

**SYNTHESIS OF INDIUM AND LEAD PHTHALOCYANINE AS
PHOTOCATALYSTS FOR PHOTODYNAMIC ANTIMICROBIAL
CHEMOTHERAPY AND PHOTO-OXIDATION OF
POLLUTANTS**

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

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By

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DEDICATION

This thesis is dedicated to the alpha and omega, the beginning and the end, the unchangeable changer, “Kabiokosi” the lily of the valley Jesus for the gift of life and his amazing grace towards the completion of this thesis. Also, I dedicate this work to:

My late Father

Paul Olatunji Osifeko

My beloved Mother

Margret Amope Osifeko

My loving and Indefatigable Wife

Olajoke Osifeko

My sweet lovely Daughters

Paulina Oreoluwa Osifeko

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*“In life, you will realize there is a role for everyone you meet. Some will test you, some will use you, some will love you, and some will teach you. **But the ones who are truly important are the people who bring out the best in you.** They are the rare and amazing people who remind you why it’s worth it”* by Anonymous

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Abstract

This thesis explores the synthesis of metallophthalocyanines as potential photosensitizers for application in photodynamic antimicrobial chemotherapy and phototransformation of environmental pollutants. The metallophthalocyanines containing amino substituent were conjugated with magnetic nanoparticle and semiconductor quantum dots via an amide bond and by chemisorption onto gold nanoparticles surface. Techniques such as time-resolved fluorescence measurements, transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), elemental analysis, fourier transform infrared (FTIR), nuclear magnetic resonance (^1H , ^{13}C , and cozy of symmetrical phthalocyanine), electronic spectroscopy, as well as mass spectroscopy were employed to characterize all metallophthalocyanines. Quarternized pyridyloxy substituted phthalocyanine and asymmetric (AB_3) metallophthalocyanines were embedded in electrospun polystyrene fiber. General trends are described for quantum yields of fluorescence, triplet, singlet oxygen and photodegradation as well as lifetimes of fluorescence and triplet state of the compounds. There is an increase in triplet quantum yield for Pcs in the presence of gold nanoparticles (AuNPs) and semiconductor quantum dots (QDs), but not in the presence of magnetic nanoparticles (MNPs). Photodynamic inactivation of *Escherichia coli* with the quarternized photosensitizers at low concentrations totally inactivate the bacteria compared to non-charged photosensitiser. Also, a similar trend was observed for the magnetic nanoparticles conjugates. Photooxidations of bisphenol A and 4-chlorophenol were carried out in this study using two asymmetric Indium(III) phthalocyanines photosensitizers. The photooxidation reactions were compared with those of a symmetrical indium(III) phthalocyanines containing four quaternized 4-pyridyloxy substituents. The complexes were embedded in electrospun

polystyrene fiber for heterogeneous photocatalysis. The immobilized photosensitizers possess good singlet oxygen generation potentials in aqueous media. The asymmetrical phthalocyanine containing 4-pyridylsulfanyl and one aminophenoxy showed the best photocatalytic behavior.

Table of Contents

TITLE PAGE	i
DEDICATION	ii
ACKNOWLEDGEMENT	iii
ABSTRACT	iv
TABLE OF CONTENTS	vi
LIST OF SYMBOLS	xiv
LIST OF ABBREVIATIONS	xvi
LIST OF FIGURES	xix
LIST OF SCHEMES	xxv
LIST OF TABLES	xxxvi
Chapter 1.....	1
1 Introduction.....	1
1.1 Phthalocyanines (MPcs)	1
1.1.1 Structure and General Applications	1
1.1.2 Synthetic Methods	1
1.1.3 Electronic Absorption Spectra of MPcs	8
1.2 Photodynamic Antimicrobial Chemotherapy (PACT)	10
1.2.1 Introduction to PACT	10
1.2.2 Photosensitizers Used in PACT	12

1.3	Photo-oxidation of Environmental Pollutants	16
1.4	Nanoparticles.....	17
1.4.1	Magnetic Nanoparticles (MNPs).....	17
1.4.2	Quantum Dot (QDs).....	18
1.4.3	Gold Nanoparticles (AuNPs)	18
1.5	Electrospinning.....	20
1.5.1	Basics of Electrospinning.....	20
1.5.2	Phthalocyanines Which Has Been Embedded in Fibers and Application.....	22
1.6	Photophysical and Photochemical Parameters.....	23
1.6.1	Fluorescence Quantum Yield (Φ_F) and Lifetime (τ_F)	24
1.6.2	Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T).....	26
1.6.3	Singlet Oxygen Quantum Yield (Φ_Δ).....	27
1.6.4	Photodegradation Quantum Yield (Φ_{Pd})	29
1.7	Summary of This Thesis	29
CHAPTER 2		31
2 Experimental.....		31
2.1	Materials.....	31
2.1.1	Solvents	31
2.1.2	Reagents for the Metallophthalocyanines synthesis.....	31
2.1.3	Quenchers/Standard for determination of Photophysical Parameters.....	31
2.1.4	Reagents for Nanoparticles Synthesis	32

2.1.5	Reagents for Photodynamic Antimicrobial Chemotherapy and Photocatalysis.	
	32	
2.2	Instrumentation.....	32
2.3	Phthalocyanines Synthesis	38
2.3.1	Synthesis of 2,9(10),16(17),23(24)-tetrakis[4-(N-pyridyloxy) phthalocyaninato] lead(II) (7, Scheme 3.1)	38
2.3.2	Quaternized phthalocyanine 2,9(10),16(17),23(24)-tetrakis[4-(4-N-ethylpyridiniumoxy) phthalocyaninato] lead (II) (7a, Scheme 3.1)	38
2.3.3	Synthesis of 2,9(10),16(17),23(24)-tetrakis[4-(pyridyloxy) phthalocyaninato] chloroindium(III) (8, Scheme 3.2).....	39
2.3.4	Synthesis of 2, 9(10), 16(17), 23(24)-tetrakis [4-(4-N-methylpyridiniumoxy) phthalocyaninato] chloroindium(III) iodide (8a, Scheme 3.2)	39
2.3.5	Synthesis of 2-[4-(pyridyloxy) phthalocyaninato] chloroindium(III) (9, Scheme 3.2)	40
2.3.6	Synthesis of 2-[4-(N-methylpyridiniumoxy) phthalocyaninato] chloroindium(III) iodide (9a, Scheme 3.2).....	41
2.3.7	Synthesis of 9(10), 16(17), 23(24)-tri-4-pyridylsulfanyl -2(3) -(4 aminophenoxy) phthalocyaninato chloroindium(III). (10, Scheme 3.3)	41
2.3.8	Synthesis of 9(10), 16(17), 23(24)-tri-N-methyl-4-pyridylsulfanyl-2(3) - (4Aminophenoxy) Phthalocyaninato Chloroindium(III) Triiodide (10a)	42
2.3.9	2,9(10),16(17),23(24)-tetrakis-(4'-(4',6'-diaminopyrimidin-2'-ylthio)) phthalocyaninato zinc (II) (11, Scheme 3.4).	43

2.3.10	2,9(10),16(17),23(24)-tetrakis-(4'-(4',6'-diaminopyrimidin-2'-ylthio)) phthalocyaninato chloroindium(III) (12, Scheme 3.4)	43
2.4	Synthesis of Nanoparticles	44
2.4.1	Synthesis of Magnetic Nanoparticles	44
2.4.2	Synthesis of AuNPs.....	45
2.5	Conjugation of Phthalocyanines to the Nanoparticles	46
2.5.1	Conjugation of 10-MPcs-MNPs conjugates (Scheme 3.6)	46
2.5.2	Conjugation of 10a-MPcs-MNPs conjugates (Scheme 3.6).....	46
2.5.3	Conjugation of complexes 11 and 12 to MNPs, Scheme 3.7	46
2.5.4	Conjugation of glutathione-capped CdTe/ZnSe/ZnO to complex 10 (10-QD), Scheme 3.8.....	47
2.5.5	Conjugation of phthalocyanine (11 or 12) to GSH/CdTe/ZnSe/ZnO QDs to form (11-QDs and 12-QDs, respectively), Scheme 3.9	48
2.5.6	Conjugation of phthalocyanine to gold nanoparticles, Scheme 3.10	48
2.6	Preparation of Electrospun Nanofibers	48
2.7	Antimicrobial Studies.....	49
2.7.1	Preparation of <i>E. Coli</i> Culture.....	49
2.7.2	Photodynamic Antimicrobial Chemotherapy Activity.....	49
2.8	Photochemical Studies	50
2.8.1	Preparation of Working Solutions.....	50
2.8.2	Photo-oxidation Experiments.....	50
2.9	Photophysical and Photochemical Parameters	50

2.9.1	Fluorescence Quantum Yield (Φ_F) and Lifetime (τ_F)	50
2.9.2	Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T).....	51
2.9.3	Singlet Quantum Yield (Φ_Δ) and Photodegradation (Φ_{Pd}).....	51
Chapter 3.....		55
3 Synthesis and characterization of Pcs and conjugates.....		56
3.1	Characterisation of phthalocyanines alone.....	56
3.1.1	Pyridyloxy Substituted Phthalocyanine (7-9, 17, 18)	56
3.1.2	Pyridyloxy and aminophenoxy substituted InPc (10 and 10a).....	62
3.1.3	Complexes 11 and 12	68
3.2	Characterization of MNPs and their conjugates to Pcs (10, 11, and 12).....	70
3.2.1	Synthesis.....	70
3.2.2	TEM images and EDX spectra of MNP and its Pcs (10, 11 and 12) conjugates 76	
3.2.3	Surface Area and Porosity Analyses of MNPs alone.....	77
3.2.4	XRD Patterns.....	79
3.2.5	Thermal Analysis	80
3.2.6	XPS Spectra.....	81
3.2.7	FT-IR spectra.....	86
3.2.8	UV–Vis Absorption Spectra.....	87
3.3	Conjugates of QDs and with Pcs (10, 11 and 12)	88
3.3.1	Synthesis.....	88

3.3.2	TEM Images	91
3.3.3	XRD Spectra	91
3.3.4	XPS Spectra Characterization of 10-QD	92
3.3.5	FT-IR spectra.....	94
3.3.6	UV–Vis Spectra.....	95
3.4	Synthesis and Conjugation to Gold Nanoparticles (AuNPs)	97
3.4.1	Synthesis.....	97
3.4.2	TEM Images	98
3.4.3	XRD Patterns.....	98
3.4.4	XPS Spectra.....	99
3.4.5	UV-Vis Spectra	101
3.5	Characterization of Phthalocyanines When Embedded in Electrospun Fiber.....	102
3.5.1	Scanning electron microscope (SEM).....	102
3.5.2	XRD Patterns.....	105
3.5.3	Surface Area and Porosity Analyses	105
3.5.4	Thermal stability	106
3.5.5	UV/Visible Spectra	108
3.6	Conclusion.....	109
Chapter 4.....		110
Photophysical and photochemical studies		110

4	Photophysical and Photochemical Studies of Phthalocyanines and their Conjugates	111
4.1	Pyridyloxy Substituted Phthalocyanines (7-9, 17, 18).....	111
4.1.1	Fluorescence Quantum Yields and Lifetimes.	111
4.1.2	Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T).	113
4.1.3	Singlet Oxygen Quantum Yield (Φ_Δ).....	115
4.1.4	Photodegradation Studies.....	116
4.2	Asymmetrical MPc (10 and 10a) alone or in the Presence of Nanomaterials.....	118
4.2.1	Fluorescence Quantum Yields (Φ_F) and Lifetimes (τ_F)	118
4.2.2	Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T).	121
4.2.3	Singlet oxygen quantum yield (Φ_Δ)	122
4.2.4	Photodegradation Studies (Φ_{Pd})	122
4.3	Photophysical and Photochemical Parameters of Symmetrical MPc (11 and 12) alone or in the Presence of Nanomaterials	123
4.3.1	Fluorescence Quantum Yield (Φ_F) and Lifetimes (τ_F).	123
4.3.2	FRET	125
4.3.3	Triplet quantum yield (Φ_T) and lifetimes (τ_T).	125
4.3.4	Singlet Oxygen Quantum Yield (Φ_Δ) and Photodegradation Quantum Yield (Φ_{Pd})	127
4.4	Singlet Oxygen Quantum Yields of Phthalocyanines When Embedded in Electrospun Fiber	127
4.5	Conclusion.....	128

CHAPTER 5.....	130
5 Application studies with synthesized phthalocyanines	130
5.1 Photodynamic Antimicrobial Chemotherapy (PACT) in Solution	131
5.1.1 Pyridyloxy MPcs	131
5.1.2 Asymmetric 10a, 10-MNPs, 10a-MNPs.	136
5.2 PACT Studies Using 7 and 7a Electrospun Fiber	139
5.3 Photocatalytic Degradation of Pollutants	140
5.3.1 UV-Vis Spectral Changes	140
5.3.2 Kinetic Studies	142
5.4 Conclusion.....	144
Chapter 6.....	145
6 Conclusions and Future Perspective.....	145
6.1 Conclusion.....	146
6.2 Future Prospects	148
References	149

List of symbols

K_{ads}	-	Adsorption coefficients
K_{a}	-	Apparent reaction rate constant
ΔA_{s}	-	Changes in the singlet state absorbance
ΔA_{T}	-	Changes in the triplet state absorbances
Φ_{F}	-	Fluorescence quantum yield
Φ_{T}	-	Triplet quantum yield
Φ_{ADMA}	-	Quantum yield of ADMA
Φ_{Δ}	-	Singlet oxygen quantum yield
Φ_{pd}	-	Photodegradation quantum yield
F	-	Area under the Fluorescence emission curves of samples
F_{std}	-	Area under the Fluorescence emission curves of standard
n	-	Refractive index of sample solvent
n_{std}	-	Refractive index of standard solvent
λ	-	Wavelength
E_{ff}	-	FRET efficiency
τ	-	Amplituted weighted average lifetimes
r	-	Donor-acceptor distance
R_0	-	Förster distance

J	-	Förster overlap integral
τ_A	-	Fluorescence lifetime of donor in the absence of acceptor
τ_P	-	Fluorescence lifetime of donor in the prescence of acceptor
ϵ_T	-	Triplet state molar extinction coefficients
$t_{1/2}$	-	Half-life
t	-	Time
k	-	Apparent rate constant
K_{obs}	-	Observed rate constant
K_A	-	Adsorption coefficient
I_{abs}	-	Light intensity

List of Abbreviations

ADMA	Anthracene-9,10-bis-methylmalonate
APTES	3-Aminopropyltriethoxysilane
AuNP	Gold Nanoparticles
BE	Binding Energy
BET	Brunauer-Emmtte-Teller
BPA	Bisphenol A
CFU	Colony Forming Units
COSY	Correlated spectroscopy
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCC	Dicyclohexylcarbodiimide
DMF-d ₆	Deuterated dimethylformamide
DMSO-d ₆	Deuterated dimethyl sulfoxide
DPBF	3-Diphenylisobenzofuran
DCM	Dichloromethane
EDC	Endocrine Disrupting Chemicals/ 1-Ethyl-3-(3-dimethylaminopropyl)- carbodiimide
EDX	Energy Dispersive X-ray

EtOH	Ethanol
FCC	Face Centered Cubic Crystal
FTIR	Fourier Transform Infrared
FRET	Förster Resonance Energy Transfer
FWHM	Full Width at Half-maximum
GSH	Glutathione
HOMO	Highest occupied molecular orbital
HAD	Hexadecylaniline
IC	Internal conversion
IR	Infrared
ISC	Intersystem crossing
LUMO	Lowest unoccupied molecular orbital
MALDI	Matrix-assisted laser desorption/ionization
MCP	Monochromator photomultiplier
MNP	Magnetic nanoparticle
MRI	Magnetic resonance imaging
MPc	Metallophthalocyanine
NHS	N-hydroxysuccinimide
NMR	Nuclear magnetic resonance
NP	Nanoparticle
OBC	Original Bacterial Culture
PACT	Photodynamic antimicrobial

	Chemotherapy
PBS	Phosphate buffer solution
PDT	Photodynamic therapy
PMT	Photomultiplier tube
PS	Polystyrene
QD	Quantum Dot
^1H NMR	Proton nuclear magnetic resonance Spectroscopy
ROS	Reactive Oxygen species
SEM	Scanning electron microscopy
SPR	Surface plasmon resonance
TCD	Tip to collector distance
TCSPC	Time-correlated single photon counting
TEM	Transmission electron microscopy
TEOS	Tetraethoxysilane
TGA	Thermo-gravimetric analysis
THF	Tetrahydrofuran
$^3\text{MPc}^*$	Triplet state of phthalocyanine
VR	Vibrational relaxation
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

List of Figures

Figure 1.1 Numbering scheme for the phthalocyanine core	3
Figure 1.2 Structures of MPcs synthesized in this thesis	6
Figure 1.3 Structures of the MPc-NPs conjugates in this thesis	8
Figure 1.4 Typical electronic absorption spectrum of metallophthalocyanine	9
Figure 1.5 Electronic energy levels in phthalocyanine complexes showing the origin of Q and B bands.	10
Figure 1.6 Jablonski diagram for generations of reactive oxygen species (ROS)	11
Figure 1.7 Show the mechanism of cell death through PACT	12
Figure 1.8 Schematic diagram of an electrospinning set-up	21
Figure 1.9 A modified Jablonski diagram showing all the major photophysical and photochemical parameters	23
Figure 2.1 Schematic diagram of TCSPC set-up.	34
Figure 2.2 Schematic diagram of photochemical set-up	35
Figure 2.3 Schematic diagram of a laser flash photolysis set-up.	36
Figure 3.1 Structures of quaternized 3-pyridyloxy tetrasubstituted (phthalocyaninato) indium(III) substituted at the α and β positions	58
Figure 3.2 Absorption spectra of (a) 7 and (b) 7a in DMF $\sim 8.00 \times 10^{-6}$ M. (c) is the spectrum of 7a in water.	59

Figure 3.3 Absorption, emission and excitation spectra for (A) 7 , (B) 7a , (C) 8 and (D) 9 in DMF.	59
Figure 3.4 Electronic absorption, excitation and emission spectra of 8a in water (a) and in water plus Triton-X 100 (b).	60
Figure 3.5 ¹ NMR spectrum for 10	64
Figure 3.6 ¹ H-H COSY NMR spectrum of compound 10	65
Figure 3.7 ¹³ C NMR spectrum of compound 10	65
Figure 3.8 ¹ H NMR spectrum of compound 10a	66
Figure 3.9 Mass spectrum of 10 (A) and 10a (B)	67
Figure 3.10 Electronic absorption (a), excitation (b) and emission (c) spectra of 10 (A) in DMSO (concentration = 2.0×10^{-6} M) and 10a (B) in water plus Triton-X. (d) in (B) is the absorption spectrum of 10a in water.	68
Figure 3.11 Electronic absorption (a), excitation (b) and emission spectra of 11	70
Figure 3.12 Photograph of the 10 -MNPs (A) and 10 (B) exhibiting magnetic property of the former	71
Figure 3.13 TEM images and the corresponding histograms showing in (A) MNP-Si, (B) MNP-NH ₂ and (C) MNP-COOH	76
Figure 3.14 EDX spectra of MNPs alone (a) and 12 -MNPs	77
Figure 3.15 Typical Nitrogen adsorption-desorption BET isotherm of MNP-Si (A) and MNP-COOH (B).	78
Figure 3.16 Powder XRD diffractograms of (A) MNP, MNP-Si, MNP-NH ₂ and MNP-COOH and (B) complex 10 , 10 -MNPs and 10a -MNPs	79

