7×10^{-7} , $[BSA] = 3 \times 10^{-6}$ M. Inset shows positive deviation from expected Stern –Volmer's plot for BSA quenching by increasing $[QD]$.

(QD) concentration using Equation 6.2, plotted against [QD] and extrapolated to [QD] = 0 to obtain K_{SV} . Plotting $F_0/F(1+K_{SV}[QD])$ against [QD] (figure not shown), gave K_a , according to Equation 6.5.

K_{SV} and K_a values were quite high as listed in Table 6.4 with TGA1 having the highest values; this may explain why the rate of quenching is quite high in these samples. K_{SV} and K_a decreased in the order TGA1 > CYS1 > MPA1. MPA1 QDs are small in size hence resulting in low values of the constants. The lack of shift in the absorption spectra

Table 6.4: Quenching parameters for BSA-QD interactions in PBS pH 7.4.

QD	K_{SV} ($\times 10^6 M^{-1}$)	K_a ($\times 10^6 M^{-1}$)	K_S ($\times 10^6 M^{-1}$)
MPA1	1.20	7.22	2.11
CYS1	1.79	12.2	3.55
TGA1	2.84	27.7	8.41

K_{SV} = Stern-Volmer quenching constant; K_a = association constant; K_S = apparent quenching constant.

of the QDs in the presence of BSA (Figure 6.9) suggests that there is no significant association between the QDs and BSA in the ground state, and that the static component of the interaction of BSA with the QDs is from close proximity of the QD and BSA at the moment of excitation. This type of apparent static quenching constant (K_S) value is usually determined by plotting $\ln (F_0/F (1+K_{SV} [QD]))$ against [QD] which is a modified S-V's plot [245,373], Equation 1.24 shown here as Equation 6.6.

$$\frac{F_0}{F(1 + K_{sv}[Q])} = e^{-K_s[Q]} \quad (6.6)$$

K_s values from the plot are listed in Table 6.4 and they represent the apparent quenching constant due to interaction of the fluorophore (BSA) and quencher (QD) at the excited state.

6.3 Conclusions

Increased efficiency of singlet oxygen generation via energy transfer from the excited triplet state of MPcs in the presence of BSA coupled with long triplet state lifetimes and large binding constants observed, suggest that MPc complexes studied strongly interact with BSA; hence they can be easily transported in the blood.

Enhanced emission was also observed in QDs when in a mixture or when linked with BSA due to radiationless recombination at the surface vacancies. Fluorescence studies reveal positive deviation behaviour from Stern-Volmer relationship, suggesting the occurrence of static and dynamic mechanisms of quenching together which was accounted for by the modified Stern-Volmer relationship.

CHAPTER 7

GENERAL CONCLUSIONS AND FUTURE PERSPECTIVE

7.1 General Conclusions

The synthesis and spectroscopic characterization of water-soluble (zinc, aluminium, silicon and germanium) MPc complexes substituted with sulfonated and carboxy groups are presented. Reasonable yields with satisfactory spectroscopic characterization confirming the purity of the complexes were obtained. The complexes have intense absorption in the visible / near-IR region though most of the sulfonated and tetracarboxy (MPcS₄ and MTCPC) complexes were highly aggregated in aqueous solution with dimerization constants estimated. The addition of cremophore EL hindered aggregation, however, it had no effect on the spectra of silicon and germanium tetracarboxy MPcs. The octacarboxy MPcs and the aluminium complexes of the sulfonated and tetracarboxy MPcs exhibited monomeric behaviour in aqueous medium. Most of the complexes exhibited monomeric behaviour in organic solvent (DMSO). Aryloxy substituted SnPcs and aminoalkanethio-substituted ZnPcs and their quaternized derivatives are also presented in this work with satisfactory spectroscopic characterization.

A comprehensive investigation of the photochemical and photophysical properties of the synthesized MPc complexes is also presented and was shown to be dependent on the central metal and solvent employed. The water-soluble aggregated complexes showed little photoactivity, however, the addition of cremophore EL resulted in increased triplet quantum yields (Φ_T), lifetimes (τ_T) and singlet oxygen quantum yields (Φ_Δ) compared with aqueous medium, suggesting an improved photoactivity of these complexes in the presence of CEL. Photoactivity was shown to be highest in DMSO, emphasizing the importance of solvent consideration on the photophysicochemical properties of MPc complexes. It was also shown that aggregated MPcs and those with large central metals

like Sn exhibited differences in the nuclear configuration of their ground and excited states leading in some cases to a loss of symmetry. Photoreduction of AlPc and the SnPcs was observed during photolysis in the absence of oxygen due to ring reduction.

Fluorescence quenching of the carboxy-substituted MPc complexes by BQ was presented and found to be diffusion-controlled. This was exploited to estimate the fluorescence lifetimes of the carboxy complexes which allowed for detailed photophysical studies of the complexes. The obtained fluorescence lifetime values were comparable to lifetimes obtained from using known software.

Behaviour of the octacarboxy MPcs as dye-sensitized solar cells on the surface of ZnO was also presented. The MOCPC complexes showed satisfactory photoelectrochemical properties. Facile electron injection from the excited dye molecules to the ZnO conduction band was demonstrated by the different MOCPCs. ZnOCPC exhibited the highest incident photon-to-current conversion (IPCE) efficiency in the set and an absorbed photon-to-current conversion (APCE) efficiency of 60%. This is the highest obtained IPCE so far with phthalocyanine-type sensitizers on nanocrystalline ZnO films.

Interaction of water-soluble MPcs with bovine serum albumin was also investigated. Spectral changes at the ground state were observed which suggested high affinity of BSA for the complexes. It was shown from the interpretation of the results that BSA binds efficiently to these MPcs in a 1:1 stoichiometry with the probability of binding varying with aggregation. It was shown that the efficiency of singlet oxygen generation of the MOCPCs increased in the presence of BSA. This was coupled with long triplet state lifetimes suggesting that the MPc complexes studied strongly interact with BSA; which can lead to an ease of transportation of these complexes in the blood.

The interaction of QDs with BSA also led to enhanced emission intensity of the QDs either as a mixture or as linked macromolecules due to radiationless recombination at the surface vacancies of the QDs.

It was also demonstrated that the interaction of nanoparticles with MPcs led to improved photophysical and photochemical properties reinforcing the idea of excellent photodynamic activity of MPc-MNH systems for PDT and local HT. Rules of photophysics were contradicted in that the MPcs in the presence of nanoparticles exhibited high triplet state quantum yields with corresponding long lifetimes. Increased photostability of the MPcs was also attained in the presence of nanoparticles.

Photoinduced energy transfer was evident from highly photoluminescence QDs to MPcs, leading to quenching of the excited state of the QDs coupled with emergence of emission for the MPcs. It was also shown that a non - Förster type energy transfer behaviour can occur in some QD-MPc donor-acceptor systems due to the involvement of the QD surface states in the energy transfer process.

It was shown that these interactions between CdTe QDs and MPc complexes are highly dependent on the substituents of the MPcs, since ion-pair complexes resulting in aggregates were formed with cationic MPcs, whereas interaction with anionic MPc complexes led to FRET.

It was shown that singlet oxygen can be produced via excitation of the QD via a FRET mechanism. Lower values of singlet oxygen via FRET mechanism were however obtained, but are speculated to produce a steady level of singlet oxygen due to the fact that QDs are photostable and can be repetitively exposed for a prolonged time to UV-vis irradiation.

It was shown that fluorescent-magnetic nanocomposites (MOCPC-QD-MNS) of different varieties can be developed and that these composites can exhibit excellent photophysical and photochemical properties which can be exploited for combined therapy (PDT and HT plus imaging) since their cell destructive abilities are enhanced.

The knowledge of these properties will allow us to design new biocompatible materials, with maximum biological activity for intravenous administration and cancer treatment.