Figure 3.17 TGA thermogravimetry of complexes MNP-COOH, 10 , 10a and 10 -MNPs.	80
Figure 3.18 Survey spectra of (A) 10 (red) and 10a (black) and (B) MNP-COOH (blue), 10 -MNPs (black) and 10a -MNPs (red).	81
Figure 3.19 High resolution of N 1s for MNP-NH ₂ (A) and MNP-COOH (B).	82
Figure 3.20 High resolution of N 1s for (A) 10 , (B) 10a , (C) 10 -MNPs and (D) 10a -MNPs.	84
Figure 3.21 High-resolution N 1s for 11 and 11 -MNPs	84
Figure 3.22 High resolution of I 3d _{5/2} for 10a -MNPs.	85
Figure 3.23 High resolution of In 3d for (A) 10 and 10 -MNPs and (B) 10a and 10a -MNPs.	86
Figure 3.24 Infrared spectra (IR) of MNPs (a), 12 (b) and 12 -MNPs (c).	87
Figure 3.25 Electronic absorption (a), excitation (b) and emission (c) spectra of 10 -MNPs (A) and 11 -MNPs (B) in DMSO	88
Figure 3.26 TEM micrographs of (a) GSH-CdTe/ZnSe/ZnO QDs and (b) 10 -QDs	91
Figure 3.27 Powder XRD diffractograms of (a) QDs and (b) 11 -QDs.	92
Figure 3.28 Survey spectra of 10 (a), QDs (b) and 10 -QDs (c).	93
Figure 3.29 High resolution N1s XPS spectra of (A) 10 and (B) 10 -QDs.	93
Figure 3.30 XPS deconvoluted N 1s for 11 -QDs	94
Figure 3.31 Infrared spectra (IR) of QDs (a), 12 (b) and 12 -QDs	95
Figure 3.32 Electronic absorption spectrum of (A) 10 -QDs (a) and 10 (b) in DMSO; (B) the overlap spectra of QDs absorption (a) and QDs emission (excitation at 400 nm) (b)	96
Figure 3.33 TEM micrographs of AuNPs alone (a) and 11 -AuNPs (b).	98
Figure 3.34 Powder XRD diffractograms of (a) AuNPs and (b) 11 -AuNPs	99

Figure 3.37 Wide scan XPS spectra of 11 (a), AuNPs (b) and 11 -AuNPs (c)	100
Figure 3.36 High resolution of N 1s for 11 -AuNPs	101
Figure 3.37 Electronic absorption (a) excitation, (b) emission (c) spectra of 11 -AuNPs in DMSO.	101
Figure 3.38 SPR band for the AuNPs in toluene	102
Figure 3.39 The SEM micrographs of electrospun fiber and the histogram showing fiber distribution (A) polystyrene polymer (PS), (B) 7 -PS, (C) 7a -PS, (D) 8a -PS, (E) 9a -PS and (F) 10a -PS	104
Figure 3.40 XRD of the polystyrene (a) 7a -PS (b) and 7a (c).	105
Figure 3.41 Typical nitrogen adsorption-desorption BET isotherm of 9a -PS fiber (A), 8a -PS fiber (B) and 10a -PS fiber (C) the inserts are the respective BET surface area plots.	106
Figure 3.42 TGA thermograms of the photosensitizers and their modified fibers	107
Figure 3.43 UV/Vis absorption spectra of complexes 7a , 8a , 9a and 10a embedded in polystyrene fiber (PS).	108
Figure 4.1 Fluorescence decay profile of the phthalocyanines; (A) 7 , 7a and (B) 8 and 9 in DMSO	111
Figure 4.2 Transient differential spectrum of complex 8a , excitation wavelength at 691 nm. Insert = corresponding triplet decay curve. Solvent= DMSO	114
Figure 4.3 Absorption spectral changes during the determination of singlet oxygen quantum yield for (A) 7 in DMF and (B) 8 in DMSO.	116
Figure 4.4 Absorption spectra during the determination of photodegradation of (A) 7 in DMF. Inset: plot of absorbance versus time. (B) complex 8 in DMF	117

Figure 4.5 Fluorescence lifetime decay curve of 10 -MNPs in DMSO at 703 nm.	119
Figure 4.6 Overlap spectra of (a) QDs emission (excitation at 400 nm) and (b) absorption spectra of 10	121
Figure 4.7 Fluorescence decay profile of the phthalocyanines; 11 (a) and 12 (b) in DMSO.	123
Figure 4.8 Overlap of (a) QDs emission (excitation at 400 nm and in water) with the absorption spectra of absorption (b) 11 and (c) 12 in DMSO. An excitation wavelength of QDs at 400 nm.	125
Figure 4.9 Transient differential spectrum of complex 11 , excitation wavelength at 679 nm. Insert = corresponding triplet decay curve. Solvent =DMSO	126
Figure 4.10 Singlet absorption spectra of (A) 7a -PS in water (30 minutes intervals) and (B) 10a -PS in water using ADMA (6.1×10^{-6} M) as the singlet oxygen quencher.	128
Figure 5.1 Survival curve of <i>E. coli</i> incubated with 5 μ M of the Photosensitizers; (A) 7 and (B) 7a	132
Figure 5.2 Micrograph of the original bacterial culture (OBC) before PACT without photosensitizer.	133
Figure 5.3 Survival curve of <i>E. coli</i> incubated with 10 μ M of the photosensitizer in (A) 1% DMSO–PBS and (B) PBS. Time 60 min	134
Figure 5.4 Electronic absorption spectra of cell culture with 10 μ M of complex 8a (1% DMSO in PBS). (A) Absorbance before incubation, (B) absorbance after 30 min incubation and (C) final absorbance after PACT	135
Figure 5.5 Photodynamic inactivation efficiency of (A) 10a in PBS and PBS/ DMSO and (B) 10a -MNPs on <i>E. coli</i> in PBS/DMSO	137

Figure 5.6 Photodynamic effect of the embedded **7** and **7a** on bacteria *E. coli*: Agar plates A and C are irradiated with light while agar plates B and D were kept in the dark, each plate contains both controls (polystyrene fiber) and photosensitized fiber. Photolysis time = 30 min. 139

Figure 5.7 Electronic absorption spectral changes of (A) 4-chlorophenol (5 μ M) and (B) bisphenol A (0.02 mM) during the photo-oxidation at 30 min intervals. Irradiation intervals using **8a**-PS fiber. 141

Figure 5.8 Plots of log concentration versus time for (A) 4-chlorophenol and (B) bisphenol A. Concentrations were monitored at 244 nm and 242 nm for 4-chlorophenol and bisphenol A, respectively; **9a**-PS fiber (a), **8a**-PS fiber (b) and **10a**-PS fiber (c) 144

List of Schemes

Scheme 1.1 Synthetic routes of metallophthalocyanines from different precursors	2
Scheme 1.2 Synthetic route for peripheral and non-peripheral substituted phthalocyanines	4
Scheme 1.3 General method for preparation of asymmetric phthalocyanines by the statistical condensation approach	5
Scheme 1.4 Reaction of a tetraazaporphyrin derivative with $^1\text{O}_2$	29
Scheme 3.1 Synthetic route for 7 and 7a	56
Scheme 3.2 Synthetic route for 8 , 8a , 9 and 9a	57
Scheme 3.3 Schematic representation of the synthesis of 10	63
Scheme 3.4 Synthetic route of the metallophthalocyanines 11 and 12 .	69
Scheme 3.5 The Scheme for the synthesis of bare MNP, MNP-Si, MNP-NH ₂ , and MNP-COOH	73
Scheme 3.6 Schematic representation of the conjugation of MNP-COOH and the photosensitizers (10 and 10a)	74
Scheme 3.7 Schematic representation of conjugation of 11 and 12 to MNPs	75
Scheme 3.8 Schematic representation of the conjugation of glutathione-capped CdTe/ZnSe/ZnO and 10 .	89
Scheme 3.9 Synthesis route to MPc-QDs conjugates	90
Scheme 3.10 Synthesis route to phthalocyanine MPc-AuNPs.	97
Scheme 5.1 Type I and II mechanisms	142

List of Tables

Table 1.1 Examples of known quaternized Pcs used for PACT	13
Table 1.2 Some examples of phthalocyanine nanoparticles conjugates use for PACT	19
Table 1.3 Examples of known electrospun nanofibers functionalized with phthalocyanines and their applications.	22
Table 3.1 Electronic absorption and emission properties of the phthalocyanines in DMSO, unless otherwise stated	61
Table 3.2 Electronic absorption and parameters of nanoparticles and MPc/conjugates in DMSO or unless otherwise stated.	72
Table 3.3 Parameters for the modified fibers	109
Table 4.1 Photophysical properties of MPcs and their quartenized MPcs	112
Table 4.2 Photophysical properties of Indium (III) phthalocyanines in DMSO, excitation at 670 nm unless otherwise stated	118
Table 4.3 Förster resonance energy transfer (FRET) parameters	120
Table 4.4 Photophysical properties of complexes/conjugates in DMSO unless otherwise stated. Excitation for emission at 640 nm, unless otherwise stated	124
Table 5.1 Log reduction values (after 60 min irradiation) for <i>Escherichia coli</i> using different phtosensitizers when cells are grown in PBS or DMSO (1%)/PBS.	136
Table 5.2 Log reduction values for the photoinactivation effect on <i>E. coli</i> inactivation	138
Table 5.3 Kinetic data of the photodegradation of the pollutants	143

Chapter 1

1 Introduction

1.1 Phthalocyanines (MPcs)

1.1.1 Structure and General Applications

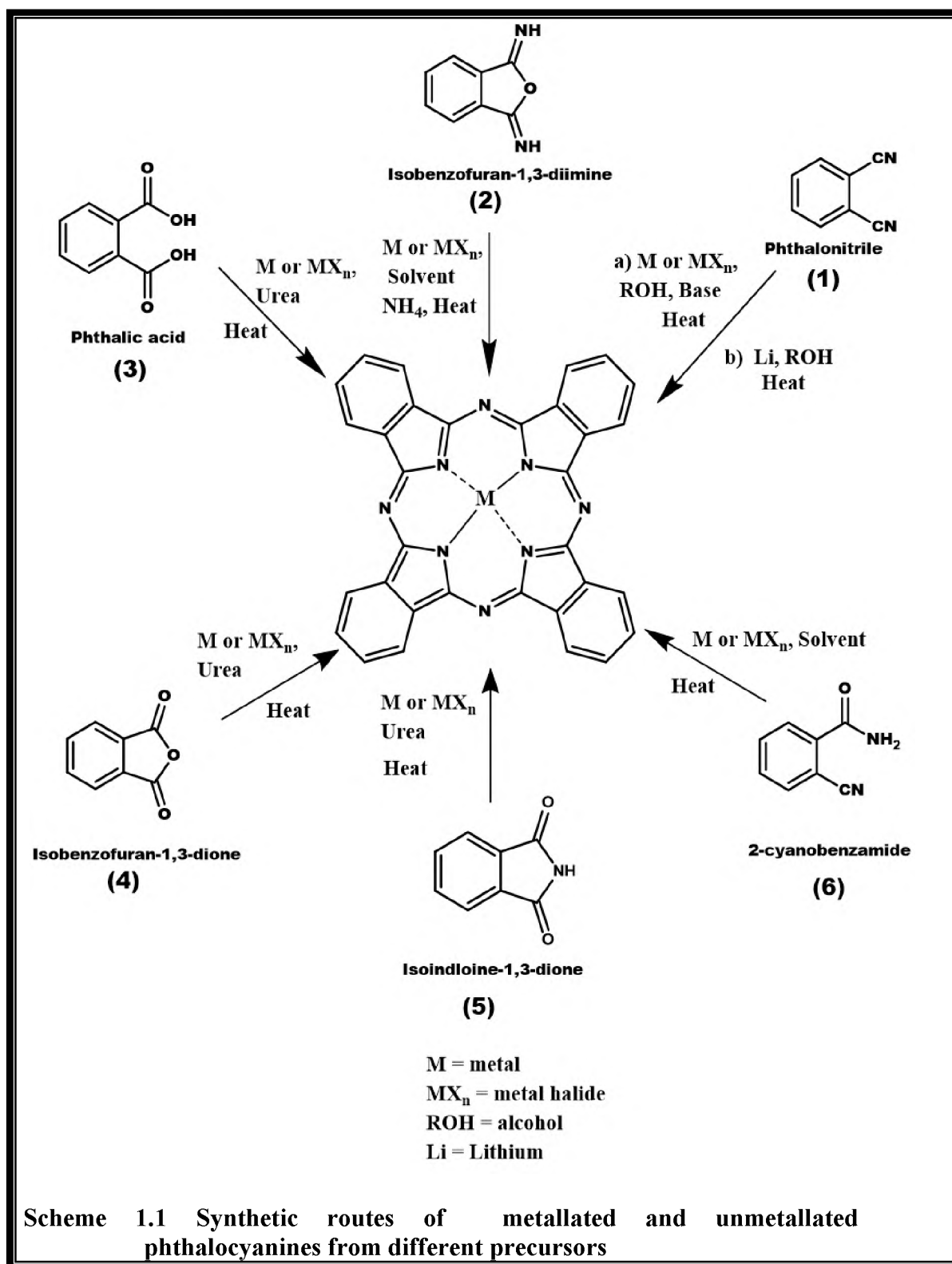
Metallophthalocyanines (MPcs) were first characterized by Linstead and co-workers [1]. MPcs consist of conjugated π -electron aromatic cloud, delocalized over an arrangement of alternating carbon and nitrogen atoms with an extensive delocalized 18π electron system [1–4]. These unique organic pigments have been extensively studied because of their tunable properties and thermal stability. Phthalocyanines also exhibit electrochromic, semiconducting, nonlinear optical and catalytic behavior [5–10]. Reported applications of MPcs include as chemical sensors in Langmuir-Blodgett films [11,12], semiconductors [13], liquid crystals [14] and in dye-sensitized solar cells (DSSC) [2]. The chemical flexibilities of MPcs enable synthesis of various complexes containing diverse substituents (either axial, α -non-peripheral or β -peripheral substitution). Also, the ability to incorporate up to 70 different metal ions or metalloids into the Pc ring is a unique advantage which enables the design of a wide range of chemical structures, capable of meeting specific needs [8].

1.1.2 Synthetic Methods

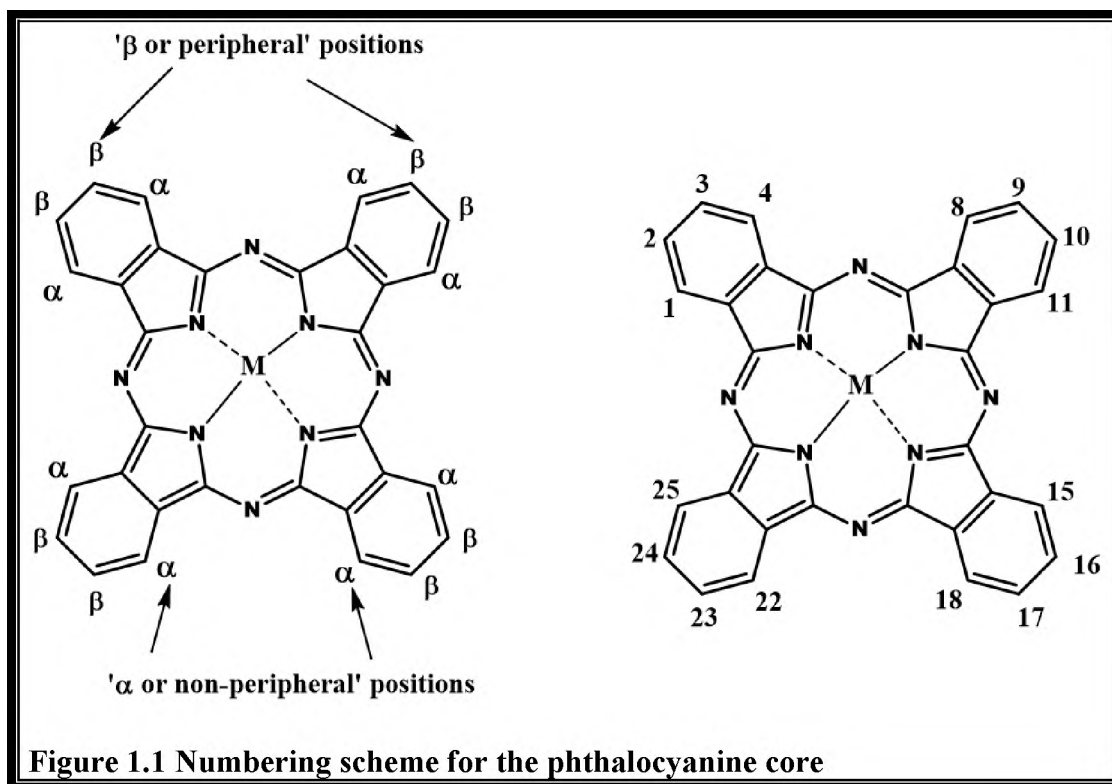
1.1.2.1 Synthesis of Symmetrical Tetrasubstituted MPcs

Synthesis of symmetrical MPcs is achieved by cyclotetramerization of phthalonitrile precursors in the presence of a metal salt (for MPcs), a base such as 1,8-diazabicycloundec-7-ene (DBU) and a suitable solvent such as dimethylformamide (DMF), dimethylsulphoxide (DMSO), hydroquinone or quinoline [15–18]. Pcs can also be obtained by the use of phthalimides, phthalic acids and other precursors such as phthalic anhydrides (**1-6**), **Scheme**

1.1 in the absence of metal for unmetallated Pc and the presence of metal for the metallated counterparts [19,20].



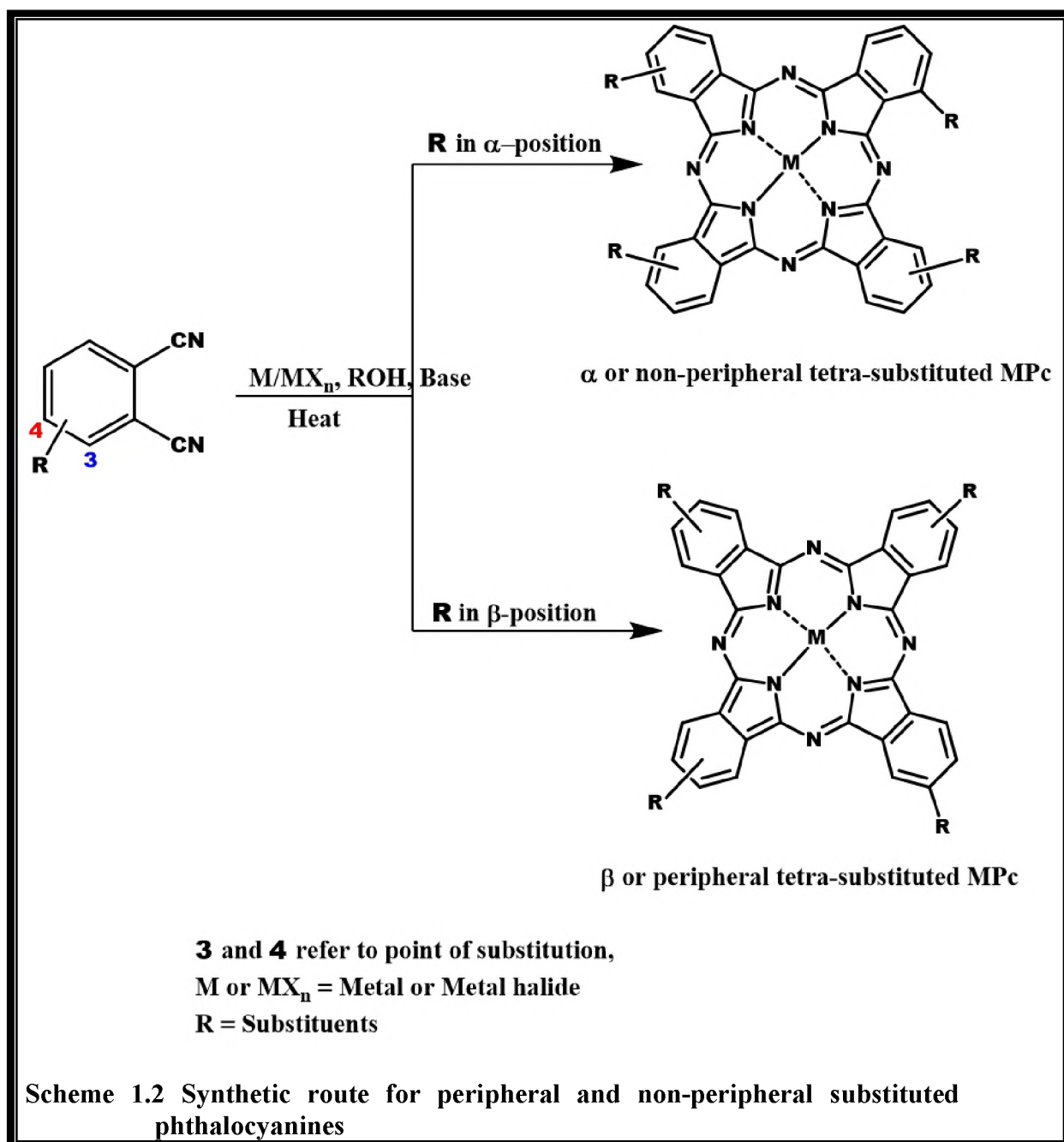
Unmetallated phthalocyanines (H_2Pc) can also be metallated by heating in the presence of metal or metal salt, using aromatic solvents such as 1-chloronaphthalene and quinoline [21]. The non-peripheral positions on the Pc ring are located at 1, 4, 8, 11, 15, 18, 22, and 25 (**Figure 1.1**); designate as α -substituents, while those located at positions 2, 3, 9, 10, 16, 17, 23, and 24 (**Figure 1.1**) are regarded as β -substituents [16,22].



A good yield of phthalocyanines depends on the choice of the precursor, a metal salt, nature of solvents, temperature, base and catalyst [23]. Phthalonitrile is the most useful precursor for designing MPc (**Scheme 1.1**) since it does not require extra nitrogen sources such as urea and a catalyst such as ammonium molybdate or boric acid before a phthalocyanine macrocycle is produced [15]. The non-peripherally (α) substituted phthalocyanines are synthesized from a 3-substituted phthalonitrile while β -substituents (peripheral) MPcs are obtained from 4-substituted phthalonitrile precursor **Scheme 1.2**.

Phthalocyanine solubility is enhanced when it is peripherally or non-peripherally substituted [24–32]. The cationic or quarternized MPcs (bearing hydrophilic moieties such as pyridinium

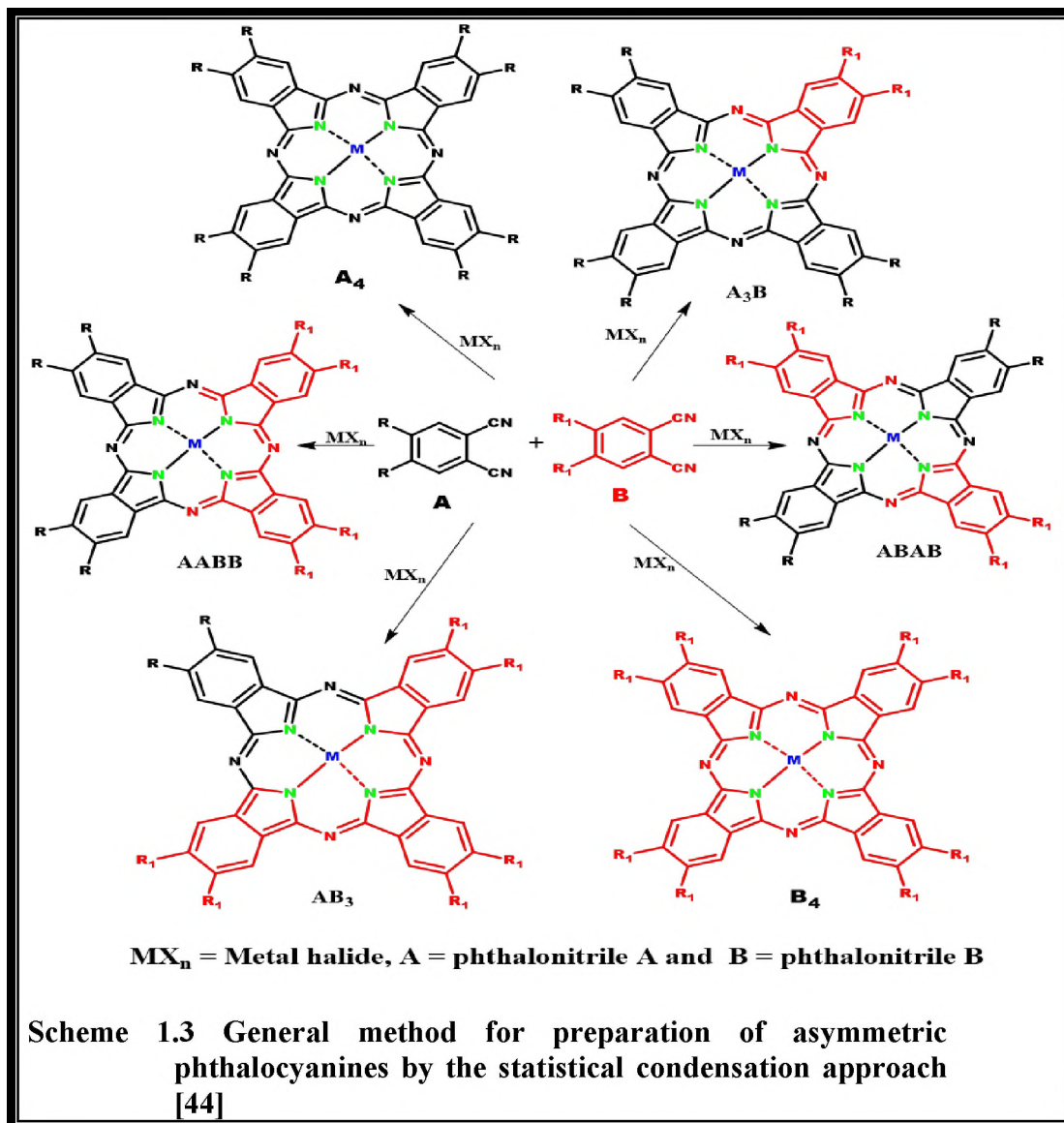
groups) have superior water solubility, low aggregation degree, and high cellular uptake efficiency [33–39].



1.1.2.2 Synthesis of Unsymmetrical MPcs

The synthesis of asymmetrical MPc with particular functional groups at a given position improves properties of the phthalocyanine [40]. The statistical condensation approach is mainly used for the preparation of the A_3B asymmetric phthalocyanine analogs [41–44]. The

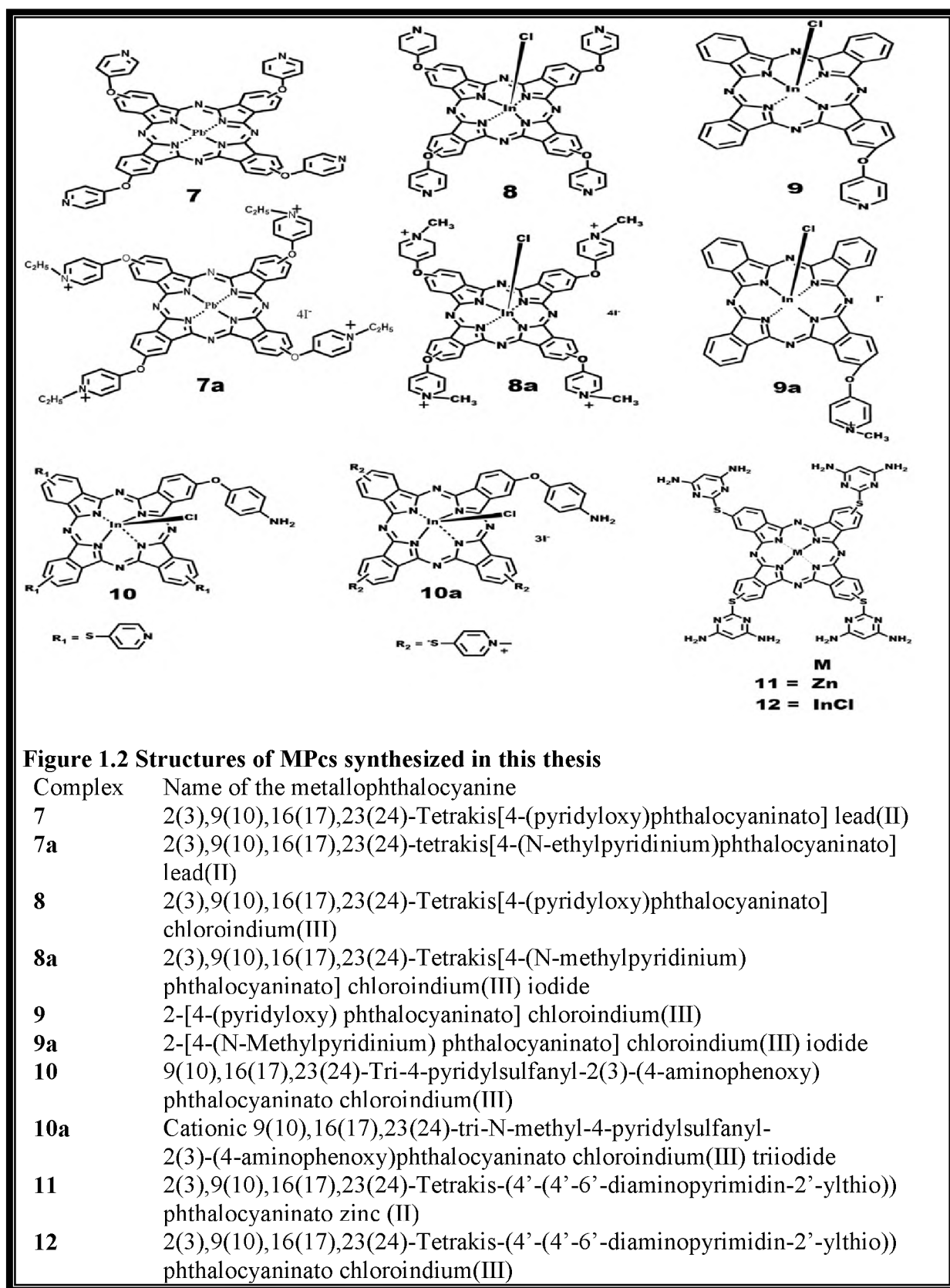
method requires two different substituted phthalonitriles (A and B, **Scheme 1.3**), which upon cyclization reaction give a mixture of six compounds, with the A₃B type Pc being in a good yield, depending on the ratio of the phthalonitriles [42,45,46].



1.1.2.3 Phthalocyanine Molecules Synthesized in This Work

The Pcs used in this work are shown in **Figure 1.2**. Low symmetry Pc have shown improved antimicrobial activity [47] hence are employed in this thesis (**9**, **9a** and **10a**). The substituent employed in this thesis is pyridyl group due to its ease of quaternization which will result in water solubility depending on the number of substituents. The heavy metal ions (Pb and In) are used in this thesis because they encourage intersystem crossing from excited singlet state

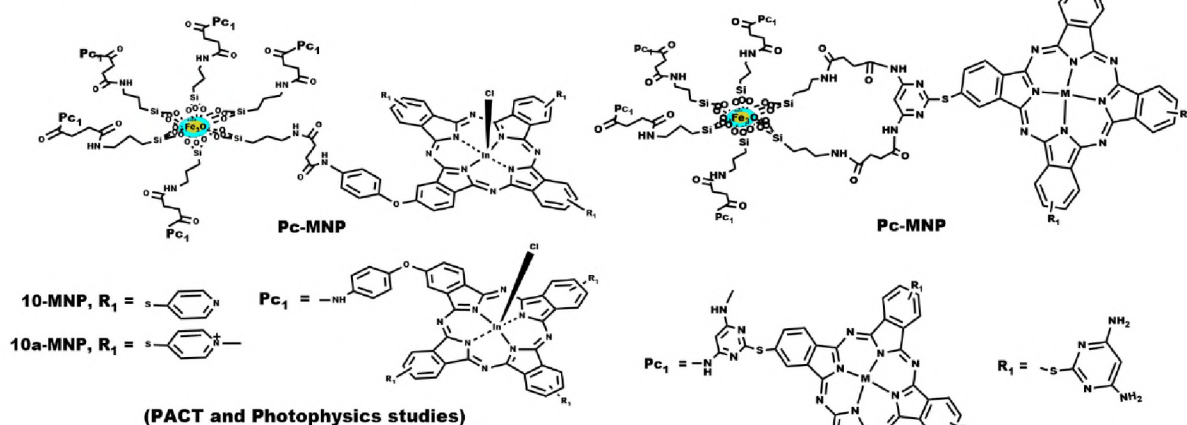
to triplet state thereby enhancing the generation of the needed cytotoxic singlet oxygen and reactive oxygen species.



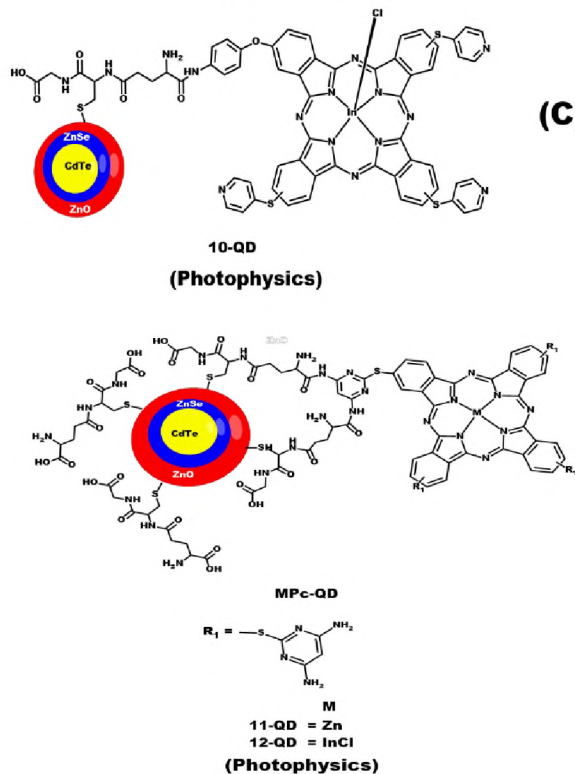
This thesis examines the photochemical or physical behavior of two symmetrically substituted pyridyloxy phthalocyanines containing lead (complex **7** and **7a**) as a central metal ion and compare them to symmetrical **8**, **8a** and asymmetrically substituted **9** and **9a**. All are new compounds. Furthermore, in this work, a new AB₃ type photosensitizer, consisting of 4-pyridylsulfanyl units (denoted as B₃) and one aminophenoxy (denoted as A) group (complex **10**) was synthesized, and its photophysical properties were compared to its cationic derivative (**10a**). The synthesis of 4,6-diaminopyrimidin-2-ylthio substituted phthalocyanines has been reported elsewhere using lutetium and cobalt as the central metal [48–50], this thesis report for the first time on the synthesis and photophysicochemical properties of the 4,6-diaminopyrimidin-2-ylthio substituted phthalocyanines containing zinc (complex **11**) and indium (complex **12**) as central metals.

The unique properties of nitrogen in pyridyl, enable easy quaternization of compounds (**7**, **8**, **9** and **10**) using alkyl halide (ethyl iodide or methyl iodide), hence making the MPcs water soluble. A moiety such as amino group affords the MPcs covalent linkage to carboxylic acid functionalized nanoparticles forming an amide bond. The ability of amino group in forming amide bond allowed the attachment of complexes **10**, **11** and **12** (**Figure 1.3A**), to carboxylic acid functionalized magnetic nanoparticles (MNPs), and glutathione-capped quantum dots (GSH-QD) (**Figure 1.3B**). The MPcs (**11** and **12**) allowed for the attachment of gold nanoparticle (AuNPs) by chemisorption onto the S of N groups (**Figure 1.3C**). All the complexes were fully characterized, and some were electrospun into solid support using polystyrene polymer for studies of either photodynamic antimicrobial chemotherapy (PACT) or photo-oxidation of bisphenol A (BPA) and 4-chlorophenol which will be discussed later in the thesis.

(A) The conjugations of phthalocyanines (10,10a, 11 and 12) to magnetic nanoparticle (MNP)



(B) The conjugations of phthalocyanines (10, 11 and 12) to quantum dot (QD)



(C) The conjugations of phthalocyanines (11 and 12) to gold nanoparticle (AuNP)

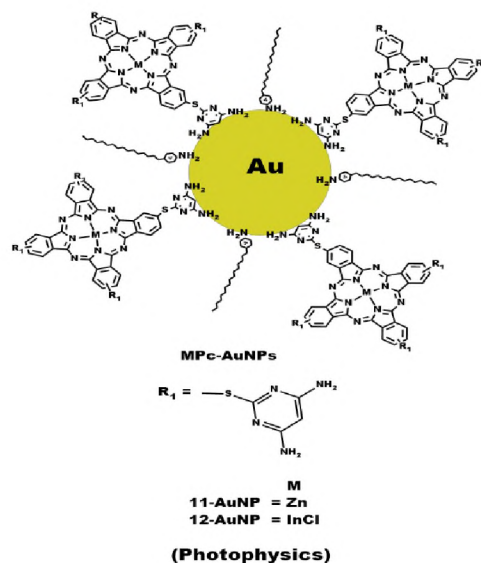
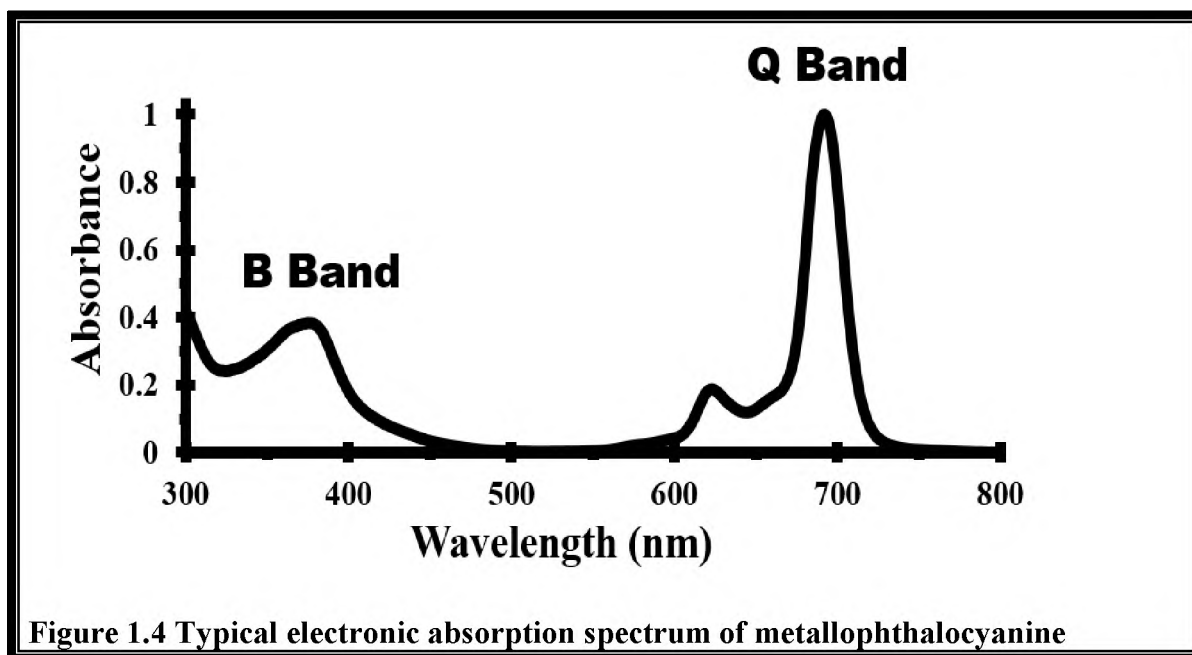


Figure 1.3 Structures of the MPC-NPs conjugates in this thesis.