7.2 Future Perspectives

Monomeric water-soluble MPcs can be synthesized to produce complexes with excellent photoactivity that can penetrate into cells easily without aggregation. The aggregated MPcs may also be applied in cases of molecular hyperthermia therapy or brachytherapy. Unsymmetrical MPcs with just one substituent that can attach to these biomolecules or nanoparticles for specificity will be excellent in these applications. Molecules with different chain lengths can be employed in monitoring FRET and potential applications of MPc-QDs by the tuning of linkages can also be looked into.

It is worth saying that these are preliminary studies considering the toxicity of the components of the QDs in this work, though many researchers are proving its biocompatibility. Toxicity is of major concern when advocating nanoparticles for any biomedical use therefore further work can look into the use of non-toxic QDs that can be tuned to emit into the near-IR region as FRET donors, and similar approaches employed in this work can be used for the development of fluorescent-magnetic composites with low toxicity that can serve as all in one diagnostic, surgery and drug delivery tools for the treatment of cancer and some other diseases.

REFERENCES

1. J.Z. Zhang, *Acc. Chem. Res.*, **30** (1997) 423.
2. A.P. Alivisatos, *Science*, **271** (1996) 933.
3. M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, *Science*, **281** (1998) 2013.
4. W. C.W. Chan, S. Nie, *Science*, **281** (1998) 2016.
5. A.L. Efros, *Sov. Phys. Semicond.*, **16** (1982) 772.
6. A.I. Ekimov, A.A. Onushchenko, *Sov. Phys. Semicond.*, **16** (1982) 775.
7. A.P. Alivisatos, *J. Phys.Chem.*, **100** (1996) 13226.
8. D.J. Norris, *Phys. Rev. B. Condens. matter*, **53** (1996) 16338.
9. S. J.Rosenthal, *Nat.Biotechnol.*, **19** (2001) 621.
10. A.J. Sutherland, *Curr. Opin. Solid State Mater. Sci.*, **6** (2002) 365.
11. X.G. G. Peng, *Adv. Mater.*, **15** (2003) 459.
12. R. E. Bailey, S.M. Nie, *J. Am. Chem. Soc.*, **125** (2003) 7100.
13. S. Kim, B. Fisher, H.J. Eisler, M. Bawendi, *J. Am.Chem. Soc.*, **125** (2003) 11466.
14. V.I. Klimov, *Los Alamos Science*, **28** (2003) 214.
15. W. Schroter, In *Handbook of semiconductor technology, Electronic structure and properties of semiconductors*, Wiley VCH, Weinheim, (2000).
16. L. E. Brus, A. I. Efros, T. J. Itoh, *Luminesc.*, **70** (1982) R7.
17. C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem.Soc.*, **115** (1993) 8706.
18. L.S. Li, J. Hu, W. Yang, A. P. Alivisatos, *Nanolett.*, **1** (2001) 349.

19. M. Kuno, J.K. Lee, B.O. Dabbousi, F.V. Mikulec, M.G. Bawendi, *J. Chem. Phys.*, **106** (1997) 9869.
20. C.J. Murphy, J.L. Coffey, *Appl. Spectrosc.*, **56** (2002) 16A.
21. A. Henglein, *Chem. Rev.*, **89** (1989) 1861.
22. Y. Wang, N. J. Herron, *Phys. Chem.*, **95** (1991) 525.
23. S. Santra, K.M. Wang, R. Tapecc, W.H. Tan. *J. Biomed. Opt.*, **6** (2001) 160.
24. A. Eychmüller, *J. Phys. Chem. B.*, **104** (2000) 6514.
25. L. Qu, Z.A. Peng, X. Peng, *Nanolett.*, **1** (2001) 333.
26. D.V. Talapin, A.L. Rogach, A. Kornowski, M. Haase, H. Weller, *Nano Lett.*, **1** (2001) 207.
27. X. Peng, J. Wickham, A. P. Alivisatos, *J. Am. Chem. Soc.*, **120** (1998) 5343.
28. R.M. Raab, G. Stephanopoulos, *Biotechnol Bioeng*, **88** (2004) 121.
29. M. Kuno, D.P. Fromm, S.T. Johnson, A. Gallagher, D.J. Nesbitt, *Phys. Rev. B*, (2003) 67.
30. A. Eychmüller, A. L. Rogach, *Pure Appl. Chem.*, **72** (2000) 179.
31. A.L. Rogach, L. Katsikas, A. Kornowski, D. Su, A. Eychmüller, H. Weller, *Ber. Bunsenges. Phys. Chem.*, **101** (1997) 1668.
32. N.N. Mamedova, N. A. Kotov, A. L. Rogach, J. Studer *Nano Lett.*, **1** (2001) 281.
33. L. R. Becerra, C.B. Murray, R.G. Griffin, M.G. Bawendi, *J.Chem.Phys.*, **100** (1994) 3297.
34. W.C.W. Chan, D.J. Maxwell, X.H. Gao, R.E. Bailey, M.Y. Han, S.M. Nie, *Curr. Opin. Biotechnol.*, **13** (2002) 40.

-
35. D. Gerion, F. Pinaud, S.C. Williams, W.J. Parak, D. Zanchet, S. Weiss, A.P. Alivisatos, *J. Phys. Chem. B*, **105** (2001) 8861.
 36. C.C. Chen, C.P. Yet, H.N. Wang, C.Y. Chao, *Langmuir*, **15** (1999) 6845.
 37. J. Aldana, Y.A. Wang, X. Peng, *J. Am. Chem. Soc.*, **123** (2001) 8844.
 38. H. Mattoussi, J. M. Mauro, E. R. Goldman, G. P. Anderson, V.C. Sundar, F.V. Mikulec, M. G. Bawendi, *J. Am. Chem. Soc.*, **122** (2000) 12142.
 39. W.J. Parak, D. Gerion, D. Zanchet, A.S. Woerz, T. Pellegrino, C. Micheel, S.C. Williams, M. Seitz, R.E. Bruehl, Z. Bryant, C. Bustamante, C. R. Bertozzi, A. P. Alivisatos *Chem. Mater.*, **14** (2002) 2113.
 40. N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmüller, H. Weller, *J. Phys. Chem. B*, **106** (2002) 7177.
 41. U. Schwertmann, R.M. Cornell In *Iron oxides in the laboratory: preparation and characterization*. Weinheim, Cambridge, VCH Publishers, (1991).
 42. C.R. Vestal, Z.J. Zhang, *Int. J. Nanotech.*, **1** (2004) 240.
 43. G.H. Kwei, R.B. von Dreele, A. Williams, J.A. Goldstone, A.C. Lawson II, W.K. Warburton, *J. Mol. Struct.*, **223** (1990) 383.
 44. Y.X. Wang, S.M. Hussain, G.P. Krestin, *Eur. Radiol.*, **11** (2001) 2319.
 45. G.F. Goya, T.S. Berquo, F.C. Fonseca, *J. Appl. Phys.*, **94** (2003) 3520.
 46. P. Tartaj, M.P. Morales, S. Veintemillas-Verdaguer, T. González-Carreño, C.J. Serna, *J. Phys. D: Appl. Phys.* **36** (2003) R182.
 47. A. Jordan, R. Scholz, K. Maier-Hauff, M. Johannsen, P. Wust, J. Nadobny, H. Schirra, H. Schmidt, S. Deger, S. Loening, W. Lanksch, R. Felix, *J. Magn. Magn. Mater.*, **225** (2001) 118.

-
48. S.E. Pratsinis, S.Vemury, *Powder Technol.*, **88** (1996) 267.
 49. S.M. Moghimi, A.C.H. Hunter, J.C. Murray. *Pharm. Rev.* **53** (2001) 283.
 50. A. Rishton, Y. Lu, R.A. Altman, A.C. Marley, C. Bian Hahnes, R. Viswanathan, G. Xiao, W.J. Gallagher, S.S.P. Parkin. *Microelectron Eng.*, **35** (1997) 249.
 51. A. B. Chin, I. I. Yaacob, *J. Mater. Process. Technol.*, **191** (2007) 235.
 52. C. Albornoz, S. E. Jacobo, *J. Magn. Magn. Mater.*, **305** (2006) 12.
 53. J. Wan, X. Chen, Z. Wang, X. Yang, Y. Qian, *J. Cryst. Growth*, **276** (2005) 571.
 54. M. Kimata, D. Nakagawa, M. Hasegawa, *Powder Technol.*, **132** (2003) 112.
 55. G. S. Alvarez, M. Muhammed, A. A. Zagorodni, *Chem. Eng. Sci.*, **61** (2006) 4625.
 56. S. Basak, D.R. Chen, P. Biswas, *Chem. Eng. Sci.*, **62** (2007) 1263.
 57. I. Martinez-Mera, M. E. Espinosa, R. Perez-Hernandez, J. Arenas-Alatorre, *Mater. Lett.*, **61** (2007) 4447.
 58. S.A. Morisson, C. L. Cahill, E. Carpenter, S. Calvin, V. G. Harris, *J. Nanosci. Nanotechnol.*, **5** (2005) 1323.
 59. J. Qiu, R.Yang, M. Li, N. Jiang, *Mater. Res. Bull.*, **40** (2005) 1968.
 60. A.K. Gupta, A.S.G. Curtis, *Biomaterials*, **25** (2004) 3029.
 61. A.K. Gupta, M. Gupta, *Biomaterials*, **26** (2005) 3995.
 62. J.P. Jolivet, C. Chaneac, E. Tronc, *Chem. Commun.*, **5** (2004) 481.
 63. C. Zhang, B. Wangler, B. Morgenstern, H. Zentgraf, M. Eisenhut H. Untenecker, R. Kruger, R. Huss, C. Seliger, W. Semmler, F. Kiessling, *Langmuir*, **23** (2007) 1427.
 64. M. Chen, S. Yamamuro, D. Farrell, S. A. Majetich, *J. Appl. Phys.*, **93** (2003) 7551.

65. A.M. Morawski, P. M. Winter, K. C. Crowder, S. D. Caruthers, R. W. Fuhrlop, M. J. Scott, J. D. Robertson, D. R. Abendschein, G. M. Lanza, S. A. Wickline, *Magn. Res. Med.*, **51** (2004) 480.
66. F. Tourinho, R. Franck, R. Massart, R. Perzynski, *Coll. Polym. Sci.*, **79** (1989) 128.
67. J.F. Banfield, S.A. Welch, H. Zhang, T.T. Ebert, R.L. Penn, *Science*, **289** (2000) 751.
68. J.F. Banfield, R.L. Penn, *Science*, **281** (1998) 969.
69. C.E. Sjogren, K. Briley-Saebo, M. Hanson, C. Johansson, *Magn. Res. Med.*, **31** (1994) 268.
70. E. Tronc, P. Belleville, J.P. Jolivet, J. Livage, *Langmuir*, **8** (1992) 313.
71. R. Massart, V. Cabuil, *J. Chim. Phys.*, **84** (1987) 7.
72. S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science*, **287** (2000) 1989.
73. M.M. Miller, G. A. Prinz, S. F. Cheng, S. Bounnak, *Appl. Phys. Lett.*, **81** (2002) 2211.
74. S.W. Charles, J. Popplewell, *Endeavour*, **6** (1982) 153.
75. J.W. Bulté, *Methods Mol. Med.*, **124** (2006) 419.
76. A. Ito, M. Shinkai, H. Honda, T. Kobayashi, *J. Biosc. Bioeng.*, **100** (2005) 1.
77. B. Lobel, O. Eyal, N. Kariv, A. Katzir, *Lasers Surg. Med.*, **26** (2000) 4.
78. M. Chastellain, A. Petri, A. Gupta, K. V. Rao, H. Hofmann, *Adv. Eng. Mater.*, **6** (2004) 235.
79. T.K. Jain, M. A. Morales, S. K. Sahoo, D. L. Leslie-Pelecky, V. Labhasetwar, *Mol. Pharm.*, **2** (2005) 194.
80. O.S. Nielsen, M. Horsman, J. Overgaard, *Eur. J. Cancer*, **37** (2001) 1587.

-
81. A. Jordan, P. Wust, H. Fahling, W. John, A. Hinz, R. Felix, *Int. J. Hyperthermia*, **9** (1993) 51.
82. P. Moroz, S. K. Jones, B. N. Gray, *Int. J. Hyperthermia*, **18** (2002) 267.
83. A.A. Luderer, N.F. Borrelli, J.N. Panzarino, G.R. Mansfield, D.M. Hess, J.L. Brown, E.H. Barnett, *Radiat. Res.*, **94** (1983) 190.
84. D.C.F. Chan, D.B. Kirpotin, P.A. Bunn Jr., *J. Magn. Magn. Mater.*, **122** (1993) 374.
85. R.T. Gordon, J.R. Hines, D. Gordon, *Med. Hypothesis*, **5** (1979) 83.
86. X. Wang, J. Zhuang, Q. Peng, Y. Li, *Nature*, **437** (2005) 121.
87. C. Pascal, J. L. Pascal, F. Favier, M. L. Elidrissi Moubtassim, C. Payen, *Chem. Mater.*, **11** (1999) 141.
88. K. Inouye, R. Endo, Y. Otsuka, K. Miyashiro, K. Kaneko, T. Ishikawa, *J. Phys. Chem.*, **86** (1982) 1465.
89. S. Calvin, E. E. Carpenter, V. G. Harris, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **68** (2003) 033411/1.
90. M. Di Marco, I. Guilbert, M. Port, C. Robic, P. Couvreur, C. Dubernet, *Int. J. Pharm.*, **324** (2006) 37.
91. *Phthalocyanines: Properties and Applications*, eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York, Vols. **1-4** (1989, 1993, 1993 and 1996).
92. A. von Braun, J. Tscherniac, *Ber. Deut. Chem. Ges.*, **40** (1907) 2709.
93. L.R. Milgrom, In *The colours of life: An introduction to the chemistry of porphyrins and related compounds*, Oxford University Press, (1997).
94. H. de Diesbach, E. von der Weid, *Helv. Chim. Acta*, **10** (1927) 886.
95. R.P. Linstead, *J. Chem. Soc.*, (1934) 1016.

-
96. P. Gregory, *J. Porphyrins Phthalocyanines*, **3** (1999) 468.
 97. N.B. McKeown, *Chem. Ind.*, (1999) 92.
 98. J.M. Robertson, *J. Chem. Soc.*, (1935) 615.
 99. J.M. Robertson, *J. Chem. Soc.*, (1936) 1195.
 100. C.C. Leznoff, In *Phthalocyanines: Properties and Applications*, eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York, **Vol. 1** (1989)1, Chp. 1.
 101. D. Wöhrle, J. Gitzel, G. Krawczyk, E. Tsuchida, H. Ohno, T. Nishisaka, *J. Macromol. Sci. Chem: A*, **25** (1998) 1227.
 102. D. Wöhrle, D. Meissner, *Adv. Mater.*, **3** (1991) 129.
 103. M.K. Emmelius, G. Pawlowski, H. Vollman, *Angew. Chem.* **28** (1989) 1445.
 104. P. Gregory, In *High-Technology Applications of Organic Colourants*, Plenum Press: New York, (1991) 759.
 105. A. Grund, A. Kaltbeitzel, A. Mathy, R. Schwartz, C. Bubeck, P. Vernmehren, M. Hanack, *J. Phys. Chem.*, **96** (1992) 7450.
 106. E.M. Maya, A.W. Snow, J.S. Shirk, R.G. Pong, S.R. Flom, G.L. Roberts, *J. Mater. Chem.*, **13** (2003) 1603.
 107. M. Iwamoto, *J. Mater.Chem.*, **10** (2000) 99.
 108. M.J. Cook, *J. Mater.Chem.*, **6** (1996) 677.
 109. N.B. McKeown, In *Phthalocyanine Materials: Synthesis, Structure and Function. Chemistry of Solid State Materials*, Cambridge University Press, New York, (1998).
 110. S. Vilakazi, T. Nyokong, *Polyhedron*, **19** (2000) 229.