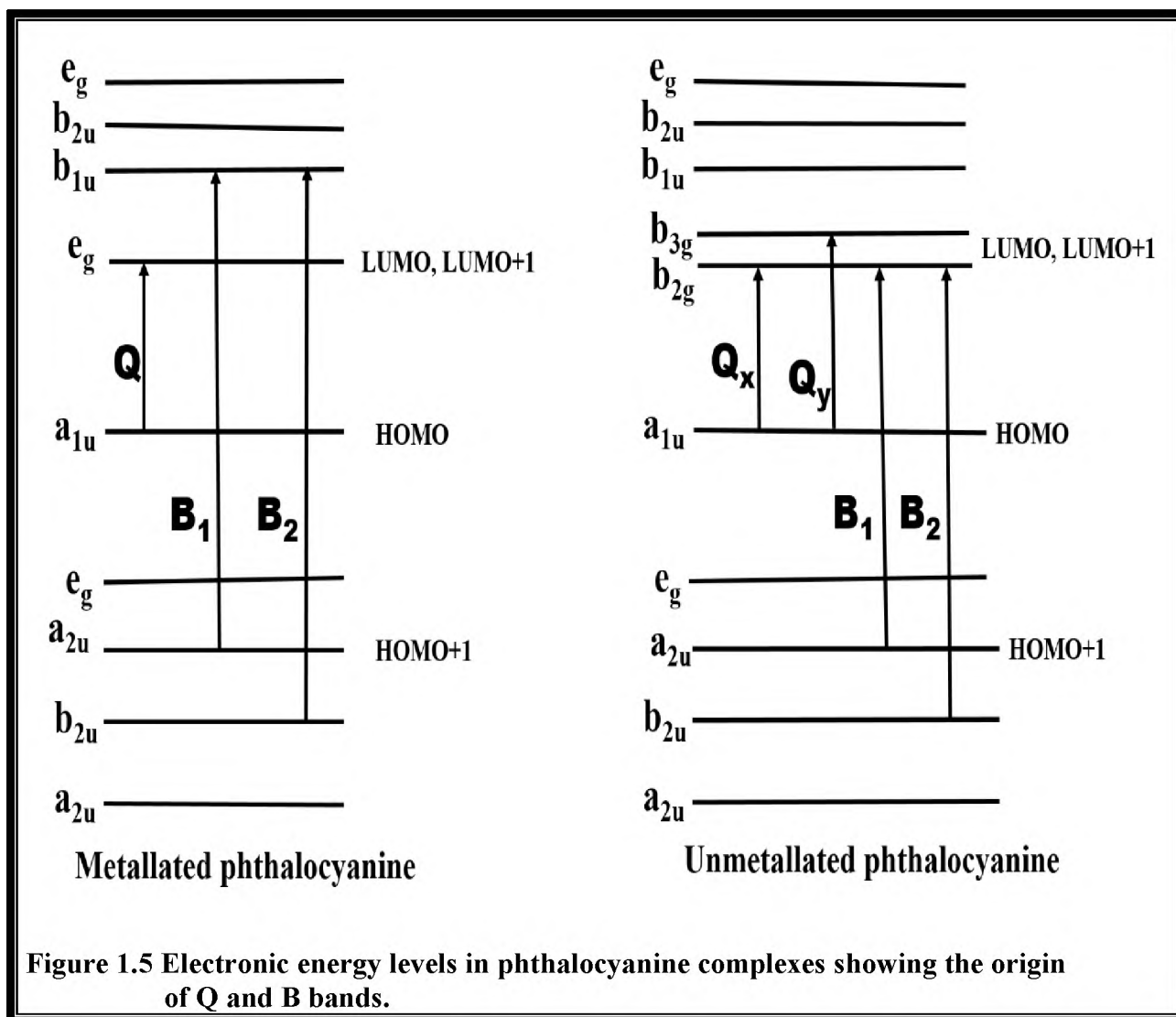
1.1.3 Electronic Absorption Spectra of MPCs

Phthalocyanines consist of intense bands in their absorption spectra (Figure 1.4). The spectral region between 300 - 800 nm for PCs has been grouped into two different areas [51]. The strongest and often conspicuous absorption band which lies in the visible region

generally at wavelengths between 650 to 800 nm in a vast number of phthalocyanines is the Q-band, while the peak observed in the region 300 – 350 nm is recognized as the B-band [52] (consisting of two bands). Metallated MPcs show a single Q-band in the visible range, whereas, for the corresponding metal free Pcs (H_2Pc), a split Q-band is usually observed as a result of their lower symmetry [8].



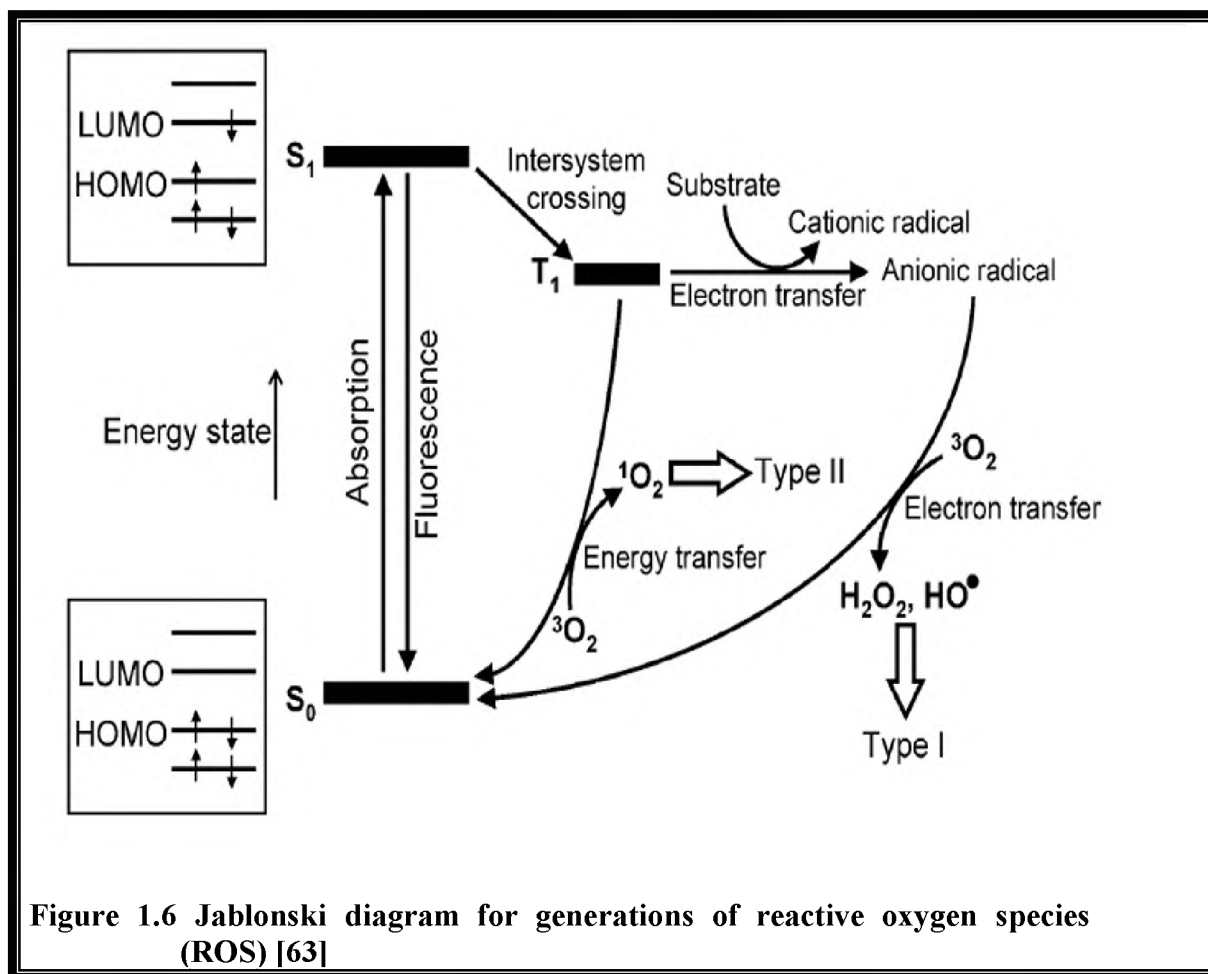
The B bands originates from the a_{2u} or b_{2u} to e_g transitions (**Figure 1.5**) while the Q-band has been reported to be due to excitation between the ground state a_{1u} highest occupied molecular orbital (HOMO) to e_g lowest unoccupied molecular orbital (LUMO) as described by Gouterman's four orbital model [53–56]. The split Q-band observed in unmetallated Pcs is denoted as Q_x and Q_y , which arises from the transitions from the a_{1u} of the HOMO to the non-degenerate b_{2g} and b_{3g} LUMO respectively (**Figure 1.5**). The nature of the central metal and the substituents can influence the position of the Q-band. [57–59].



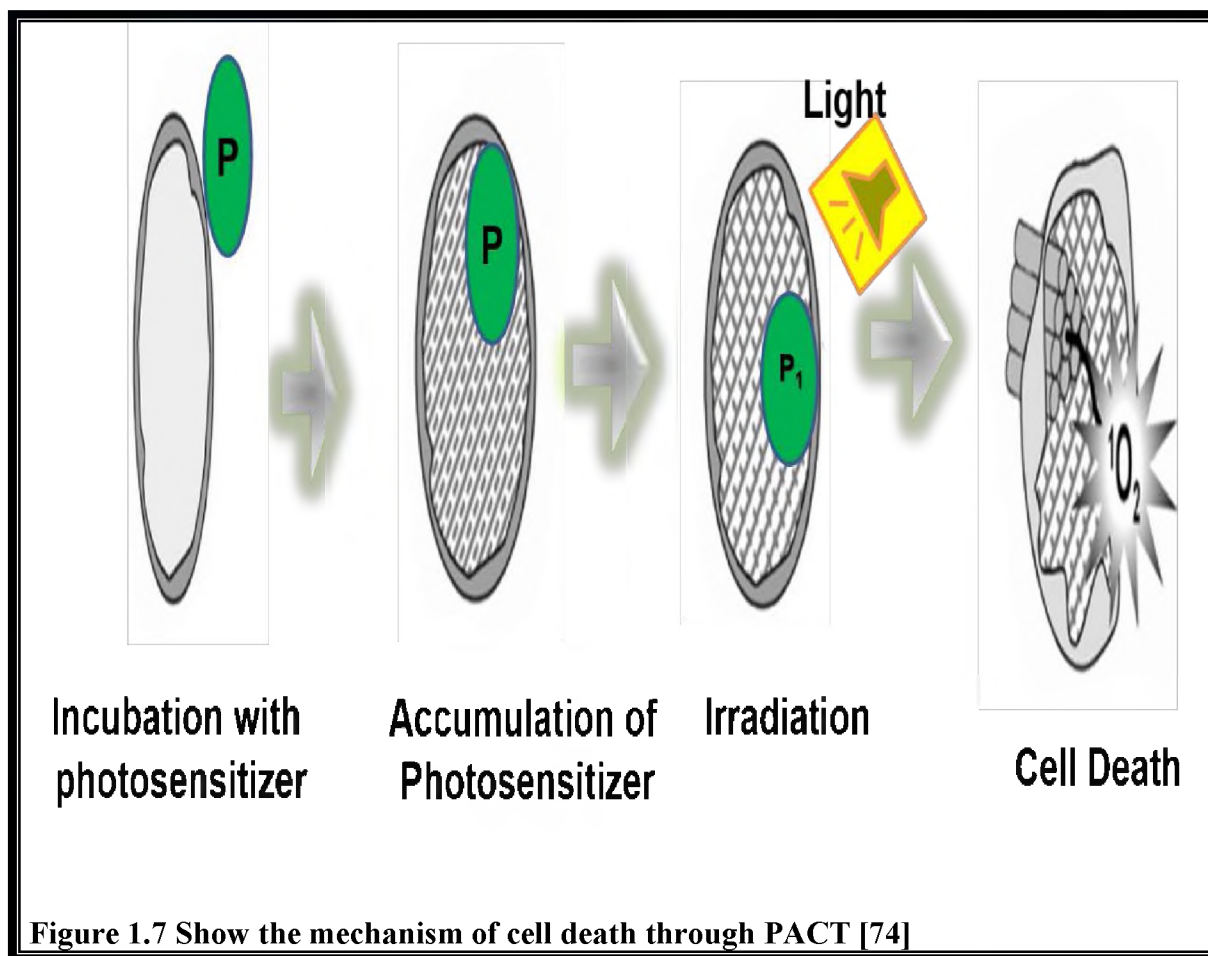
1.2 Photodynamic Antimicrobial Chemotherapy (PACT)

1.2.1 Introduction to PACT

Photodynamic therapy (PDT) consist of a combination of a photosensitizing drug (dye) and light, in the presence of molecular oxygen, to obtain a therapeutic effect. PDT has been proposed as a treatment substitute to complement conventional protocols in the management of malignant tumors and many other non-oncologic diseases [60–62].



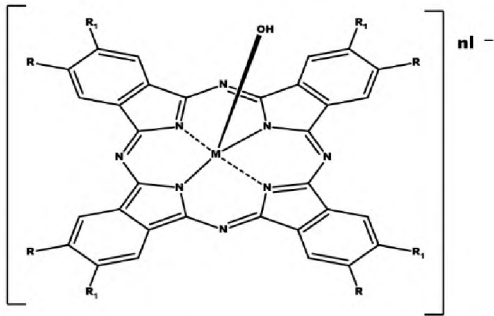
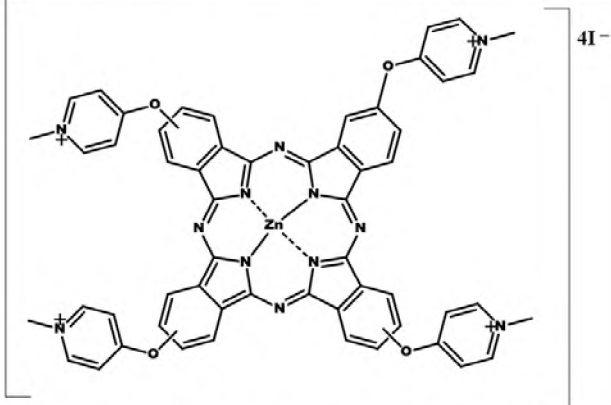
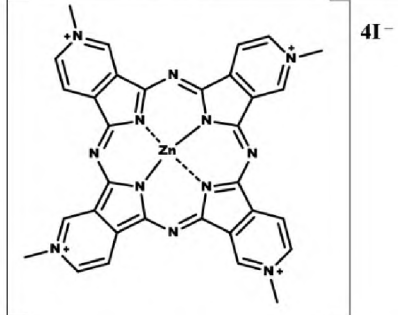
Photodynamic antimicrobial chemotherapy (PACT) is based on the same concept as PDT. A drug localized in microorganisms can be activated by visible light of appropriate wavelength to generate reactive oxygen species (ROS) such as radicals and singlet oxygen through Type I or Type II mechanism, **Figure 1.6** [63] which are cytotoxic to these microorganisms [64–69]. The interest in PACT is increasing due to some bacteria being resistance to routine antibiotics [70–72]. Of interest in this thesis is the use of Pcs and their conjugates (with nanomaterials) as photosensitizers in PACT. The properties (such as increased singlet oxygen quantum yield) exhibited by Pcs and their conjugates makes them excellent photosensitizers [73]. **Figure 1.7** shows the mechanism of cell death during PACT which involves incubation of the photosensitizer allowing their accumulation inside the cytoplasm of the bacteria and upon irradiation, resulting in cell death [74].

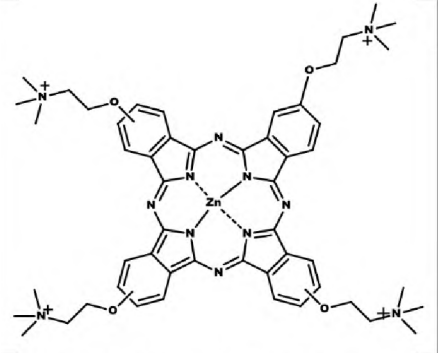
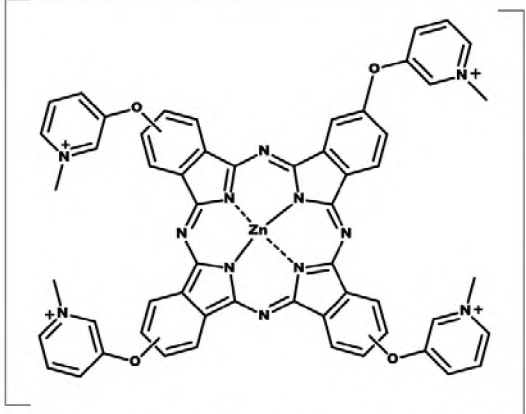
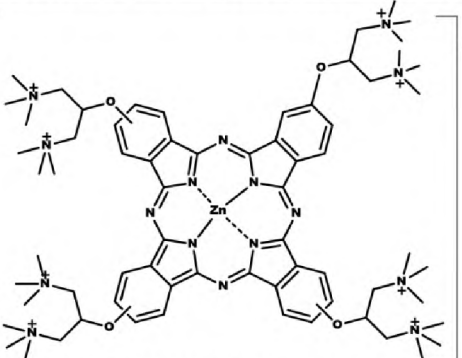
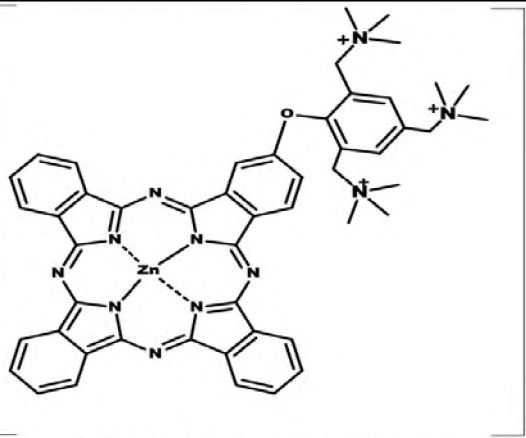


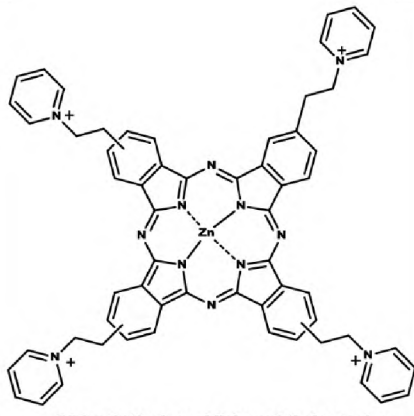
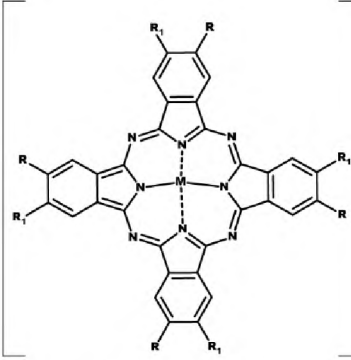
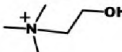
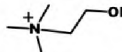
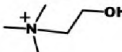
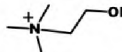
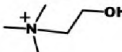
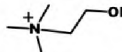
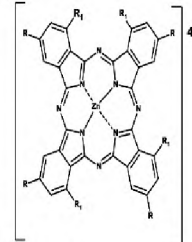
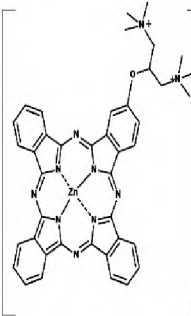
1.2.2 Photosensitizers Used in PACT

Pc derivatives have gained significance in some fields including their use as photosensitizers in PDT of cancer [75–78]. Pcs are efficient photosensitizers for both PACT [65,79] and PDT. Cationic photosensitizers are more active than their anionic and neutral counterparts against Gram (-) bacteria, such as *E. coli* [66,68,80–82], hence cationic (quaternized) metallophthalocyanine derivatives are employed in this work for PACT. Table 1.1 shows quaternized Pcs, which have been used for PACT [66,80,82–91].