111. A.W. Snow, W.R. Barger, In *Phthalocyanines: Properties and Applications* eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York, **Vol. 1** (1989) 341, Chp. 5.
112. Md. K. Nazeeruddin, M. Humphry-Baker, M. Grätzel, D. Wöhrle, G. Schnurpfeil, G. Schneider, A. Hirth, N. Trombach, *J. Porphyrins Phthalocyanines*, **3** (1999) 230.
113. J.F. Van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Notte, W. Drenth, J. Aerts, R. Visser, S. J. Picken, *Liq. Cryst.*, **6** (1989) 577.
114. J.H. Zagal, *J. Electroanal. Chem.*, **109** (1980) 389.
115. O.L. Kaliya, E.A. Luk'yanets, G.N. Vorozhtsov, *J. Porphyrins Phthalocyanines*, **3** (1999) 592.
116. A. Sorokin, B.J. Meunier, *J. Chem. Soc., Chem. Commun.*, (1994) 1799.
117. G. Schneider, D. Wöhrle, W. Spiller, J. Stark, G. Schulz-Ekloff, *Photochem. Photobiol.*, **60** (1994) 333.
118. I. Rosenthal, *Photochem. Photobiol.*, **53** (1991) 859.
119. B.W. Henderson, T.J. Dougherty, *Photochem. Photobiol.*, **55** (1992) 145.
120. I. Rosenthal, E. Ben-Hur, In *Phthalocyanines: Properties and Applications* eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York, **Vol. 1** (1989) 393, Chp.6.
121. I.J. MacDonald, T. Dougherty, *J. Porphyrins Phthalocyanines*, **5** (2001) 105.
122. R. Bonnett, In *Chemical Aspects of Photodynamic Therapy*, Gordon and Breach Science Publishers, Amsterdam, (2000).
123. G.P. Moss, *Eur. J. Biochem.*, **178** (1988) 277.
124. T. Nyokong, Z. Gasyna, M.J. Stillman, *Inorg. Chem.*, **26** (1987) 548.

-
125. M.J. Stillman, T. Nyokong, In *Phthalocyanines: Properties and Applications*, eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York, **Vol. 1** (1989) 133, Chp.3.
126. P.N. Day, Z.Q. Wang, R. Pachter, *J. Mol. Struct. (Theochem)*, **455** (1998) 33.
127. M.K. Friedel, B.F. Hoskins, R.L. Martin, S.A. Mason, *J. Chem. Soc., Chem. Commun.*, (1970) 400.
128. Y. Zhang, X. Zhang, Z. Liu, H. Xu, J. Jiang, *Vib. Spectrosc.*, **40** (2006) 289.
129. J. Mack, M.J. Stillman, *J. Am. Chem. Soc.*, **116** (1994) 1292.
130. T. Kobayashi, T. Ashida, N. Uyeda, E. Surro, M. Kakuda, *Bull. Chem. Soc. Jpn*, **44** (1971) 2095.
131. D. Wöhrle, G. Schnurpfeil, G. Knothe, *Dyes and Pigments*, **18** (1992) 91.
132. F. Yilmaz, D. Atilla, V. Ahsen, *Polyhedron*, **23** (2004) 1931.
133. M. Brewis, M. Helliwell, N.B. McKeown, S. Reynolds, A. Shawcross, *Tetrahedron Lett.*, **42** (2001) 813.
134. P. Yiru, H. Fenghua, L. Zhipeng, C. Naisheng, H. Jinling, *Inorg. Chem. Commun.* **7** (2004) 967.
135. M. Hanack, M. Lang, *Adv. Mater.*, **6** (1994) 819.
136. M.J. Cook, A.J. Dunn, S.D. Howe, A.J. Thomson, K.J. Harrison, *J. Chem. Soc., Perkin Trans. 1*, (1988) 2453.
137. N.B. McKeown, I. Chambrier, M.J. Cook, *J. Chem. Soc. Perkin Trans. 1*, (1990) 1169.
138. C.H. Lee, D.K.P. Ng, *Tetrahedron Lett.*, **43** (2002) 4211.
139. H. Vollman: In *Chemistry of Synthetic Dyes*, ed. K. Venkataraman, Academic Press, New York, (1971) 283.

-
140. F. Henari, A. Davey, W. Blau, P. Haisch, M. Hanack, *J. Porphyrins Phthalocyanines*, **3** (1999) 331.
141. C.C. Leznoff, S.M. Marcuccio, S. Greenberg, A.B.P. Lever, K.B. Tomer, *Can. J. Chem.*, **63** (1985) 623.
142. D. Wöhrle, V. Schmidt, *J. Chem. Soc. Dalton Trans.*, (1988) 549.
143. A. Louati, M.E.I. Meray, J.J. Andre, J. Simon, K.M. Kadish, M. Gross, A. Giraudeau, *Inorg. Chem.*, **24** (1985) 1175.
144. D. Schlettwein, N.R. Armstrong, *J. Phys. Chem.*, **98** (1994) 11771.
145. S. Foley, G. Jones, R. Luizzi, D.J. McGarvey, M.H. Perry, T.G. Truscott, *J. Chem. Soc., Perkin Trans. 2*, (1997) 1725.
146. G. Torres, A.T. Torres *J. Porphyrins Phthalocyanines*, **1** (1997) 221.
147. G. Schmid, M. Sommerauer, M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **32** (1993) 1422.
148. M. Sommerauer, C. Rager, M. Hanack, *J. Am. Chem. Soc.*, **118** (1996) 10085.
149. A.G. Dandridge, H.A.E. Drescher, J. Thomas, *Scottish Dyes Ltd.*, (1929) GB322169.
150. J.H. Weber, D.H. Busch, *Inorg. Chem.*, **4** (1965) 469.
151. S.K. Saini, A. Jena, J. Dey, A.K. Sharma, R. Singh, *Mag. Res. Imag.*, **13** (1995) 985.
152. S.V. Kudrevich, M.G. Galpern, J.E. van Lier, *Synthesis*, (1994) 779.
153. K. Sakamoto, E. Ohno, *Prog. Org. Coating*, **31** (1997) 139.
154. R.W. Boyle, J.E. van Lier, *Synlett*, (1993) 351.

-
155. M. Ambroz, A. Beeby, A.J. MacRobert, M.S.C. Simpson, R.K. Svensen, D. Phillips, *J. Photochem. Photobiol. B: Biol.*, **9** (1991) 87.
156. H. Ali, R. Langlois, J.R. Wagner, N. Brasseur, B. Paquette, J.E. van Lier, *Photochem. Photobiol.*, **47** (1988) 713.
157. R.P. Linstead, E.G. Noble, J.M. Wright, *J. Chem. Soc.*, (1937) 911.
158. K. Sakamoto, F. Shibamiya, *J. Jpn. Soc. Colour Mater.*, **59** (1986) 517.
159. D. Wöhrle, N. Iskander, G. Grasclew, H. Sinn, E. Friedrich, W. Maier-Borst, J. Stern, P. Schlag, *Photochem. Photobiol.*, **51** (1990), 351.
160. Z.A. Bayir, *Dyes and Pigment*, **65** (2005) 235.
161. L. Zhang, J. Huang, L. Ren, M. Bai, L. Wu, B. Zhai, X. Zhou, *Bioorg. Med. Chem.*, **16** (2008) 303.
162. D.A. Makarov, O.A. Yuzhakova, L.K. Slivka, N.A. Kuznetsova, V.M. Negrimovsky, O.L. Kaliya, E.A. Lukyanets, *J. Porphyrins Phthalocyanines*, **11** (2007) 586.
163. M.P. De Phillips, D. Dei, L. Fantetti, G. Roncucci, *Tetrahedron Lett.*, **41** (2000) 9143.
164. J.G. Avila-Zárraga, R. Martínez, *Syn. Commun.*, **31** (2001) 2177.
165. J.R. Darwent, P. Douglas, A. Harriman, G. Porter, M.C. Richoux, *Coord. Chem. Rev.*, **44** (1982) 83.
166. A. Ogunsipe, T. Nyokong, *J. Photochem. Photobiol. A: Chem.*, **173** (2005) 211.
167. S. E. Maree, D. Phillips, T. Nyokong, *J. Porphyrins Phthalocyanine*, **6** (2002) 17.

168. S. Khene, A.N. Cammidge, M.J. Cook, T. Nyokong, *J.Porphyrins Phthalocyanines*, **11** (2007) 761.
169. E.A. Ough, Z. Gasyna, M.J. Stillman, *Inorg. Chem.*, **30** (1991) 2301.
170. T.H. Huang, K.E. Reickhoff, E.M. Voight, *J. Chem. Phys.*, **77** (1982) 3424.
171. A.B.P. Lever, S.R. Pickens, P.C. Minor, S. Licoccia, B.S. Ramaswamy, K. Magnell, *J. Am. Chem. Soc.*, **103** (1981) 6800.
172. M. Stillman, J. Mack, N. Kobayashi, *J. Porphyrins Phthalocyanines*, **6** (2002) 296.
173. K. Kasuga, N. Matsura, K Inoue, M. Handa, T. Sugimori, K. Isa, M. Nakata, *Chem.Lett.*, (2002) 352.
174. G.A. Kumar, J. Thomas, N.V. Unnikrishnan, V.P.N. Nampouri, C.P.G. Vallabhan, *J. Porphyrins Phthalocyanines*, **5** (2001) 456.
175. N. Kobayashi, H. Ogata, N. Nonaka, E.A. Luk'yanets, *Chem. Eur. J.*, **9** (2003) 5123.
176. N. Kobayashi, H. Konami, In *Phthalocyanines: Properties and Applications*, eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York, **Vol. 4** (1999) 343, Chp.9.
177. A. Ogunsipe, D. Maree, T. Nyokong, *J. Mol. Struc.*, **650** (2003) 131.
178. J.E. van Lier, J.D. Spikes, In *Photosensitizing compounds: their chemistry, biology and clinical use*, eds. G.S. Buck, S. Harnett, John Wiley and Sons, Chichester, (1989) 17.
179. M. Kasha, *Radiat. Res.*, **20** (1960) 55.
180. Z. Gasyna, N. Kobayashi, M.J. Stillman, *J. Chem. Soc., Dalton Trans.*, (1989) 2397.

181. N. Kobayashi, A.B.P. Lever, *J. Am. Chem. Soc.*, **109** (1987) 7433.
182. W.E. Ford, B.D. Rihter, M.E. Kenney, M.A.J. Rodgers, *Photochem. Photobiol.*, **50** (1989) 277.
183. A. Ferencz, D. Neher, M. Schulze, G. Wegner, L. Viaene, F.C. Achryver, *Chem. Phys. Lett.*, **245** (1995) 23.
184. S. Dhami, D. Phillips, *J. Photochem. Photobiol. A: Chem.*, **100** (1996) 77.
185. W.A. Nevin, W. Liu, S. Greenberg, M.R. Hempstead, S.M. Maruccio, M.M. Melnik, C.C. Leznoff, A.B.P. Lever, *Inorg. Chem.*, **26** (1987) 291.
186. Z. Li, M. Lieberman, *Inorg. Chem.*, **40** (2001) 932.
187. A.B.P. Lever, M.R. Hempstead, C.C. Leznoff, W. Liu, M. Melnik, W.A. Nevin, P. Seymour, *Pure Appl. Chem.*, **58** (1986) 1467.
188. K. Kasuga, M. Tsutsui, *Coord. Chem. Rev.*, **32** (1980) 67.
189. N. Nensala, T. Nyokong, *Polyhedron*, **17** (1998) 3467.
190. I. Szymczyk, H. Abramczyk, *Pure Appl. Chem.*, **76** (2004) 183.
191. O.T.E. Sielcken, M.M. van Tilborg, M.F.M. Rocks, R. Hendricks, W. Drenth, R.J.M. Nolte, *J. Am. Chem. Soc.*, **109** (1987) 4261.
192. D. Wöhrle, In *Phthalocyanines: Properties and Applications*, eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York, **Vol. 1** (1989) 55, Chp. 2.
193. Y. Yang, J.R. Ward, R. Seiders, *Inorg. Chem.*, **24** (1985) 1765.
194. A.R. Monahan, J.A. Brado, A.F. DeLuca, *J. Phys. Chem.*, **76** (1972) 446.
195. N. A. Wiederkehr, *J. Braz. Chem. Soc.*, **7** (1996) 7.
196. R.B. Ostler, A.D. Scully, A.G. Taylor, I.R. Gould, T.A. Smith, A. Waite, D. Phillips, *Photochem. Photobiol.*, **71** (2000) 397.

197. M.E. Daraio, P.F. Aramendia, E.A. San Roman, S.E. Braslavsky, *Photochem. Photobiol.*, **54** (1991) 367.
198. J. Devila, H. Harriman, *Photochem. Photobiol.*, **51** (1990) 9.
199. T.G. Truscott, *J. Chem. Soc., Faraday Trans. 2*, **82** (1986) 2177.
200. J.P. Zelina, J.F. Rusling, *Microporous Mesoporous Mater.*, **5** (1995) 203.
201. A.W. Snow In *The Porphyrin Handbook*, eds. K.M. Kadish, K.M. Smith, R. Guilard Academic Press, San Diego, **Vol. 17** (2003) 129, Chp. 109.
202. H. Dummin, Th. Cernay, H.W. Zimmermann, *J. Photochem. Photobiol. B: Biol.*, **37** (1997) 219.
203. H.M. Aliabadi, A. Mahmud, A. D. Sharifabadi, A. Lavasanifar, *J. Control. Release*, **104** (2005) 301.
204. D. Wörhle, S. Muller, M. Shopova, B. Mantareva, G. Spassova, F. Vietri, F. Ricchelli, G. Jori , *J. Photochem. Photobiol. B: Biol.*, **50** (1999) 124.
205. M. Soncin, L. Polo, E. Reddi, G. Jori, M.E. Kenney, G. Cheng, M.A.J. Rodgers, *Cancer Lett.*, **89** (1995) 101.
206. G. Jori, In *Photodynamic Therapy: Basic Principles and Clinical Applications*, eds. B.W. Henderson, T.J. Dougherty, Marcel Dekker, New York, (1992) 173.
207. S. Khene, E. Antunes, A. Ogunsipe, T. Nyokong, *J. Porphyrins Phthalocyanines*, **11** (2007) 109.
208. A.R. Monahan, D.F. Blossey, *J. Phys. Chem.*, **74** (1970) 4014.
209. S. M. T. Nunes, F. S. Squilla, A. C. Tedesco., *Braz. J. Med. Biol. Res.*, **37** (2004) 273.
210. X.F. Zhang, *Sci. China. Ser. B*, **37** (1994) 1298.