Table 1.1 Examples of known quaternized Pcs used for PACT

Compound	Microorganisms	Ref.
 M R R_1 n MPc 1 Ga or In  H 4 MPc 2 Ga or In   8 GaPc 1 = Hydroxy Ga(III) 2,9,16,23-tetrakis-[3-(N methyl)pyridyloxy] phthalocyanine tetraiodide GaPc 2 = Hydroxy Ga(III) 2,9,16,23-octakis-[3-(N methyl)pyridyloxy] phthalocyanine tetraiodide InPc 1 = Hydroxy In(III) 2,9,16,23-tetrakis-[3-(N methyl)pyridyloxy] phthalocyanine tetraiodide InPc 2 = Hydroxy In(III) 2,9,16,23-octakis-[3-(N methyl)pyridyloxy] phthalocyanine tetraiodide	<i>Staphylococcus aureus</i> <i>Enterococcus faecalis</i> <i>Candida albicans</i>	[66] [82]
 ZnPPc4+ = Zinc(II) 2,9,16,23-tetrakis[4-(N-methylpyridyloxy)]-phthalocyanine iodide	<i>Escherichia coli</i>	[80,83,84]
 ZnTpyPc4+ = Zinc(II) tetramethyltetrapyrroline porphyrin iodide	<i>Escherichia coli</i> <i>Streptococcus mitis</i>	[84]

 ZnEPc⁴⁺ = Zinc(II) 2,9,16,23-tetrakis[2-(N,N,N trimethylamino)ethoxy] phthalocyanine iodide iodide	<i>Escherichia coli</i> <i>Streptococcus mitis</i>	[84]
 ZnPcMe = Zinc(II) tetrakis-(3-methylpyridinium)-phthalocyanine	<i>Staphylococcus aureus</i> <i>Pseudomonas aeruginosa</i> <i>Candida albicans</i>	[85]
 [2(3),9(10),16(17),23(24)-tetrakis[1,3-bis(N,N,N-trimethylammonium)-2-propyloxy]phthalocyaninato] zinc(II) iodide	<i>Staphylococcus aureus</i> <i>Escherichia coli</i>	[86]
 2-[2,4,6-tris(trimethylammoniummethyl)phenoxy]phthalocyaninatozinc(II) triiodide	<i>Staphylococcus aureus</i> <i>Escherichia coli</i> <i>Pseudomonas aeruginosa</i> <i>Staphylococcus epidermidis</i>	[87]

 PPC = Cationic pyridinium phthalocyanine	<i>Escherichia coli</i> <i>Pseudomonas aeruginosa</i> <i>Enterococcus seriolicida</i>,	[88,89]																				
 <table><thead><tr><th></th><th>M</th><th>R</th><th>R₁</th><th>n</th></tr></thead><tbody><tr><td>(MPcPym)₄</td><td>Zn or AlCl₃</td><td></td><td>H</td><td>4</td></tr><tr><td>(MPcPym)₈</td><td>Zn or AlCl₃</td><td></td><td></td><td>8</td></tr><tr><td>(MPcChol)₈</td><td>Zn</td><td></td><td></td><td>8</td></tr></tbody></table> ZnPcPym⁴⁺ = Zinc (II) tetrakis-(pyridiniummethyl) chlorophthalocyanine ZnPcPym⁸⁺ = Zinc (II) octakis-(pyridiniummethyl) chlorophthalocyanine AlClPcPym⁴⁺ = Chloroaluminium tetrakis-(pyridiniummethyl) phthalocyanine AlClPcPym⁸⁺ = Chloroaluminium octakis-(pyridiniummethyl) phthalocyanine ZnPcChol⁸⁺ = Zinc (II) octakis-(cholinyl) chlorophthalocyanine		M	R	R ₁	n	(MPcPym) ₄	Zn or AlCl ₃		H	4	(MPcPym) ₈	Zn or AlCl ₃			8	(MPcChol) ₈	Zn			8	<i>Proteus mirabilis</i> <i>Escherichia coli</i> <i>Salmonella enteritidis</i>	[90]
	M	R	R ₁	n																		
(MPcPym) ₄	Zn or AlCl ₃		H	4																		
(MPcPym) ₈	Zn or AlCl ₃			8																		
(MPcChol) ₈	Zn			8																		
  β-ZnPc α-ZnPc Cationic Zinc, [2-[(29H,31H-phthalocyanin-2-yl-$\kappa N^{P2}, \kappa N^{P3}, \kappa N^{P1}, \kappa N^{P2}$)oxy]-N',N',N',N'-tetramethyl-1,3-propanediaminato(2-)]-iodide β-ZnPc = Cationic Zinc, [(3,3',3'',3''')-(29H,31H-phthalocyanine-1,8,16,25-tetrayl-$\kappa N^{P2}, \kappa N^{P3}, \kappa N^{P1}, \kappa N^{P2}$)tetrakis(oxy)] tetrakis[N,N-dimethylbenzenaminato]] α-ZnPc = Cationic Zinc, [(3,3',3'',3''')-(29H,31H-phthalocyanine-2,9,16,23-tetrayl-$\kappa N^{P2}, \kappa N^{P3}, \kappa N^{P1}, \kappa N^{P2}$)tetrakis(oxy)] tetrakis[N,N-dimethylbenzenaminato]]	<i>Candida albicans</i>	[91]																				

As shown in the Table, many symmetric quaternized Pcs have been employed, compared to limited asymmetric quaternized Pc. Asymmetric MPcs are known to improve intersystem crossing to the triplet state [40], where needed cytotoxic singlet oxygen species [92] are generated. Thus, asymmetric complexes **9**, **10** and their quaternized form (**9a** and **10a**) are used in this work. There have been no studies of PACT in the presence of MNPs, the later enhances intersystem crossing, but also allows for separation following use. The PACT study using quaternized Pcs embedded in electrospun fiber has not been reported before, and this was done for the first time in this thesis.

1.3 Photo-oxidation of Environmental Pollutants

Photocatalytic oxidation of pollutants using molecular oxygen is one of the most important methodologies, since it does not liberate any additional pollutants, hence it is employed in this work for degradation or phototransformation of bisphenol A (endocrine disrupting chemical) and 4-chlorophenol. Endocrine disrupting chemicals (EDCs) are exogenous substances or mixture that alter the functions of the endocrine system and consequently causes adverse health effects [93,94]. EDCs are emerging man-made pollutants in water [95]. Bisphenol A (BPA) has been demonstrated to have endocrine disrupting effects [96]. On the other hand, phenolic compounds are common environmental contaminants as by-products of numerous manufacturing products such as pesticides, pharmaceuticals, plastics and dyes [97]. There are many reported methods of removal of EDC and chlorophenol from water, such as biological, chemical oxidation, electrochemical oxidation and photocatalytic processes [98]. The application of photosensitized oxidation processes may be considered as one of the emerging green technologies for water treatment, due to the possibility of using two natural resources: dissolved oxygen and solar energy. MPc containing non-transition metals have proved to be good photocatalysts for the degradation of a wide range of pollutants including chlorophenol and BPA [98–100]. Singlet oxygen generated by photoexcited Pc is a

particularly good candidate for these applications. However, some disadvantages should be overcome, such as the need to recover the dissolved sensitizer from the treated water. Photochemical transformation of chlorophenol using phthalocyanines embedded in fibers has been reported but using symmetrical Pcs [101–107]. Also, photodegradation of 4-chlorophenol using anionic resin-immobilized AlPc tetra-sulfonated has been reported elsewhere [108]. This work reports for the first time on the use of asymmetric cationic phthalocyanine embedded in electrospun fibers for the degradation of BPA and 4-chlorophenol.

1.4 Nanoparticles

In this work Pcs are linked to QDs, magnetic nanoparticles (MNPs) or gold nanoparticles (AuNPs) for photophysical and MNP for PACT studies. **Figure 1.3** shows the conjugates employed and studies carried out.

1.4.1 Magnetic Nanoparticles (MNPs)

Magnetic nanoparticles are non-toxic, biocompatible, injectable and have a high-level accumulation in the target tissue or organ hence are suitable for medical applications [109]. Magnetic nanoparticles have potential for use in various fields such as magnetic resonance imaging, hyperthermia, drug delivery and cell separation [110–113].

The route for MNPs synthesis are top down or physical methods such as breaking bulk materials to the desired size distribution and bottom-up approach or chemical route such as co-precipitation [114–116]. The chemical route is employed in this work due to its capability to produce consistent particles with a uniform shape and small size dispersion in less time than the physical process [117]. The co-precipitation method is the most common and simplest route for synthesizing MNPs [116]. By increasing the pH (8-14) of an aqueous solution of ferrous and ferric salt in an inert atmosphere, magnetite precipitates [116,118]. MNPs have been linked to Pcs for the photocatalytic application or photophysical studies

Table 1.2A [119–130]. The table shows that MNP-Pc conjugates have been used as photosensitizers for applications such as in PDT and photocatalysis. This thesis reports for the first time on their use for PACT. Conjugates of **10** and **10a** with MNPs are employed for PACT while MNPs conjugates to **11** and **12** are employed for photophysical studies only.

1.4.2 Quantum Dots (QDs)

QDs are zero-dimensional inorganic semiconductive fluorescent nanoparticles that are 1-20 nm in size. The small size of the semiconductor QDs enables them to provide a higher surface to volume ratio [131]. Hence, QDs have been widely used in numerous application including imaging [132–134], diagnostics and PDT therapy [135–137]. QDs have unique optical properties that can be tuned from the UV to the infrared region by changing their size and composition [137,138]. QDs improve triplet state parameters of phthalocyanines [139,140] due to the heavy atom effect. QDs transfer energy to Pcs through Förster resonance energy transfer (FRET) [132,137,139–143]. Many Pcs have been linked to QDs. A selection of conjugates is shown in Table 1.2B [119,141,144–146]. This work report for the first time on the photophysical properties of QDs conjugated to asymmetric InPc. QDs are also fluorescent. Hence, imaging is possible when linked to phthalocyanines. Complexes **11** and **12** are linked to QDs (**Figure 1.3B**), via amide bond for photophysical studies.

1.4.3 Gold Nanoparticles (AuNPs)

Au nanoparticles (AuNPs) have attracted considerable attention in the fields of electronics, catalysis, and biosensors because of their high active surface area, excellent catalytic properties and their ability to enhance electrode conductivity [147]. AuNPs have tuneable optical properties, which depend on the size, shape and capping agent [148–150]. AuNPs are known to enhance intersystem crossing, and accumulation (into tissue) of photosensitizers [151] hence are of importance in this work. AuNPs have been linked to Pcs for PDT and

photophysical studies, Table 1.2C [152–158]. AuNPs are linked to complex **11** and **12** (Figure 1.3C) for photophysical studies. Adsorption could be through NH₂ or S group; NH₂ is shown in **Figure 1.3C**.

Table 1.2 Some examples of phthalocyanine nanoparticles conjugates use for PACT

Phthalocyanines	Applications	Ref.
(A) MPc-MNP Conjugates		
Indium octacarboxy phthalocyanine (ClInPc(COOH) ₈)	Photophysics Multi-Functional Quantum Dots-Magnetic Nanoparticles	[119]
Zinc pyridyloxy phthalocyanine-MNPs	Photophysics parameters	[120]
Zinc octacarboxy phthalocyanine-MNPs	Photodegradation of azo dye (Orange-G)	[121,127]
2,9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)phthalocyaninato indium(III)chloride	Nonlinear optic	[122]
Silicon-phthalocyanine-MNPs	PDT and Hyperthermia	[123,124]
Zinc-phthalocyanine-MNPs		[125]
Aluminium-phthalocyanine-MNPs Aluminium-phthalocyaninetetrasulfonate-MNPs		[126]
Cu(II) phthalocyanine-tetrasulfonic acid tetrasodium	epoxidation of olefins and oxidation of hydrocarbons and sulfides	[128]
Aluminium-tetracarboxyphthalocyanine-folate-MNPs	Imaging/ cell targeting/ drug delivery & PDT	[129]
Copper-phthalocyaninetetrasulfonate- MNPs	Photodegradation of Rhodamine B and methyl orange	[130]
(B) MPc-QDs Conjugates		
Indium octacarboxyphthalocyanine (ClInPc(COOH) ₈)	Photophysical properties	[119,141]
2,9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)phthalocyaninato indium(III) chloride(InPc)	Nonlinear optic	[144]
Indium tetracarboxyphenoxy phthalocyanines ((OH)InTCPPc)	Photophysical properties	[145]
Indium tetraamino phthalocyanines(InTAPc)	Photophysical properties	[146]
(C) MPc-AuNPs Conjugates		
Pc-4	drug and gene delivery	[152]
1,4,8,11,15,18-Hexahexyl-22- methyl-25-(11-	PDT	[153,154]

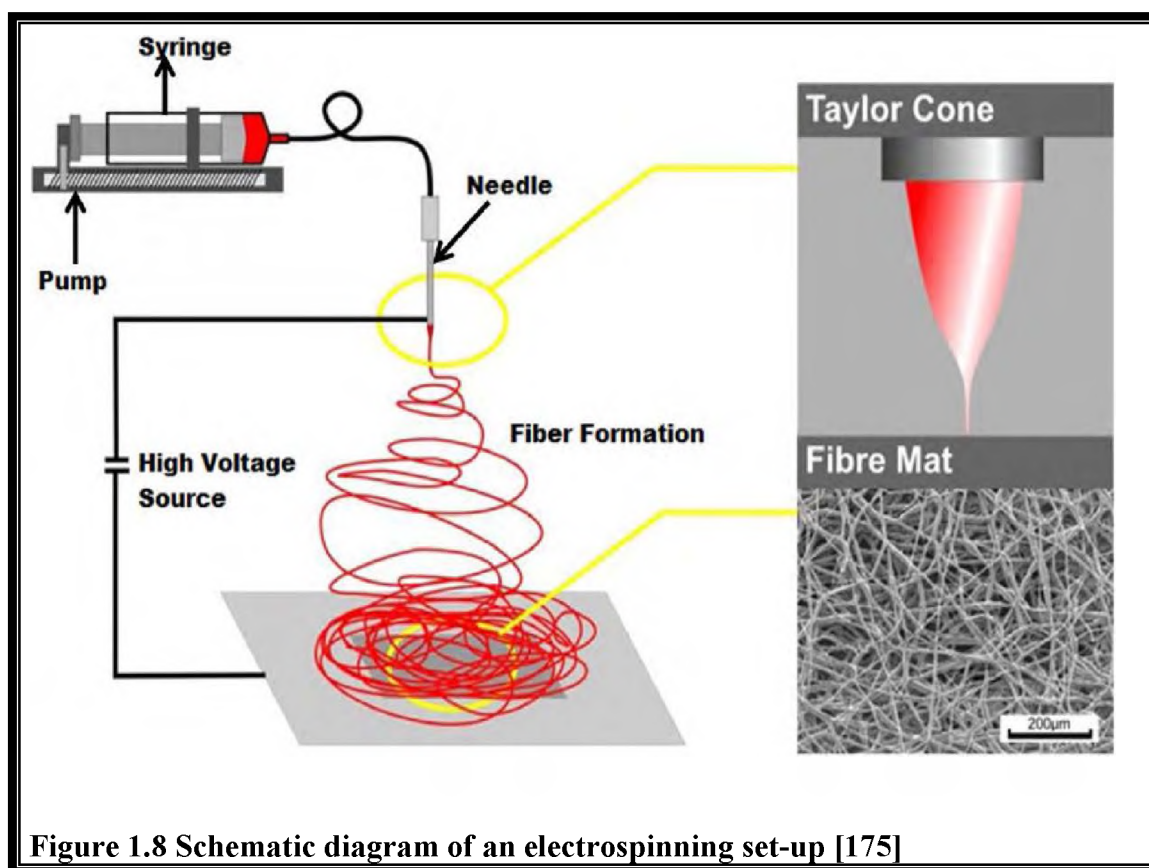
mercaptoundecyl phthalocyaninato zinc		
2,9(10),16(17),23(24)-tetrakis2,(3)[(1,6-hexanedithiol) phthalocyanine]zinc(II)	Photophysical and photochemical properties	[155]
2,(3)-[tetra-(mercaptoacetic acid phthalocyaninato) zinc(II)] 2,(3)-[tetra-(mercaptopropanoic acid phthalocyaninato) zinc(II)]	Photophysical and photochemical properties	[156]
1,(4)-(2-Mercaptopyridine)phthalocyaninato titanium (IV) oxide 2,(3)-(2-Mercaptopyridine)phthalocyaninato titanium (IV) oxide 2,(3)-(2-Mercaptopyridine)phthalocyaninato tantalum (V) hydroxide	Photocatalytic oxidation of cyclohexene	[157]
1,4,8,11,15,18,22,25-Octaoctylthiophthalocyaninato tantalum (V) butoxide	Photocatalytic oxidation of cyclohexene	[158]

1.5 Electrospinning

1.5.1 Basics of Electrospinning

Formhals invented electrospinning technique in 1934 [159]. Electrospinning is a specialized process of fabricating reproducible submicron-sized nanofibers. In electrospinning, a high voltage is applied to a polymer fluid such that charges are induced within the fluid. When a charged polymer solution is fed through the spinneret under an external electric field, a fluid jet will erupt from the droplet resulting in the formation of a Taylor cone (a suspended conical droplet, which is formed due to applied electrostatic force overcoming the surface tension of the polymer) [160–166] **Figure 1.8**. It is also possible to create nanofibers with different morphology by varying the parameters [164,167–169]. Electrospinning is a promising and highly flexible technique for incorporation of functional molecules (such as phthalocyanines) into solid polymer fiber supports. Parameters such as solution concentration and molecular weight of the polymer [170,171] can be fine-tuned to obtain fibers of varying diameters to meet the requirements for different applications with the functionality of the

phthalocyanines maintained in the solid fiber core [172]. Specifically, the technique is a unique and cost-effective approach for fabricating fibers with large surface area for a variety of sensor applications [173,174]. Other variables in the electrospinning process include solvent volatility, tip to collector distance (TCD) and magnitude of the voltage supplied. Other factors include temperature, humidity of the environment and nature of substance added to the polymer solution [175].



There are various known applications of modified electrospun fiber among which are: protective clothing [176,177], sensors [106,178–180], drug delivery system [181–184], wound dressings [185] and scaffolding [186]. Phthalocyanines have been embedded in electrospun polymer fibers without separation of the phthalocyanine from the fiber during electrospinning [47,101,107,121,187–194] and with the photoactivity of the Pcs maintained within the polymer fiber.

1.5.2 Phthalocyanines Which Has Been Embedded in Fibers and Application

In this work, phthalocyanines are embed in electrospun fibers as a solid support and for ease of recovery. Table 1.3 gives some examples of work reported in the literature where phthalocyanines are embedded in polymers for various applications. The reported embedded Pc utilized for PACT [47] contained Ge, Ti, and Sn as metal ions. This work reports on low symmetry Pc containing heavy In atom which will improve singlet oxygen generation. Also, this thesis reports another novel initiative with the embedding of cationic (water soluble) asymmetric and symmetric phthalocyanines in polystyrene polymer for photo-oxidation of pollutants and antimicrobial photodynamic inactivation, respectively.