211. Y. Kaneko, T. Arai, T. Katsumi, D. Matsunaga, H. Sakuragi, *Chem. Lett.*, (1996) 345.
212. K. Bernauer, S. Fallab, *Helv. Chim. Acta*, **44** (1961) 1287.
213. M. Yoon, Y. Cheon, D. Kim, *Photochem. Photobiol.*, **58** (1993) 31.
214. J.F. Lipskier, T.H. Trans-Thi, *Inorg. Chem.*, **32** (1993) 722.
215. C.A.T. Laia, S.M.B. Costa, D. Phillips, A.W. Parker, *Photochem. Photobiol. Sci.*, **2** (2003) 555.
216. S.L. Lugunov, M.A. Rodgers, *J. Phys. Chem.*, **96** (1992) 8697.
217. W. W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.*, **15** (2003) 2854.
218. E.A. Kapp, S. Daya, C.G. Whitley, *Biochem. Biophys. Res. Commun.*, **167** (1990) 1383.
219. A.C.S. Samia, X. Chen, C. Burda, *J. Am. Chem. Soc.*, **125** (2003) 15736.
220. S. Dayal, R. Krolicki, Y. Lou, X. Qiu, J.C. Berlin, M.E. Kenney, C. Burda, *Appl. Phys. B*, **84** (2006) 309.
221. S. Dayal, C. Burda, *Photochem. Photobiol. Sci.*, **7** (2008) 605.
222. S. Dayal, C. Burda, *J. Am. Chem. Soc.*, **130** (2008) 2890.
223. S. Dayal, C. Burda, *J. Am. Chem. Soc.*, **129** (2007) 7977.
224. A.C.S. Samia, S. Dayal, C. Burda, *Photochem. Photobiol.*, **82** (2006) 617.
225. S. Dayal, Y. Lou, A.C.S. Samia, J.C. Berlin, M.E. Kenney, C. Burda, *J. Am. Chem. Soc.*, **128** (2006) 13974.
226. L. Shi, B. Hernandez, M. Selke, *J. Am. Chem. Soc.*, **128** (2006) 627.
227. A.O. Orlova, V.G. Maslov, I.E. Skaletskaya, A.V. Baranov, *Opt. Spectros.*, **101** (2006) 582.

228. D.R. Arnold, N.C. Baird, J.R. Bolton, J.C.D. Brand, P.W.M. Jacobs, P. de Mayo, W.R. Ware, *Photochemistry: An Introduction*, Academic Press, New York, (1974).
229. A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, *Chem. Rev.*, **97** (1997) 1515.
230. K. Ishii, N. Kobayashi, In *The Porphyrin Handbook*, eds., K.M. Kadish, K.M. Smith, R. Guilard, Elsevier Sc., USA, **Vol. 16** (2003) 1, Chp.102.
231. C. Farren, S. Fitzgerald, A. Beeby, M.R. Bryce, *Chem. Commun.*, **6** (2002) 572.
232. M. Durmus, T. Nyokong, *Tetrahedron*, **63** (2007) 1385
233. S. Fery-Forgues, D. J. Lavabre, *Chem. Ed.*, **76** (1999)1260.
234. A. Ogunsipe, J.Y. Chen. T. Nyokong, *New J. Chem.*, **7** (2004) 822.
235. S. Dhami, A.J. De Mello, G. Rumbles, S.M. Bishop, D. Phillips, A. Beeby, *Photochem. Photobiol.*, **61** (1995) 341.
236. T. Nyokong, *Coord. Chem. Rev.*, **251** (2007) 1707.
237. C.A. Barker, K.S. Findlay, S. Bettington, A.S. Batsanov, I.S. Perepichka, M.R. Bruce, A. Beeby, *Tetrahedron*, **62** (2006) 9433.
238. M. Durmus, T. Nyokong, *Polyhedron*, **26** (2007) 2767
239. T. Minami, M. Kawahigashi, Y. Sakai, K. Shimamoto, S. Hirayama, *J. Lumin.*, **35** (1986) 347.
240. G. Valduga, E. Reddi, G. Jori, R. Cubeddu, P. Taroni, G. Valentini, *J. Photochem. Photobiol. B: Biol.*, **16** (1992) 331.
241. S.J. Strickler, R.A. Berg, *J. Phys. Chem.*, **37** (1962) 814.
242. D. Wróbel, A. Boguta, *J. Photochem. Photobiol. A: Chem.*, **150** (2002) 67.
243. J.M. Dixon, M. Taniguchi, J.S. Lindsey, *Photochem. Photobiol.*, **81** (2005) 212.

244. J.C. Swarts, M.D. Maree, *J. Porphyrins Phthalocyanine*, **11** (2007) 613.
245. J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd edn. Springer, New York, (2006).
246. S. L. Murov, I. Carmichael, G.L. Hug, In *Handbook of Photochemistry*, 2nd edn., M. Decker, New York, (1993) 207.
247. J. Rose, In *Advanced Physico-chemical Experiments*, 1st edn. Sir Isaac Pitman and Sons Ltd., London (1964) 257.
248. M.A.R.B. Castanho, M.J.E. Prieto, *Biochemica Biophysica Acta.*, **1373** (1998) 1.
249. A. Ogunsipe, T. Nyokong, *J. Porphyrins Phthalocyanines*, **9** (2005) 121.
250. I. Gürol, M. Durmus, V. Ahsen, T. Nyokong, *Dalton Trans.*, (2007) 3782.
251. M. Durmus, T. Nyokong, *Spectrochim. Acta Part A*, **69** (2008) 1170.
252. M. Kongshaug, J. Moan, S.B. Brown, *Br. J. Cancer*, **59** (1989) 184.
253. E. Reddi, C. Zhou, R. Biolo, *Br. J. Cancer*, **61** (1990) 407.
254. U. Kragh-Hansen, *Pharmacol. Rev.*, **33** (1981) 17.
255. A.A. Bhattacharya, S. Curry, N.P. Franks. *J. Biol. Chem.*, **275** (2000) 38731.
256. G. Guo, J.W. Zou, P.G. Yi, Z.C. Shang, G.X. Hu, Q.S. Yu. *Anal. Sci.*, **20** (2004) 465.
257. D.C. Carter, B. Chang, J.X. Ho, K. Keeling, Z. Krishnasami *Eur. J. Biochem.*, **226** (1994) 1049.
258. J.D. Huang, W.P. Fong, E.Y.M. Chan, M.T.M. Choi, W.K. Chan, M.C. Chan, D.K.P Ng, *Tetrahedron Lett.*, **44** (2003) 8029.
259. A.O. Ogunsipe, T. Nyokong, *Photochem. Photobiol. Sci.*, **4** (2005) 510.

260. Y. Peng, F. Huang, J. Wen, B. Huang, X. Ma, Q. Wang, *J. Coord. Chem.*, **61** (2008) 1503.
261. L. Tan, L.Y. Liu, Q. Xie, Y.Y. Zhang, S.Z. Yao, *Anal. Sci.*, **20** (2004) 441.
262. J.H. Wang, H.Q. Wang, H.L. Zhang, X.Q. Li, X.F. Hua, Y.C. Cao, Z.L. Huang, Y.D. Zhao, *Anal. Bioanal. Chem.*, **388** (2007) 969.
263. Q. Wang, Y. Kuo, Y. Wang, G. Shin, C. Ruengruglikit, Q. Huang, *J. Phys. Chem. B*, **110** (2006) 16860.
264. T. Jamieson, R. Bakhshi, D. Petrova, R. Pocock, M. Imani, A.M. Seifalian, *Biomaterials*, **28** (2007) 4717.
265. M. Grimm, E. Eybl, M. Grabenwoger, H. Spreitzer, W. Jager, G. Grimm, P. Bock, M.M. Muller, E. Wolner, *Surg.*, **111**(1992) 74.
266. C.S. Osborn, W.H. Reid, M.H. Grant, *Biomaterials*, **20** (1999) 283.
267. Th. H. Förster, *Disc. Far. Soc.*, **27** (1959) 7.
268. J. Turro, In *Modern Molecular Photochemistry*, The Benjamin / Cummings Publishing Co., Inc., New York (1978).
269. A. Periasamy, In *Molecular Imaging: FRET Microscopy and Spectroscopy*, ed. N.R. Day, Oxford University Press, New York, (2005).
270. J.S. Hsiao, B.P. Krueger, R.W. Wagner, T.E. Johnson, J.K. Delaney, D.C. Mauzerall, G.R. Fleming, J.S. Lindsey, D.F. Bocian, R.J. Donohoe, *J. Am. Chem. Soc.*, **118** (1996) 11181.
271. A.R. Clapp, I.L. Medintz, J.M. Mauro, B.R. Fisher, M.G. Bawendi, H. Mattoussi, *J. Am. Chem. Soc.*, **126** (2004) 301.