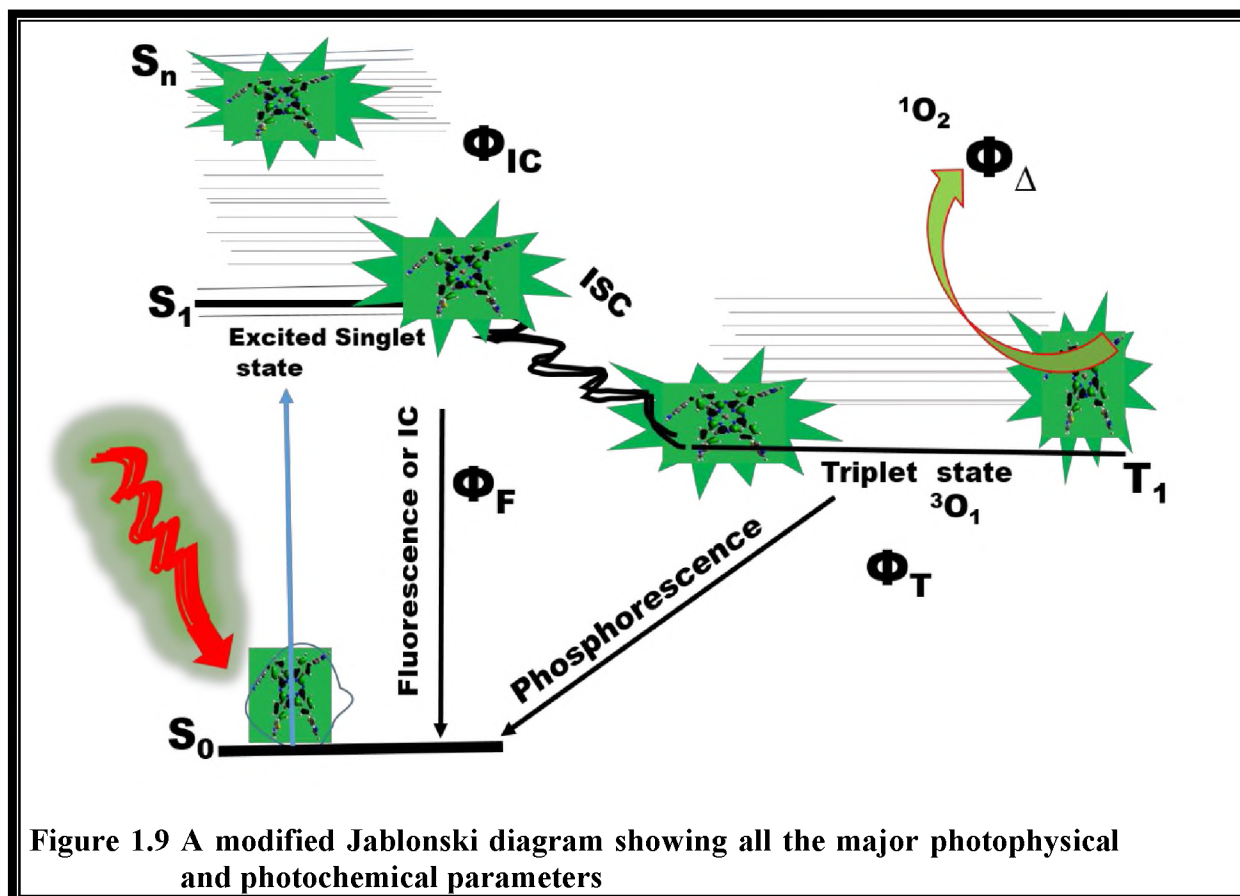
Table 1.3 Examples of known electrospun nanofibers functionalized with phthalocyanines and their applications.

MPcs	Support system	Application	Ref.
(OH) ₂ GeMCPc (OTi)MCPc (ac) ₂ SnMCPc	Polystyrene	PACT	[47]
CuTsPc	Polyvinyl alcohol (PVA)-sodium alginate (SA)	water splitting	[102]
CuTcPc	polyvinyl alcohol(PVA)-sodium alginate (SA)	water splitting	[102]
CuTAPc	polyvinyl alcohol-chitosan	water splitting	[102]
LuTPPc	Polyurethane polymer Polystyrene Polymer	Photoconversion of 4-chlorophenol Photoconversion of 4-nitrophenol	[101,103] [104]
LuTPyPc	Polystyrene Polymer Polysulfone polymer Polyacrylic acid	Photoconversion of 4-nitrophenol and methyl orange	[104] [105]
LuTAPc	Polyacrylic acid	NO ₂ gas sensing	[106]
CoTAPc	Cellulose fiber	Photoconversion of Reactive Red X-3B	[107]

TPPc = tetraphenoxy phthalocyanine, TPyPc = Tetrapyridyloxy phthalocyanine, TAPc = tetraamino phthalocyanine, TNPc = Tetrinitro phthalocyanine, TcPc = Tetracarboxy phthalocyanine, TsPc = Tetrasulfonic acid phthalocyanine, MCPc = Monocarboxy phthalocyanine

1.6 Photophysical and Photochemical Parameters

When the light of appropriate wavelength is absorbed by MPcs, physical changes that are described by the Jablonski diagram [195] shown in **Figure 1.9** are observed.



When an MPc absorbs a photon, it is excited from ground state (S_0) to the excited state (S_1); the molecules undergo a non-radiative vibration within the excited state electronic level (S_1) where its presence is short-lived due to the collisions. The excited molecule (MPc)* can either dissipate energy by emitting light through fluorescence (F) or by releasing heat to the surrounding via internal conversion (IC), or undergoes intersystem crossing (ISC) to the excited triplet state T_1 .

The lifetime of the T_1 state is long. Hence, it allows phthalocyanines in the T_1 state to interact with molecular oxygen to generate ROS via two pathways [196]. Type I reactions uses electron transfer to form the cytotoxic radicals while Type II results in the formation of

singlet oxygen, **Figure 1.6**. MPcs containing non-transition metals have proved to be suitable photosensitizers for Type II processes, this is because they have high triplet quantum yield coupled with longer triplet lifetimes [197].

1.6.1 Fluorescence Quantum Yield (Φ_F) and Lifetime (τ_F)

The fluorescence quantum yield (Φ_F) this is defined as the ratio of photons absorbed to photons emitted through fluorescence. The quantum yield is the probability of the excited state being deactivated by fluorescence [198]. The fluorescence quantum yields (Φ_F) may be determined using comparative methods [199], Equation 1.1 and ZnPc is used as a standard ($\Phi_F = 0.20$ in DMSO [200]) and ($\Phi_F = 0.3$ in DMF [201]).

$$\Phi_F = \Phi_F^{std} \frac{F A_{std} n^2}{F_{std} A n_{std}^2} \quad (1.1)$$

where F and F_{std} are the areas under the fluorescence emission curves of the sample and the standard, respectively. A and A_{std} are the respective absorbances of the sample and standard at the excitation wavelength. The fluorescence quantum yield in water was determined using AlSmixPc (a mixture of differently substituted aluminium sulfonated phthalocyanines) as the standard ($\Phi_{F(std)} = 0.44$ in aqueous media [202]). For excitation where QDs absorb, the fluorescence quantum yields in water were determined using Rhodamine 6G as the standard ($\Phi_F (Std) = 0.95$ in ethanol [195]). The fluorescence quantum yields of the QDs in the conjugates ($\phi_{FQD}^{Conjugate}$) with MPc were calculated using Equation (1.2),

$$\Phi_{F(QD)}^{Conjugate} = \Phi_{F(QD)} \frac{F_{QD}^{Conjugate}}{F_{QD}} \quad (1.2)$$

where $\Phi_{F(QD)}$ represents the fluorescence quantum yield of the QDs alone and was used as a standard, F_{QD} is the fluorescence intensity of the QDs alone, $F_{QD}^{Conjugate}$ represent the QDs fluorescence intensity of the quantum dots in the conjugate.

Fluorescence lifetimes are usually of the order of nanoseconds (10^{-9} s). Several techniques are available for the determination of fluorescence lifetimes [203–205]. In this work, the time-correlated single photon counting (TCSPC) technique is used [206–208]. Pcs were studied in the presence of nanomaterials such as QDs, MNPs, and AuNPs.

The Förster resonance energy transfer (FRET) efficiency (Eff) between QDs and MPc was obtained using the fluorescence lifetime of the donor (QD) in the absence (τ_A) and presence (τ_P) of the acceptor, using Equation 1.3 [195,209–211].

$$Eff = 1 - \frac{\tau_P}{\tau_A} \quad (1.3)$$

In Equation 1.3, the amplitude weighted average lifetimes (τ) were used and were obtained via Equation 1.4; [195,209–211]

$$\tau = \sum_i \alpha_i \tau_i \quad (1.4)$$

where α_i is the relative amplitude contribution to the lifetimes (τ).

The donor-acceptor distance r (Å), is extrapolated from the Equation 1.5 [195,209–211]

$$Eff = \frac{R_0^6}{R_0^6 + r^6} \quad (1.5)$$

where R_0 is 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 and it is quantified using Equation 1.6. [195,209–211]

$$R_0^6 = 8.8 \times 10^{23} \kappa^2 n^{-4} \Phi_F^{QD} J \quad (1.6)$$

where κ^2 is the dipole orientation factor (the value in liquid media is given as 2/3), n is the solvent's refractive index, Φ_F^{QD} is the donor quantum yield and J (cm^6) is the Förster overlap integral defined by Equation 1.7

$$J = \int f_{QD}(\lambda) \epsilon_{MPc}(\lambda) \lambda^4 d\lambda \quad (1.7)$$

where f_{QD} is the normalized QD emission spectrum, ε_{MPc} is the molar extinction coefficient ($M^{-1} cm^{-1}$) of the MPc and λ is the wavelength (nm) at the absorption maximum of the acceptor i.e the Q-band.

1.6.2 Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T)

The triplet quantum yield is defined as the number of molecules that successfully undergo intersystem crossing from excited singlet state to triplet excited state per quanta of light. The length of resident time of the photons in the triplet state is known as triplet lifetime (τ_T). The triplet quantum yields were determined in DMSO and DMF using a comparative method [99], and ZnPc as a standard in DMSO (Φ_T 0.65 [99]), using Equation 1.8

$$\Phi_T = \Phi_T^{Std} \frac{\Delta A_T \varepsilon_T^{Std}}{\Delta A_T^{Std} \varepsilon_T} \quad (1.8)$$

where ΔA_T^{Std} and ΔA_T are the changes in the triplet state absorbances of the standard and the sample, respectively, Φ_T^{Std} is the triplet quantum yield for the standard. ε_T and ε_T^{Std} are the triplet state molar extinction coefficients for the sample and the standard, respectively and are determined using the Equations 1.9 and 1.10, from there respective ground state molar extinction coefficients (ε_s and ε_s^{Std}), changes in absorbances of the ground singlet states (ΔA_s and ΔA_s^{Std}) and changes in the triplet state absorptions (ΔA_T and ΔA_T^{Std}).

$$\varepsilon_T = \varepsilon_s \frac{\Delta A_T}{\Delta A_s} \quad (1.9)$$

$$\varepsilon_T^{Std} = \varepsilon_s^{Std} \frac{\Delta A_T^{Std}}{\Delta A_s^{Std}} \quad (1.10)$$

The triplet lifetimes were determined by exponential fitting the kinetic curves using ORIGIN 8 software.

1.6.3 Singlet Oxygen Quantum Yield (Φ_{Δ})

The singlet oxygen quantum yield (Φ_{Δ}) could be defined as the amount of singlet oxygen generated per photon absorbed by the phthalocyanine complex [212], and the value of Φ_{Δ} may be evaluated using a chemical or optical (luminescence at 1270 nm) method. The singlet oxygen ($^1\text{O}_2$) is generated via photosensitization, where a photosensitizer absorbs light to induce a chemical and physical alteration of another chemical entity [213–223].

In this work, a chemical method for Φ_{Δ} determination was employed using 1,3-diphenylisobenzofuran (DPBF) in organic media or anthracene-9,10-bis-methylmalonate (ADMA) in aqueous media using Equation 1.11. The chemical method requires a suitable singlet oxygen sensitive compound (quencher) that can react quickly with the singlet oxygen in a 1:1 ratio without any side reactions. The decomposition product of the quencher should not react with the generated singlet oxygen and is not expected to interfere with the Q-band of MPcs (the MPc must remain stable). The experiment is usually carried out by irradiating a sample solution containing the phthalocyanine and the quencher. The degradation of the quencher is typically monitored spectroscopically [221,224].

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \frac{RI_{Abs}^{Std}}{R^{Std}I_{Abs}} \quad (1.11)$$

where Φ_{Δ}^{Std} is the singlet oxygen quantum yield of a known standard, $\mathbf{R}$ and $\mathbf{R}^{Std}$ are the singlet oxygen quencher photobleaching rates in the presence of the respective MPcs and their conjugates under investigation and of the standard, respectively. I_{Abs} and I_{Abs}^{Std} are the rates of light absorption by the MPcs, MPcs conjugates and the standards, respectively and are defined by Equation 1.12 and 1.13.

$$I_{Abs} = \frac{\alpha \cdot A \cdot I}{N_A} \quad (1.12)$$

$$I_{Abs}^{Std} = \frac{\alpha \cdot A \cdot I}{N_A} \quad (1.13)$$

where, $\alpha = 1 - 10^{-A(\lambda)}$, $A(\lambda)$ is the absorbance of the sensitizer (MPc, MPc conjugates and standard) at the irradiation wavelength, A is the irradiated area (2.5 cm^2). I is the intensity of light calculated using the $\lambda_{Q\text{-band}}$ of MPc (expressed as photons $\text{cm}^{-2}\text{s}^{-1}$), and N_A is the Avogadro's constant.

For singlet oxygen quantum yield (Φ_Δ) determinations in fibers, the absolute method was used due to lack of a standard. The experiments were carried out in unbuffered aqueous media using ADMA as a quencher, and its degradation was monitored at 380 nm [121,225]. The quantum yields (Φ_{ADMA}) were calculated using Equation (1.14),

$$(\Phi_{\text{ADMA}}) = \frac{(C_o - C_t)V_R}{I_{\text{Abs}} \cdot t} \quad (1.14)$$

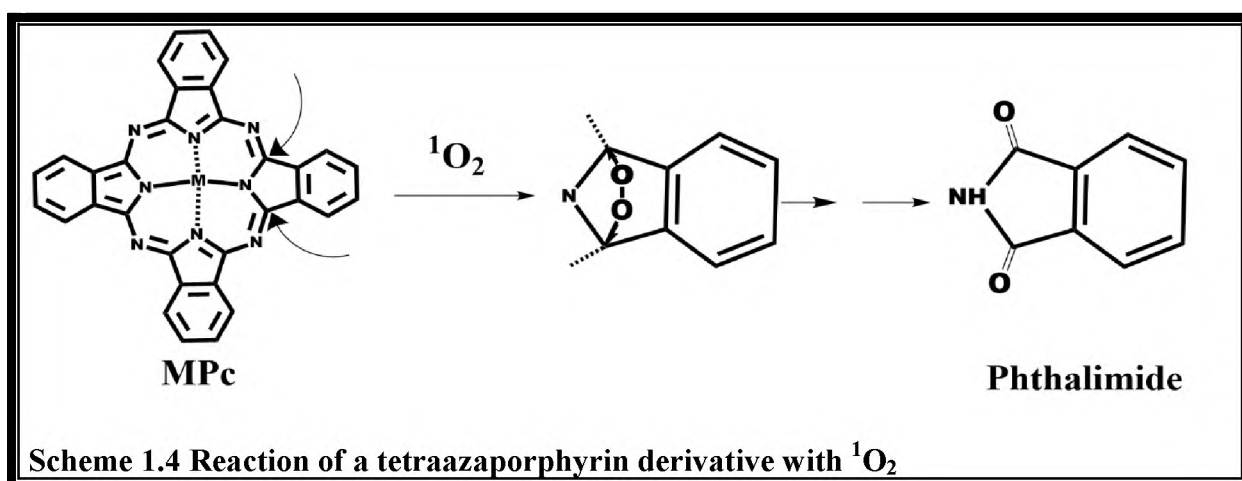
where C_o and C_t are the ADMA concentrations before and after irradiation, respectively; V_R is the solution volume; t is the irradiation time per cycle, and I_{Abs} is as defined above. The absorbance used for Equation 1.14 is that of the phthalocyanines in the fibers (not in solution) measured by placing the modified fiber directly on a glass slide or solid state UV spectrophotometer. The light intensity measured refers to the light reaching the spectrophotometer cells, and it is expected that some of the light may be scattered. Hence, the Φ_Δ values of the phthalocyanines in the fiber are estimates. The singlet oxygen quantum yields (Φ_Δ) were calculated using Equation 1.15.

$$\frac{1}{\Phi_{\text{ADMA}}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi_\Delta} \cdot \frac{k_d}{k_a} \cdot \frac{1}{[\text{ADMA}]} \quad (1.15)$$

where k_d is the decay constant of singlet oxygen and k_a is the rate constant for the reaction of ADMA with $^1\text{O}_2$ ($^1\Delta_g$). The intercept obtained from the plot of $1/\Phi_{\text{ADMA}}$ versus $1/[\text{ADMA}]$ gives $1/\Phi_\Delta$.

1.6.4 Photodegradation Quantum Yield (Φ_{Pd})

Photodegradation is a photochemical process similar in experimental and evaluation of the value as for singlet oxygen quantum yield except that there is no quencher needed. The conjugated chromophore of the phthalocyanine ring gets degraded into smaller molecular fragments. This process is driven by singlet oxygen in the presence of light to afford the photo-oxidation products, phthalimide, as suggested by Schnurpfeil et al. [226], Scheme 1.4. Singlet oxygen reacts with tetraazaporphyrin derivatives in a Diel-Alder [4+2]-cycloaddition, with the phthalocyanine acting as a diene and the singlet oxygen as the dienophile. For determination of photodegradation quantum yields (Φ_{Pd}), the usual Equation 1.14 was employed [99], using Φ_{Pd} instead of Φ_{Δ} and other parameters maintained the status quo.



1.7 Summary of This Thesis

The aims of this thesis can be summarized as follows:

1. Synthesis and characterization of novel low symmetry and symmetrical Pcs as shown in Figure 1.2. (complexes **7**, **7a**, **8**, **8a**, **9**, **9a**, **10**, **10a**, **11** and **12**).
2. Synthesis and characterization of semiconductors glutathione-capped CdTe/ZnSe/ZnO QDs, hexadecylaniline capped gold (HAD-AuNPs) and carboxylic acid functionalized Fe_3O_4 magnetic nanoparticle (MNPs).

3. Conjugation and characterization of the as-synthesized nanoparticles via amide linkage for semiconductors QDs to complexes **10**, **11** and **12** or Fe₃O₄ magnetic nanoparticle (MNPs) to complexes **10**, **10a**, **11** and **12** as well as chemisorption for gold (AuNPs) to complexes **11** and **12**, **Figure 1.3**.
4. Investigation of the photophysical behavior of symmetrical and asymmetrical phthalocyanine alone or when conjugated to QDs (**10**, **11** and **12**), AuNPs (**11** and **12**) or MNPs (**10**, **10a**, **11** and **12**).
5. PACT studies of selected Pcs alone or with MNPs when in solution or fiber (compounds **7**, **7a**, **8**, **8a**, **9** and **9a**).
6. Photocatalytic transformation of pollutants (BPA or 4-chlorophenol) using cationic modified electrospun fiber of compounds **8a**, **9a**, and **10a**.

CHAPTER 2

2 Experimental

2.1 Materials

2.1.1 Solvents

Dimethyl sulfoxide (DMSO), dichloromethane (DCM), N, N-dimethylformamide (DMF) absolute ethanol (EtOH), sulphuric acid (98%), fuming nitric acid, toluene, thionyl chloride, ammonia solution (25%), methanol, n-pentanol, n-hexanol, cyclohexane, n-hexane, and acetone were purchased from SAARCHEM. Deuterated dimethyl sulfoxide (DMSO-d₆) was purchased from Sigma-Aldrich. Ultrapure water was obtained from a Milli-Q Water System (Millipore Corp, Bedford, MA, USA).

2.1.2 Reagents for the Metallophthalocyanines synthesis

The following chemicals were purchased from Sigma-Aldrich: 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), methyl iodide, lead(II) acetate, indium(III) chloride, zinc acetate dihydrate, 1,2-dicyanobenzene (**1**). The precursors used in this work 4-(4-pyridyloxy)phthalonitrile (**13**) [80], 4-aminophenoxyphthalonitrile (**14**) [227], 4-(4-pyridylsulfanyl)phthalonitrile (**15**) [228] and 4-(4,6-diaminopyrimidin-2-ylthio)phthalonitrile (**16**) [48], are known and were synthesized as reported in literature.

2.1.3 Quenchers/Standard for determination of Photophysical Parameters

Anthracene-9,10-bis-methylmalonate (ADMA), Rhodamine 6G, and 1,3-diphenylisobenzofuran (DPBF), zinc phthalocyanine (ZnPc) from Sigma-Aldrich. AlPcSmix was synthesized according to literature [229].

2.1.4 Reagents for Nanoparticles Synthesis

Iron (II) sulphate heptahydrate, iron (III) chloride hexahydrate, 3-aminopropyltriethoxysilane (APTES), tetraethoxysilane (TEOS), succinic anhydride, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), *N,N'*-dicyclohexylcarbodiimide (DCC), N-hydroxysuccinimide (NHS), gold (III) chloride trihydrate, hexadecylaniline (HDA), sodium borohydride, zinc acetate dihydrate, cadmium chloride (CdCl_2), and tellurium granules were purchased from Sigma-Aldrich; selenium powder was from Riedel-de-Haen®. Glutathione (GSH) capped semiconductor quantum dots (GSH/CdTe/ZnSe/ZnO) were synthesized as reported in literature [145].