272. I.L. Medintz, S.A. Trammell, H. Mattoussi, J.M. Mauro, *J. Am. Chem. Soc.*, **126** (2004) 30.
273. J.M. Tsay, M. Trzoss, L. Shi, X. Kong, M. Selke, M.E. Jung, S. Weiss, *J. Am. Chem. Soc.*, **129** (2007) 6865.
274. S. Moeno, T. Nyokong, *Polyhedron*, **27** (2008) 1953.
275. M.G. Lagori, L.E. Dixelio, E.S. Román, *J. Photochem. Photobiol. A: Chem.*, **72** (1993) 153.
276. M.D. Maree, T. Nyokong, K. Suhling, D. Phillips, *J. Porphyrins Phthalocyanine*, **6** (2002) 373.
277. M.D. Maree, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol. A: Chem.*, **140** (2001) 117.
278. S.M. Bishop, A. Beeby, H. Meunier, A.W. Parker, M.S.C. Foley, D. Phillips, *J. Chem. Soc., Faraday Trans.*, **92** (1996) 2689.
279. F.L. Primo, P.P. Macaroff, Z.G.M. Lacava, R.B. Azevedo, P.C. Morais, A.C. Tedesco, *J. Magn. Magn. Mater.*, **310** (2007) 2838.
280. D.M. Oliveira, Z.G.M. Lacava, E.C.D. Lima, P.C. Morais, A.C. Tedesco, *J. Nanosci. Nanotechnol.*, **6** (2006) 2432.
281. D.M. Oliveira, P.P. Macaroff, K.F. Ribeiro, Z.G.M. Lacava, R.B. Azevedo, E.C.D. Lima, P.C. Morais, A.C. Tedesco, *J. Magn. Magn. Mater.*, **289** (2005) 476.
282. P.P. Macaroff, D.M. Oliveira, K.F. Ribeiro, Z.G.M. Lacava, E.C.D. Lima, P.C. Morais, A.C. Tedesco, *IEEE. Trans. Magn.*, **41** (2005) 4105.
283. S.I. Park, J.H. Lim, J.H. Kim, H.I. Yun, C.O. Kim, *IEEE. Trans. Magn.*, **41** (2005) 4111.

284. H. Gu, K. Xu, Z. Yang, C.K. Chang, B. Xu, *Chem. Commun.*, (2005) 4270.
285. S. Liu, X. Jiang, G. Zhuo, *New J. Chem.*, **31** (2007) 916.
286. S. Corr, A. O'Byrne, Y.K. Gun'ko, S. Ghosh, D.F. Brougham, S. Mitchell, Y. Volkov, A. Prina- Mello, *Chem. Commun.*, (2006) 4474.
287. C. Schweitzer, R. Schmidt, *Chem. Rev.*, **103** (2003) 1685.
288. A. A. Frimer, *The Spectrum*, **13** (2000), 9.
289. N. Kuznetsova, N. Gretsova, O. Yuzhakova, V. Negrimovsky, O. Kaliya, E. Lukyanets, *Russ. J. Gen. Chem.*, **71** (2001) 36.
290. W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Röder, G. Schnurpfeil, *J. Porphyrins Phthalocyanines*, **2** (1998) 145.
291. N. Kuznetsova, N. Gretsova, V.M. Derkacheva, O.L. Kaliya, E.A. Lukyanets *J. Porphyrins Phthalocyanines*, **7** (2003) 147.
292. J.W. Verhoeven, *Pure Appl. Chem.*, **68** (1996) 2223.
293. A.K. Sobbi, D. Wöhrle, D. Schlettwein, *J. Chem. Soc., Perkin Trans. 2*, (1993) 481.
294. G. Schnurpfeil, A.K. Sobbi, W. Spiller, H. Kliesch, D. Wöhrle, *J. Porphyrins Phthalocyanines*, **2** (1998) 145.
295. G.S. Cox, M. Krieg, D.G. Whitten, *J. Am. Chem. Soc.*, **104** (1982) 6930.
296. T.S. Mang, T.J. Dougherty, W.R. Potter, D.G. Boyle, S. Somer, J. Moan *Photochem. Photobiol.*, **45** (1987) 501.
297. S. E. Maree, T. Nyokong, *J. Porphyrins Phthalocyanine*, **5** (2001) 782.
298. Y. Hongying, W. Fuyuan, Z. Zhiyi, *Dyes and Pigments*, **43**, (1999) 109.
299. R. Slota, G. Dyrda, *Inorg. Chem.*, **42** (2003) 5743.

300. P. Tau, A.O. Ogunsipe, S. Maree, M.D. Maree, T. Nyokong, *J. Porphyrins Phthalocyanines*, **7** (2003) 439.
301. I. Seotsanyana-Mokhosi, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol. A: Chem.*, **140** (2001) 215.
302. C.W. Dirk, T. Inabe, K.F. Schoch, T.J. Marks, *J. Am. Chem. Soc.*, **105** (1983) 1539.
303. H.I. Beltran, R. Esquivel, A. Sosa-Sanchez, J.L. Sosa-Sanchez, H. Hoepfl, V. Barba, N.Farfan, M.G. Garcia, O. Olivares-Xometl, S.L. Zamudio-Rivera, *Inorg. Chem.*, **43** (2004) 3555.
304. T. Nyokong, *J. Chem. Soc. Chem. Comm.*, (1994) 1983.
305. D.D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 2nd edn. Pergamon: Oxford, (1989).
306. R.F. Kubin, A.N. Fletcher, *J. Lumin.*, **27** (1982) 455.
307. T.H. Tran Thi, C. Desforge, C. Thiec, S. Gaspard., *J. Phys. Chem.*, **93** (1989) 1226.
308. A. Harriman, M.C. Richoux, *J. Chem. Soc., Faraday Trans., 2*, **76** (1980) 1618.
309. F. Wilkinson, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data*, **22** (1993)113.
310. N. Kuznetsova N. Gretsova, E. Kalmykova, E. Makarova, S. Dashkevich, V.Negrimovskii, O. Kaliya, E. Lukyanets, *Russ. J. Gen. Chem.*, **70** (2000) 133.
311. K. Gollnick, T. Franken, M.F.R. Fouda, H.R. Paur, S.J. Held, *J. Photochem. Photobiol. B: Biol.*, **12** (1992) 57.
312. P. C. Morais, V.K. Garg, A.C. Oliveira, L.P. Silva, R.B. Azevedo, A.M.L. Silva, E.C. D.Lima, *J. Magn. Magn. Mater.*, **225** (2001) 37.

313. M. Yamaura, R.L. Camilo, L.C. Sampaio, M.A. Macedo, M. Nakamura, H.E. Toma, *J. Magn. Magn. Mater.*, **279** (2004) 210.
314. M. E. Azim-Araghi, A. Krier, *Appl. Surf. Sci.*, **119** (1997) 260.
315. H. Tomoda, S. Saito, S. Shiraishi, *Chem. Lett.*, **12** (1983) 313.
316. M.G. Lagorio, L.E. Dixelio, E.A. San Román, S.E. Braslavsky, *J. Photochem. Photobiol. B: Biol.*, **3** (1989) 615.
317. X. Song, Y. She, H. Ji, Y. Zhang, *Org. Pro. Res. Dev.*, **9** (2005) 297.
318. R.D. George, A.W. Snow, *J. Heterocyclic Chem.*, **32** (1995) 495.
319. J.G. Young, W. Onyebuagu, *J. Org. Chem.*, **55** (1990) 2155.
320. P.Tau, T. Nyokong, *Polyhedron*, **25** (2006) 1802.
321. A. L. Spek Platon, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, (2001).
322. L. Guo, Q. Huang, X. Li, S. Yang, *Phys. Chem. Chem. Phys.*, **3** (2001) 1661.
323. S. Li, J. Zhang, Y. Shen, B. Ni, J. Zhang, *J. Mater. Sci. Technol.*, **22** (2006) 659.
324. M. C. Blanco, A. Meira, D. Baldomir, J. Rivas, M. A. Lopez, *IEEE: Trans. Magn.*, **30** (1994) 739.
325. M.S.C. Foley, A. Beeby, A.W. Parker, S.M. Bishop, D. Phillips, *J. Photochem. Photobiol. B: Biol.*, **38** (1997) 10.
326. A.G. Gurek, G. Appel, R.P. Mikalo, D. Schmeiber, *J. Porphyrins Phthalocyanines*, **5** (2001) 751.
327. G. Schnurpfeil, A.K.Sobbi, W.Spiller, H.Kliesch, D. Worhle, *J. Porphyrins Phthalocyanines*, **1** (1997) 159.