2.1.5 Reagents for Photodynamic Antimicrobial Chemotherapy and Photocatalysis.

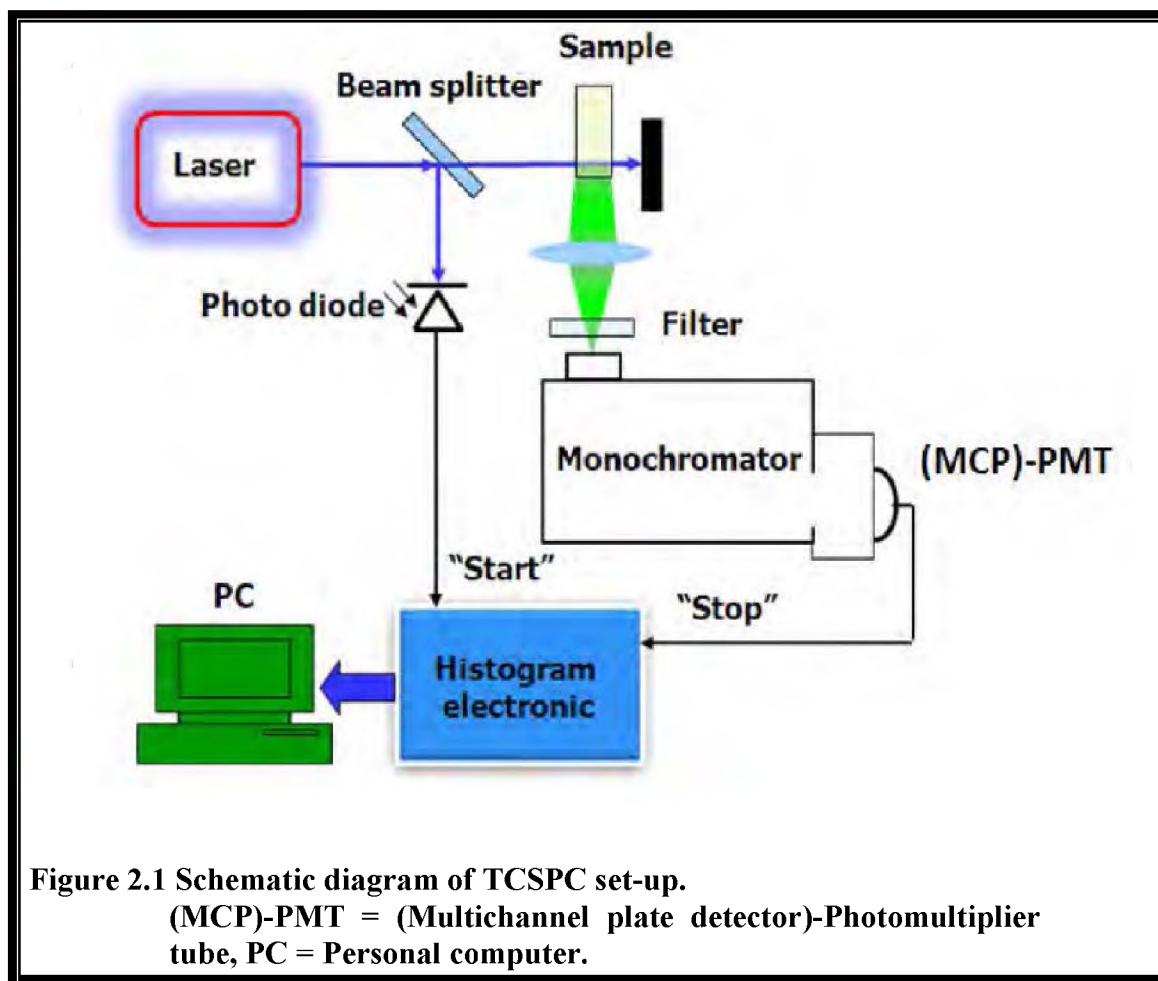
Escherichia coli (ATCC 25922) was purchased from Microbiologic; bisphenol A and polystyrene (PS, $M_w \sim 35\,000\text{ g/mol}$) were purchased from Sigma-Aldrich and 4-chlorophenol (99%) was from Fluka, phosphate buffer saline (10 mM PBS, pH 7.4) was prepared by dissolving appropriate quantity of Na_2HPO_4 , KH_2PO_4 and chloride salts in ultra-pure water obtained from Milli-Q Water System (Millipore Corp, Bedford, MA, USA).

2.2 Instrumentation

The following instruments were used during the research work;

1. The absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Quartz cells of 1 cm path lengths were employed.
2. Transmission electron microscopy (TEM) micrographs were obtained using a ZEISS LIBRA® transmission electron microscope.
3. Infrared (IR) spectra were collected on either Perkin-Elmer Fourier transform-IR (100 FT-IR) spectrophotometer or Bruker Alpha model FT-IR spectrometer with platinum-ATR.

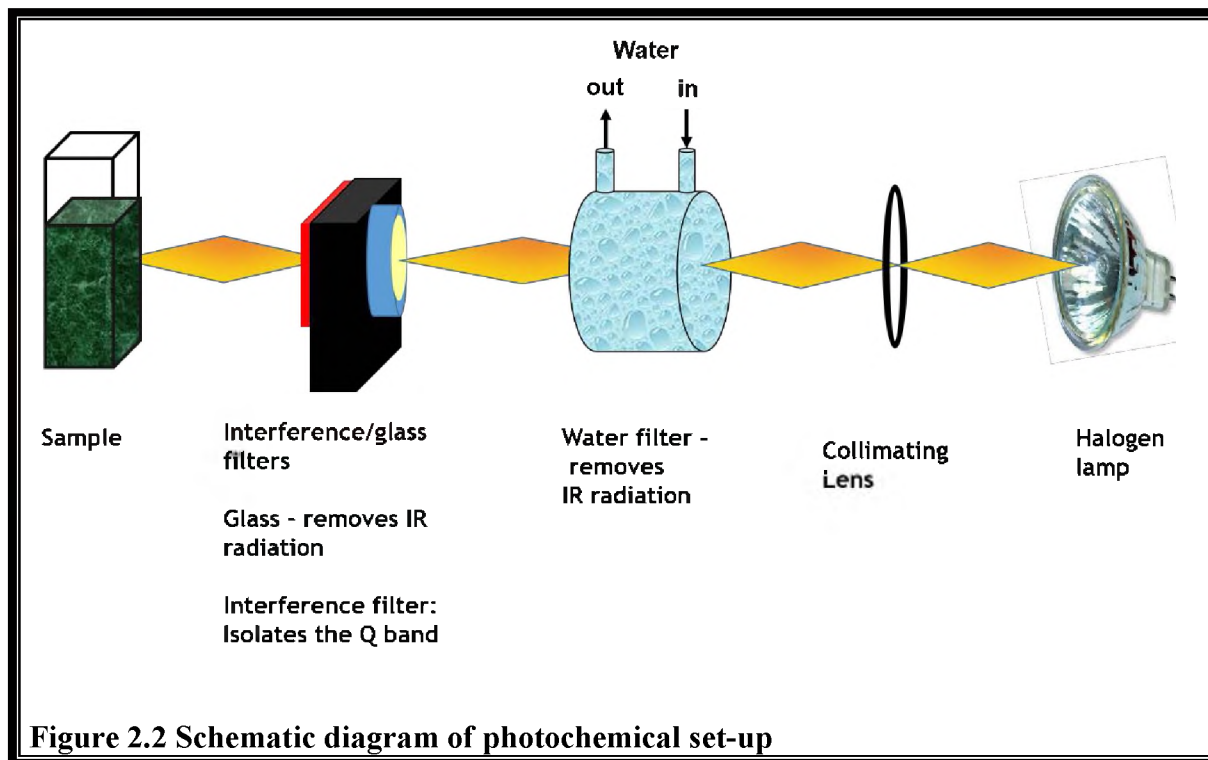
4. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorometer.
5. Mass spectra data were collected on Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer operated in positive ion or negative mode using dithranol as the MALDI matrix.
6. ^1H , ^{13}C and COSY nuclear magnetic resonance spectra were recorded using either a Bruker AMX400 MHz NMR spectrometer or a Bruker AVANCE II 600 MHz spectrometer.
7. Fluorescence lifetimes were measured using a time-correlated single photon counting set-up (TCSPC), **Figure 2.1** (FluoTime 300, Picoquant GmbH) with a diode laser as the excitation source (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, 44 ps pulse width, Pico quant GmbH). Fluorescence was detected under the magic angle with a peltier cooled photomultiplier tube (PMT) (PMA-C 192-N-M, Picoquant GmbH) and integrated electronics (PicoHarp 300E, Picoquant GmbH). A monochromator with a spectral width of about 4 nm was used to select the required measured emission wavelength. The response function of the system, which was with a scattering Ludox solution (DuPont), had a full width at half-maximum (FWHM) of about 300 ns. The ratio of stop to start pulses was kept low (below 0.05) to ensure good statistics. All luminescence decay curves were measured at the maximum of emission peak. The data were analyzed with the program FluoFit (Picoquant GmbH). The support plane approach [195] was used to estimate the errors of the decay times.



8. The X-ray (XRD) diffractograms were collected on a Bruker D8 Discover diffractometer, equipped with a Lynx Eye detector, under Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$). Data were collected in the range from $2\theta = 10^\circ$ to 100° , scanning at $0.010^\circ \text{ min}^{-1}$ and 192 s per step. The samples were placed on a zero background silicon wafer slide.
9. Elemental analyses were done using a Vario-Elementar Microcube ELIII.
10. Irradiations for singlet oxygen, photodegradation quantum yield determinations, and phototransformation of pollutants (BPA and 4-chlorophenol) were performed using a general electric quartz lamp (300 W), 600 nm glass (Schott) and water filters were used to filter off ultraviolet and far infrared radiations respectively

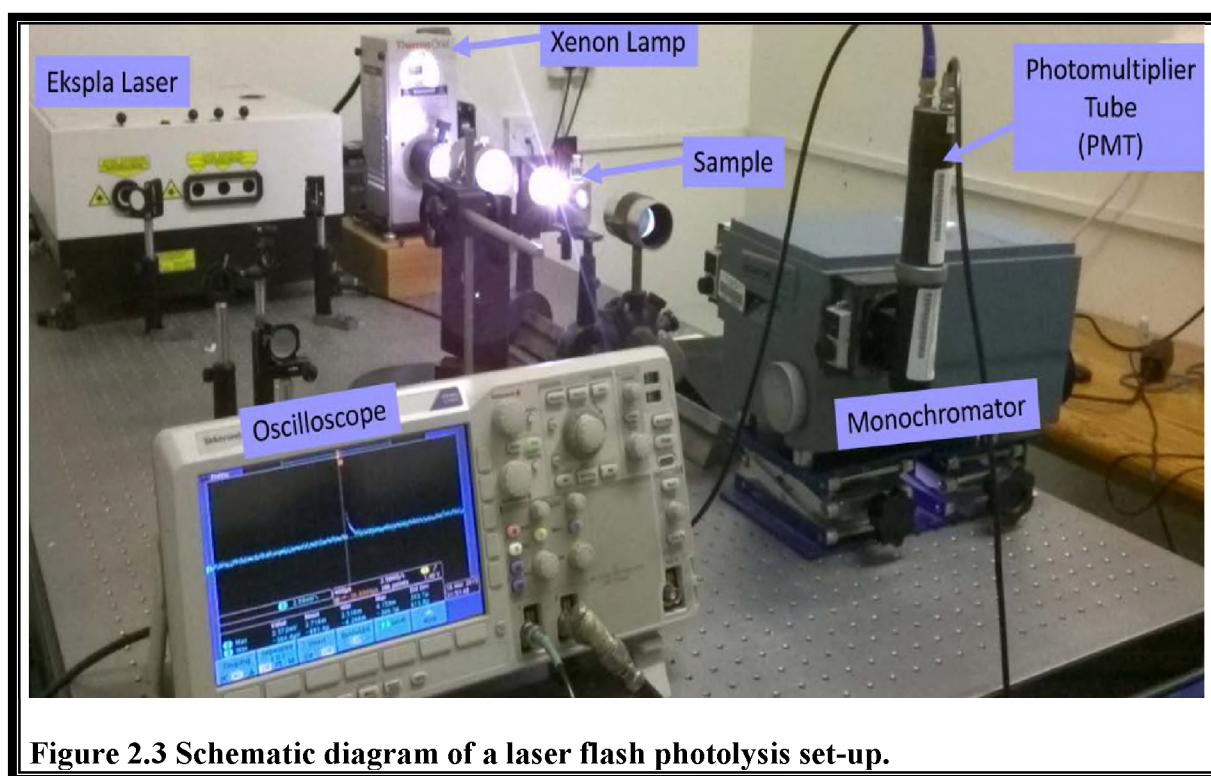
Figure 2.2. An interference filter, 700 nm with a band of 40 nm, was placed in the

light path just before the cell containing the sample. Light intensities were measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter



11. HERMLE Z233M-2 centrifuge was used for the harvesting of the bacteria cells by centrifugation process.
12. The homogenization of the bacteria suspension was done using PRO VSM-3 Lab plus Vortex mixer.
13. The incubation processes for the photodynamic antimicrobial chemotherapy was done using the thermostatic oven.
14. The optical density of the bacteria culture was determined using the LEDETECT 96 from LABXIM PRODUCTS.
15. Laser flash photolysis system was used for the determination of triplet decay kinetics and transient curve were performed with light pulses produced by either Quanta-Ray Nd: YAG laser providing 400 mJ, 9 ns pulses of laser light at 10 Hz,

pumping a Lambda-Physik FL3002 dye laser (Pyridin 1 dye in methanol), single pulse energy ranged from 2 to 7 mJ or EKSPLA NT342N-20-AW tunable wavelength laser with excitation pulses (3-5 ns) **Figure 2.3**. The analyzing beam source was from a Thermo Oriel Xenon arc lamp, and photomultiplier tube (a Kratos Lis Projekte MLIS-X3) was used as a detector. Signals were recorded with a two channel 300 MHz digital real time oscilloscope (Tektronix TDS 3032C); the kinetic curves were averaged over 256 laser pulses. For laser flash photolysis studies, the absorbance of solutions of the Pcs and the ZnPc standard were ~ 1.5 at the Q-band. The solution was introduced into a 1 cm path length UV-visible spectrophotometric cell and de-aerated using argon for 15 min.



16. The X-ray photoelectron spectroscopy (XPS) analysis was done using an AXIS Ultra DLD, with Al (monochromatic) anode equipped with a charge neutralizer, supplied by Kratos Analytical. The following parameters were used: the emission was 10 mA, the anode (HT) was 15 kV and the operating pressure below 5×10^{-9}

- torr. A hybrid lens was used and resolution to acquire scans was at 160 eV pass energy in slot mode. The center used for the scans was at 520 eV with a width of 1205 eV, with steps at 1 eV and dwell time at 100 ms as reported before [230]. The high-resolution scans were acquired using 80 eV pass energy in slot mode.
17. Nitrogen adsorption/desorption isotherms were measured at 77 K using a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. Before each measurement, degassing was carried at 90⁰C for four days. The Brunauer–Emmett–Teller (BET) method was employed to determine surface area and porosity. The Brunauer-Emmette-Teller (BET) surface area and total pore volume were calculated from the isotherms obtained. The details of the set-up have been previously described [230].
 18. Autoclave RAU-530D was utilized for the sterilization and autoclaving of nutrient broth, nutrient agar and phosphate buffer as well as various apparatus for PACT studies.
 19. Scan[®] 500 automatic color colony counter was used for the evaluation of the colony forming units (CFU)/mL of the bacteria.
 20. Thermo-gravimetric analysis (TGA) was performed using a Perkin-Elmer TGA 7 analyzer. The analysis were carried out under nitrogen/air mixture at a flow rate of 120 cm³ min⁻¹. The weighed sample masses were heated from 100 to 500 °C at a heating rate of 10 °C min⁻¹.
 21. Electrospun polymer fibers were obtained from a set-up, consisting of a high voltage source (Glassman High Voltage. Inc., EL series, 0-40 kV), a pump (Kd Scientific, KDS-100-CE), a plastic syringe connected to a steel needle of the internal diameter of 0.584 mm and aluminum foil as a collector.
 22. A Metrohm Swiss 827 pH meter was used for pH measurements.

2.3 Phthalocyanines Synthesis

2.3.1 Synthesis of 2,9(10),16(17),23(24)-tetrakis[4-(N-pyridyloxy) phthalocyaninato] lead(II) (7, Scheme 3.1)

Lead phthalocyanine (7) was synthesized by the cyclotetramerization of 4-(4-pyridyloxy) phthalonitrile (**13**, 2.5 g, 11.3 mmol) with lead(II) acetate (1.1 g, 2.8 mmol) in the presence of organic base 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU) (0.5 mL) and n-pentanol (20 mL) under argon. The mixture was heated under reflux for 18 h. The reaction mixture was cooled to room temperature and precipitated with 50 ml of cyclohexane. The solid was washed respectively with hexane, water, acetone, and diethyl ether by centrifugation and was oven dried. The dried crude sample was further purified using Soxhlet apparatus set-up for three days using methanol as an extraction solvent. The obtained pure residue was air dried in the fume hood.

Yield: (13 %). IR (KBr, cm^{-1}): 3064 (C-H), 2914, 1598, 2634, 1723 (C=O), 1638, 1588, 1482, 1373, 1199 (C-O-C), 1121, 1065. NMR (DMSO- d_6): δ {ppm} 6.19-6.20 (dd, 8H), 7.90 (m, 8H), 7.97 (m, 4H), 8.07-8.08 (dd, 8H). UV/Vis (DMF) λ_{max} nm (log ϵ): 709 (5.16), 638 (4.63), 332 (4.02). Calc. for $\text{C}_{52}\text{H}_{28}\text{N}_{12}\text{O}_4\text{Pb}$: C 57.19, H 2.58, N 15.39 Found: C 58.43, H 2.83, N 14.16. MALDI-TOF MS m/z : Calcd: 1092.07 Found: $[\text{M}+2\text{H}^+] = 1094.77$. Calc.

2.3.2 Quaternized phthalocyanine 2,9(10),16(17),23(24)-tetrakis[4-(4-N-ethylpyridiniumoxy) phthalocyaninato] lead (II), (7a, Scheme 3.1)

The complex was obtained by treating the 7 (138 mg, 0.13 mmol) with ethyl iodide (40 ml, 0.5 mmol) for 48 h at reflux temperature in acetone (20 ml). The reaction mixture was cooled to room temperature and precipitated out with 50 ml of cyclohexane and filtered. The solid was washed with hexanes, diethyl ether, and acetone and was dried in the oven.

Yield: (13 %). IR (KBr, cm^{-1}): 3062 (C-H), 2910, 2604, 1722 (C=O), 1635, 1588, 1480, 1374, 1186 (C-O-C), 1062, 1009. NMR (DMSO- d_6): δ {ppm} 2.8-3.0 (m, 28H), 7.8-8.2 (br, 13H), 9.5-9.8 (br, 9H). UV/Vis (DMF) λ_{max} nm (log ϵ): 705 (5.24), 635 (4.45), 344 (4.85). Calc. for $\text{C}_{60}\text{H}_{48}\text{I}_4\text{N}_{12}\text{O}_4\text{Pb}$: C 42.00, H 2.82, N 9.78 Found: C 41.97, H 2.25, N 9.35

2.3.3 Synthesis of 2,9(10),16(17),23(24)-tetrakis[4-(pyridyloxy) phthalocyaninato] chloroindium(III) (8, Scheme 3.2)

The complex was synthesized by the cyclotetramerization of 4-(4-pyridyloxy) phthalonitrile (**13**, 4.2 g, 18.8 mmol) with indium(III) chloride (1.04 g, 4.7 mmol) in n-pentanol (20 mL) and in the presence of 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU, 0.5 mL) as an organic base. The reaction was carried out under argon atmosphere and heated for 18 h at reflux temperature. The reaction mixture was cooled to room temperature and precipitated out of the solution with 50 mL of cyclohexane.