328. Y. Yamamoto, K. Yoshini, Y. Inuishi, S. Ichimura, *Phys. Stat. Sol. A*, **59** (1980) 305.
329. A. Suchan, J. Hurek, W. Wacławek, J. Nackiewicz, K. Ejsmont, *Polish J. Chem.*, **73** (1999) 2013.
330. K. Ozoemena, N. Kuzetnova, T. Nyokong, *J. Photochem. Photobiol. A: Chem.*, **139** (2001) 217.
331. A.N. Sidorov, M. P. Kotliar, *Opt. Spektrosk.*, **11** (1961) 175.
332. S. Gaspard, P. Maillard, *Tetrahedron*, **43** (1987) 1083.
333. G. Chen, X. Peng, G. Hao, V. O. Kennedy, I. N. Ivanov, K. Knappenberger, J. J. Hill, M. A. J. Rodgers, M. E. Kenney, *J. Phys. Chem. A*, **107** (2003) 3503.
334. M. Aoudia, G. Cheng, V. O. Kennedy, M. E. Denney, M. A. J. Rodgers, *J. Am. Chem. Soc.*, **119** (1997) 6029.
335. M. Durmus, T. Nyokong, *Inorg. Chem. Comm.*, **10** (2007) 332.
336. H. Li, T. J. Jensen, F.R. Fronczek, M. G. H. Vicente, *J. Med. Chem.*, **51** (2008) 502.
337. Z. Petrasek, D. Phillips, *Photochem. Photobiol. Sci.*, **2** (2003) 236.
338. R. D. George, A. W. Snow, J. S. Shirk, W. R. Barger, *J. Porphyrins Phthalocyanines*, **2** (1998) 1.
339. A. Alqudami, S. Annapoorni, *Plasmonics*, **2** (2007) 5.
340. H. Fei, X. Ai, M. Gao, Y. Yang, T. Zhang, J. Shen, *J. Lumin.*, **66,67** (1996) 345.
341. J.R. Darwent, I. McCubbin, D.J. Phillips, *Chem. Soc. Faraday Trans. 2*, **78** (1982) 347.
342. K. Morishige, S. Tomoyasu, G. Iwano, *Langmuir*, **13** (1997) 5184.

343. G.B. Dutt, N. Periasamy, *J. Chem. Soc., Faraday Trans.*, **87** (1991) 3815.
344. M. G. Debacker, O. Deleplanque, B. Van Vlierberge, F. X. Sauvage, *Laser Chem.*, **8** (1988) 1.
345. M.J. Stillman, In: *Phthalocyanines: Properties and Applications*, eds. C.C. Leznoff, A.B.P. Lever, VCH publishers, New York **Vol. 3** (1993) 227, Chp. 5.
346. S. Peulon, D. Lincot, *J. Electrochem. Soc.*, **145** (1998) 864.
347. T. Yoshida, T. Oekermann, K. Okabe, D. Schlettwein, K. Funabiki, H. Minoura, *Electrochemistry*, **70** (2002) 470.
348. M. Izaki, T. Omi, *J. Electrochem. Soc.*, **3** (1996) 143.
349. T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wöhrle, H. Minoura, *Chem. Commun.*, (2004) 400.
350. T. Loewenstein, K. Nonomura, T. Yoshida, E. Michaelis, D. Wöhrle, J. Rathousky, M. Wark, D. Schlettwein, *J. Electrochem. Soc.*, **153** (2006) A699.
351. K. Nonomura, T. Loewenstein, E. Michaelis, D. Wöhrle, T. Yoshida, H. Minoura, D. Schlettwein, *Phys. Chem. Chem. Phys.*, **8** (2006) 3867.
352. S. Griveau, J. Pavez, J.H. Zagal, F. Bedioui, *J. Electroanal. Chem.*, **497** (2001) 75.
353. T. Yoshida, M. Tachimoto, D. Schlettwein, D. Wöhrle, T. Sugiura, H. Minoura, *Chem. Mater.*, **11** (1999) 2657.
354. L.M. Peter, D. Vanmaekelbergh, In *Advances in Electrochemical Science and Engineering*, **Vol. 6**, eds. R. C. Alkire, D Kolb, Wiley-VCH, London, (1999).
355. H. Qin, S.Wenger, M. Xu, F. Gao, X. Jing, P. Wang, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.*, **130** (2008) 9202.

356. Md. K. Nazeeruddin, R. Humphry-Baker, D.L. Officer, W.M. Campbell, A.K. Burrell, M. Grätzel, *Langmuir*, **20** (2004) 6514.
357. Md. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.*, **115** (1993) 6382.
358. L. Stryer, *Annu. Rev. Biochem.*, **47** (1978) 819.
359. J. Ma, J.Y. Chen, Y. Zhang, P.N. Wang, J. Guo, W.L. Yang, C.C. Wang, *J. Phys. Chem. B*, **111** (2007) 12012.
360. M.N. Yarasir, M. Kandaz, A. Koca, B. Salih, *Polyhedron*, **26** (2007) 1139.
361. D.K. Geiger, C.A. Kelly, *Inorg. Chim. Acta.*, **154** (1988) 137.
362. M. Kaneko, H. Ueno, S. Masuda, K. Suzuki, H. Okimi, M. Hoshino, L. Lapok, D. Wöhrle, *J. Porphyrins Phthalocyanines*, **9** (2005) 667.
363. Y.J. Hu, Y. Liu, R.M. Zhao, J.X. Dong and S.S. Qu, *J. Photochem. Photobiol. A:Chem.*, **179** (2006) 324.
364. D.C. Hone, P. I. Walker, R. Evans-Growing, S. FitzGerald, A. Beeby, I. Chambrier, M. J. Cook, D. A. Russell, *Langmuir*, **18** (2002) 2985.
365. I. Roy, T. Y. Ohulchanskyy, H. E. Pudavar, E. J. Bergey, A.R. Oseroff, J. Morgan, T. J. Dougherty, P. N. Prasad, *J. Am. Chem. Soc.*, **125** (2003) 7860.
366. J. Guo, W. Yang, C.Wang, J. He, J.Y. Chen, *Chem.Mater.*, **18** (2006) 5554.
367. D.R. Tackley, G. Dent, W.E. Smith, *Phys. Chem. Chem. Phys.*, **3** (2001) 1419.
368. G. Dent, F. Farrell, *Spectrochim. Acta Part A*, **53** (1997) 21.
369. A.I. Filyasova, I.A. Kudelina, A.V. Feofanov, *J. Mol. Struct.*, **565-566** (2001) 173.
370. F. Seker, K. Meker, T.F. Kuech, A.B. Ellis, *Chem. Rev.*, **100** (2000) 2505.

371. Y. Wang, Z. Tang, M. A. Correa-Duarte, I. Pastoriza-Santos, M. Giersig, N. A. Kotov, L. M. Liz-Marzan, *J. Phys. Chem. B*, **108** (2004) 15461.
372. Y. Yu, Y. Lai, X. Zheng, J. Wu, Z. Long, C. Liang, *Spectrochim. Acta Part A*, **68** (2007) 1356.
373. M. Balsera, J. B. Arellano, F. Pazoz, D. Devos, A. Valencia, J. De Las Rivas, *Eur. J. Biochem.*, **270** (2003) 3916.