The solid was washed several times with hexane, methanol-water (1:9), 1 M HCl, water and acetone by centrifugation and then dried in the oven. Yield: 2.37 g (45.30 %). IR (KBr, cm^{-1}): 3069(C-H), 1634, 1608, 1555, 1522, 1482, 1346, 1253 (C-O-C), 1183, 1086. ^1H NMR (DMSO- d_6): δ {ppm} 6.27 (d, 8H Pc-H), 7.97-7.99 (br, 8H pyridyl-H), 8.03-8.05 (br, 4H Pc-H), 8.15 (d, 8H pyridyl-H). UV/Vis (DMF) λ_{max} nm (log ϵ): 693 (4.94), 623 (4.15), 362 (4.50), UV/Vis (DMSO) λ_{max} nm (log ϵ): 692 (5.12), 623 (4.36), 376 (4.75). Calc. for $\text{C}_{52}\text{H}_{28}\text{ClInN}_{12}\text{O}_4$: C 60.34, H 2.73, N 16.24 Found: C 60.53, H 3.44, N 16.02. MALDI-TOF MS m/z: Calcd: 1036 Found: $[\text{M}+\text{H}]^+ = 1037.09$.

2.3.4 Synthesis of 2, 9(10), 16(17), 23(24)-tetrakis [4-(4-N-methylpyridiniumoxy) phthalocyaninato] chloroindium(III) iodide (8a, Scheme 3.2)

A mixture containing complex **8**, (106 mg, 0.10 mmol), methyl iodide (1.0 mL), DMF (10 mL) and acetone (20 mL) was heated under reflux for 48 h. The reaction mixture was cooled

to room temperature and precipitated with diethyl ether, filtered and washed with diethyl ether and acetone and dried in the oven.

Yield: 68.9 mg (65 %). IR (KBr, cm^{-1}): 3065 (C-H), 1722, 1634, 1557, 1485, 1347, 1255 (C-O-C), 1183, 1062, 1011. ^1H NMR ($\text{D}_2\text{O}-d_6$): δ {ppm} 3.81-3.35 (m, 12H, CH_3), 6.77-6.48 (m, 16H, pyridyl-H), 7.84-7.75 (m, 8H, Pc-H), 8.20-8.08, (m, 4H, Pc-H). UV/Vis (DMF) λ_{max} nm (log ϵ): 691 (5.27), 622 (4.57), 365 (4.92), UV/Vis (DMSO) λ_{max} nm (log ϵ): 690 (5.53), 622 (4.86), 363 (5.24). Calc. for $\text{C}_{56}\text{H}_{40}\text{ClI}_4\text{InN}_{12}\text{O}_4$: C 41.96, H 2.52, N 10.49 Found: C 41.47, H 2.51, N 10.60.

2.3.5 Synthesis of 2-[4-(pyridyloxy) phthalocyaninato] chloroindium(III) (9, Scheme 3.2)

Complex **9** was synthesized by heating a mixture of 1, 2-dicyanobenzene (**1**, 0.87 g, 6.8 mmol), 4-(4-pyridyloxy) phthalonitrile (**13**, 0.5 g, 2.3 mmol) and indium(III) chloride (0.5 g, 4.7 mmol) 20 mL n-pentanol and in the presence of 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU) (0.5 mL) as an organic base. The reaction was carried out under an argon atmosphere and heated for 18 h at reflux temperature. After cooling to room temperature, the reaction mixture was precipitated with cyclohexane and further washed several times as described above for **8** and was dried in the oven. The filtered crude product was purified via silica column chromatography using DCM/methanol (98:2).

Yield: 1.22 g (65 %). IR (KBr, cm^{-1}): 3048(C-H), 1634, 1609, 1562, 1473, 1406, 1285, 1256 (C-O-C), 1189, 1162, 1115, 1080, 1059, 886. ^1H NMR ($\text{DMSO}-d_6$): δ {ppm} 6.48-6.53 (d, 2H, pyridyl-H), 8.20-8.32 (m, 7H, Pc-H), 8.54-8.60 (d, 2H, pyridyl-H), 9.29-9.41 (m, 8H, Pc-H). UV/Vis (DMF) λ_{max} nm (log ϵ): 684 (5.04), 616 (4.27), 361 (4.63); UV/Vis (DMSO) λ_{max} nm (log ϵ): 686 (5.09), 616 (4.35), 361 (4.64). Calc. for $\text{C}_{37}\text{H}_{19}\text{ClInN}_9\text{O}$: C 58.79, H 2.53, N 16.68 Found: C 58.40, H 2.78, N 15.79 MALDI-TOF MS m/z : Calcd: 755.88 Found: $[\text{M}+\text{H}]^+ = 756.01$.

2.3.6 Synthesis of 2-[4-(N-methylpyridiniumoxy) phthalocyaninato] chloroindium(III) iodide (**9a**, Scheme 3.2)

A mixture containing complex **9**, (533 mg, 0.71 mmol), methyl iodide (1.0 mL), DMF (10 mL) and acetone (20 mL) was heated under reflux for 48 h. The reaction mixture was cooled to room temperature and precipitated with diethyl ether, filtered and washed with diethyl ether and acetone and dried in the oven.

Yield: 403 mg (76 %). IR (KBr, cm^{-1}): 3052 (C-H), 1636, 1609, 1568, 1475, 1408, 1331, 1285, 1256 (C-O-C), 1189, 1153, 1115, 1081, 1051, 900, 886. ^1H NMR (DMSO- d_6): δ {ppm} 1.93 (s, 3H, CH_3), 6.65-6.52 (b, 1H, Pc-H), 8.21-8.03(b, 8H, Pc-H), 8.64-8.53, (b, 2H, Pc-H), 8.95-9.11 (b, 4H, Pyridyl), 9.20-9.13 (b, 4H, Pc-H). UV/Vis (DMF) λ_{max} nm (log ϵ): 684 (5.23), 616 (4.46), 361 (4.83), UV/Vis (DMSO) λ_{max} nm (log ϵ): 684 (5.16), 616 (4.37), 360 (4.77). Calc. for $\text{C}_{38}\text{H}_{22}\text{ClInN}_9\text{O}$: C 50.84, H 2.47, N 14.04 Found: C 50.31, H 2.48 N 14.04

2.3.7 Synthesis of 9(10), 16(17), 23(24)-tri-4-pyridylsulfanyl -2(3) -(4 aminophenoxy) phthalocyaninato chloroindium(III). (**10**, Scheme 3.3)

A mixture of 4-(4-aminophenoxy)phthalonitrile (**14**, 0.06 g, 0.23 mmol), 4-(4-pyridylsulfanyl)phthalonitrile (**15**, 0.17 g, 0.70 mmol), Indium(III) chloride (0.05 g, 0.23 mmol) and 0.5 mL DBU in 20 mL of n-pentanol was heated at reflux temperature under an argon atmosphere for 24 h with constant stirring. The product obtained was precipitated with methanol and subsequently washed with water and dried in the oven. The filtered crude product was purified via Soxhlet extractor for 4 days using absolute ethanol then the dried extract was further purified with silica packed column chromatography using isocratic eluent of dichloromethane/methanol (95:5).

Yield: 0.16 g (63%). IR [(ATR), $\nu_{\text{max}}/\text{cm}^{-1}$]: 3332 (N-H), 1723, 1666, 1597, 1480, 1385, 1330, 1225 (C-O-C), 1064, 1011, 910, 813. ^1H NMR (DMSO- d_6): δ {ppm} 6.64-6.62 (s, 2H,

NH₂-H), 6.88-6.86 (s, 4H, Pc-H), 7.26-7.23 (dd, 7H, *J*= 4.8, 1.4 Hz; Phenyl-H and Pc-H), 7.85-7.83 (s, 3H, Pc-H), 7.91-7.89 (d, 6H, *J*= 2.5 Hz, Pyridyl-H), 8.44-8.48 (dd, 8H, *J*= 4.7, 1.3 Hz; pyridyl-H and Pc-H). ¹³C NMR (DMSO-d₆): δ {ppm} 122.92 (aromatic phenyl-CH), 124.59 (aromatic pyridyl-CH), 126.74 (aromatic C), 132.74, 134.32, 138.16, 138.44 (aromatic C), 146.26 (aromatic phenyl-CH), 150.12 (aromatic pyridyl-C=N), 150.27, 162.62 (aromatic Pc-C), 168.57 (aromatic Pc-C), 168.73 (aromatic Pc-C).

UV/Vis (DMSO) λ_{max} nm (log ε): 696 (5.22), 628 (4.57), 369 (4.93). Calc. for C₅₃H₃₀ClInN₁₂OS₃: Expected: C 58.01, H 2.76, N 15.32, Found: C 58.79, H 2.53, N 15.68. MALDI-TOF MS *m/z*: Calcd: 1097 Found: [M+3H]⁺ = 1100.

2.3.8 Synthesis of 9(10), 16(17), 23(24)-tri-N-methyl-4-pyridylsulfany-2(3)-(4Aminophenoxy) Phthalocyaninato Chloroindium(III) Triiodide (10a)

Complex **10a** (quaternization of **10**) was synthesized by refluxing a mixture of complex **10** (106 mg, 0.10 mmol), methyl iodide (1.0 mL), DMF (10 mL) and acetone (20 mL) for 48 h. The reaction mixture was cooled to room temperature and precipitated with diethyl ether and washed with acetone then oven dried.

Yield: 68.9 mg (65 %). IR [(ATR), ν_{max}/cm⁻¹]: 3403 (N-H stretch), 3020 (C-H), 1714, 1626 (N-H Bend), 1488, 1383, 1326, 1304, 1226, 1138, 1088, 1041 (C-O-C), 908. ¹H NMR (DMSO-d₆): δ {ppm} 4.38-4.12 (s, 9H Methyl-H), 6.78-9.92 (br, 30H Ar-H and NH₂-H). UV/Vis (DMSO) λ_{max} nm (log ε): 698 (4.89), 629 (4.28), 368 (4.63). Calc. for C₅₆H₃₉ClI₃InN₁₂OS₃: C 44.16, H 2.58, N 11.03 Found: C 44.68, H 2.86, N 10.07. MALDI-TOF MS *m/z*: Calcd: 1523.17; Found: (1) [M-3I⁻, -3H] = 1140, (2) [M-Cl, +CH₄I⁺, -Cl⁻] = 1244 and (3) [M-Cl⁻, -8H] = 1480.

2.3.9 2,9(10),16(17),23(24)-tetrakis-(4'-(4',6'-diaminopyrimidin-2'-ylthio)) phthalocyaninato zinc (II) (11, Scheme 3.4).

The synthetic procedure adapted for the complex **11** was similar to previously reported methods for lutetium (III) and cobalt (II) (diaminopyrimidin-2-ylthio) phthalocyanines [48,49], with some modifications. Briefly, a mixture **16** (1.0 g, 1.467 mmol), $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.081 g, 0.368 mmol) and 0.3 mL of catalytic DBU in 20 mL n-hexanol was heated to 180 °C under nitrogen for 6 h. The reaction mixture was cooled to room temperature. The product was precipitated out of solution with methanol and subsequently washed with methanol and acetone. The crude green product was further purified using silica-packed column chromatography and eluted with diethyl ether/DMF (5:1) as eluents, to isolate the required product **11**. Yield: (48%). UV-Vis (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 689 (5.21), 622 (4.51), 356 (4.91). FT-IR [KBr disc ($\nu_{\text{max}}/\text{cm}^{-1}$)]: 3320, 3189 (N–H str), 2929 (C–H aromatic), 1613, 1572 (N–H bend), 1348 (C–N aryl) Anal. Calc. for $\text{C}_{48}\text{H}_{32}\text{N}_{24}\text{S}_4\text{Zn}$: C 50.63, H 2.83, N 29.52, S 11.26; Found: C 50.05, H 3.75, N 28.96, S 11.25. MS (MALDI-TOF) m/z : Calcd. 1139; Found: 1140 $[\text{M} + \text{H}]^+$. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ , ppm: 5.20 (s, 16H, NH), 8.97 (s, 4H, pyrimidinyl-H), 7.77–7.89 (m, 12H, Ar-H).

2.3.10 2,9(10),16(17),23(24)-tetrakis-(4'-(4',6'-diaminopyrimidin-2'-ylthio)) phthalocyaninato chloroindium(III) (12, Scheme 3.4)

The synthesis and purification of compound (**12**) is as outlined for zinc phthalocyanine complex (**11**) except that indium chloride is used as the central metal. The amounts used as well as purification are as discussed for compound (**11**). Yield: (45%). UV-Vis (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 704 (5.23), 673 (4.55), 360 (4.92). FT-IR [KBr disc ($\nu_{\text{max}}/\text{cm}^{-1}$)]: 3322, 3182 (N–H str), 2917 (C–H aromatic), 1695, 1579 (N–H bend), 1462, 1287, 1075, 974. Calc. for $\text{C}_{48}\text{H}_{32}\text{ClInN}_{24}\text{S}_4$: C 47.12, H 2.64, N 27.48, S 10.48; Found: C 47.55, H 2.98, N 28.41, S 11.25. MS (MALDI-TOF) m/z : Calcd. 1224; Found: 1228 $[\text{M} + 4\text{H}]^+$. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ , ppm: 5.20 (s, 16H, NH), 8.97 (s, 4H, pyrimidinyl-H), 7.77–7.89 (m, 12H, Ar-H).

DMSO-d₆): δ , ppm: 7.25-7.41 (d, 12H, Ar-H), 8.14-8.54 (d, 16H, NH), 9.05-9.21 (s, 4H, pyrimidinyl-H).

2.4 Synthesis of Nanoparticles

2.4.1 Synthesis of Magnetic Nanoparticles

2.4.1.1 Bare MNPs (Scheme 3.5)

The magnetite nanoparticles were prepared by the conventional co-precipitation method, using previously reported procedures [231,232] with some modifications. Briefly, 4.17 g (25.70 mmol) of iron (III) chloride hexahydrate and iron (II) sulfate tetrahydrate (1.95 g, 12.84 mmol) were dissolved in 80 ml of previously degassed Millipore water under nitrogen gas. Then aqueous ammonia (25%, 7.5 mL) was added dropwise. The mixture was stirred for 3 h under an argon atmosphere at the temperature of 60 °C. Following this, the slurry was repeatedly washed with distilled water, and the particles were magnetically separated from the supernatant and re-dispersed in aqueous solution three times, until pH 7 was obtained. The MNPs were then finally dispersed in ethanol, magnetically isolated and dried under vacuum at room temperature. The dried bare magnetic nanoparticles are represented as MNPs, Scheme 3.5.

2.4.1.2 Silica coated magnetic nanoparticles (MNP-Si, Scheme 3.5)

The bare MNPs surface were encapsulated with silica for easy functionalization as follows: MNPs (0.26 g) were dispersed in a degassed mixture of 80 ml absolute ethanol and water (4:1), followed by ultrasonication of the mixture for 30 min. Afterwards tetraethoxysilane (TEOS, 5 mL) was added to the mixture and pH was adjusted to 9 using ammonium hydroxide. The mixture was stirred in an inert argon environment for 12 h. This was followed by refluxing at 130 °C for 24 h. The brown precipitate was separated and dried and is represented as MNP-Si in Scheme 3.4. IR [(ATR), $V_{\max}/\text{cm}^{-1}$]: 3234 (O-H), 2160, 1055 (Si-O-Si), 951 (Si-OH), 797.

2.4.1.3 Amino coated magnetic nanoparticles (MNP-NH₂, Scheme 3.5)

A mixture of silica coated magnetic nanoparticle (0.15 g) and absolute ethanol (100 mL) was ultrasonicated for 30 min to form a homogeneous colloid suspension. Then APTES (0.5 mL) was added and the mixture heated under reflux in a nitrogen atmosphere at 130 °C for 7 h. The precipitate was separated magnetically. The resulting solid product (represented as MNP-NH₂, Scheme 3.5), was washed with distilled water and dried in the vacuum for 24 h. IR [(ATR), $V_{\max}/\text{cm}^{-1}$]: 3282 (N-H), 1065 (Si-O-Si), 794 (N-H).

2.4.1.4 Carboxylic acid functionalized magnetic nanoparticles (MNP-COOH, Scheme 3.5)

To a stirring solution of succinic anhydride (0.1 M, 20 ml) in dry DMF, the dispersed solution of MNP-NH₂ (0.1 g) in dry DMF was added dropwise. The mixture was stirred for 24 h then poured into absolute ethanol. The MNP-COOH were magnetically separated, washed several times with absolute ethanol and dried under vacuum. IR [(ATR), $V_{\max}/\text{cm}^{-1}$]: 3215 (O-H), 2160, 1646, 1058 (Si-O-Si), 796

2.4.2 Synthesis of AuNPs

AuNPs were synthesized according to the methods previously reported [154,233–235] with slight modifications. Briefly, to 100 mL solution of 1.0×10^{-4} M HAuCl₄ in de-ionised water (Milli-Q®), NaBH₄ (0.01 g, previously refrigerated for 20 min) was added followed by vigorous stirring. This reaction is accompanied by the immediate appearance of a deep ruby red color characteristic of gold nanoparticles. This solution was allowed to stand for 24 h before further use. The nanoparticle solution was mixed with 10 mL of HDA (1×10^{-3} M) in toluene and stirred vigorously for 6 h until the phase transfer from aqueous media into

toluene was achieved [235]. The binding of HDA to the nanoparticle surface occurs through the amine functionality [236]. The purple organic phase which contains the nanoparticles was separated and washed with water using a separating funnel.

2.5 Conjugation of Phthalocyanines to the Nanoparticles

2.5.1 Conjugation of 10-MPcs-MNPs conjugates (Scheme 3.6)

The conjugate was synthesized by a previously reported procedure within our group [122]. A mixture of MNP-COOH (0.10 g) and DCC (0.02 g, 0.097 mmol) was stirred in DMF (4 mL) at room temperature for 48 h. Compound **10** (0.10 g, 0.091 mmol) dissolved in DMF (2 mL) was added dropwise to the mixture and stirring continued for a further 48 h. The crude product was collected and washed several times by centrifugation with acetone, methanol and absolute ethanol in succession to remove DMF, unbound complex **10** and excess DCC. The dry nanocomposite (**10**-MNPs) was obtained by oven drying at 110 °C for 48 h. Yield: 0.12 g. IR [(ATR), $\nu_{\text{max}}/\text{cm}^{-1}$]: 3064 (-CONH-), 1725, 1599, 1572 (N-H bend), 1479, 1330, 1064 (Si-O-Si), 909.

2.5.2 Conjugation of 10a-MPcs-MNPs conjugates (Scheme 3.6).

10a-MNPs was synthesized following literature methods for quaternized porphyrin magnetic nanoparticle conjugates [237]. **10**-MNPs (0.075 g) was dissolved in a solvent mixture of 2 ml of DMF and acetone (10 ml). Then methyl iodide (1 ml) was added to the flask and the mixture heated at reflux at 40 °C for 48 h. The reaction mixture was cooled to room temperature (~25 °C) and precipitated with diethyl ether and washed with acetone then oven dried. Yield: 0.052 g. IR [(ATR), $\nu_{\text{max}}/\text{cm}^{-1}$]: 3060 (-CONH-), 1630 (N-H bend), 1472, 1036 (Si-O-Si).

2.5.3 Conjugation of complexes 11 and 12 to MNPs, Scheme 3.7

The conjugate synthesis was in accordance with a previously reported procedure within our group [122]. A mixture MNPs (0.10 g) and DCC (0.02 g, 0.097 mmol) was stirred in DMF (4 mL) at room temperature for 48 h. Compounds **11** (0.10 g, 0.088) or **12** (0.10 g, 0.082 mmol) dissolved in DMF (2 mL) were added dropwise to the mixture and stirring continued for a further 48 h. The crude products were collected and purified several times by centrifugation in acetone, methanol and absolute ethanol in succession to remove DMF, unbound complexes **11** or **12** and excess DCC. The dry nanocomposites (**11**-MNPs or **12**-MNPs) were obtained by oven drying at 110 °C for 48 h.

11-MNPs: UV-Vis (DMSO): FT-IR [KBr disc ($\nu_{\max}/\text{cm}^{-1}$): 3329, 3205, 2161, 2029, 1656, 1621, 1580, 1542 (N–H bend), 1489, 1387, 1297, 1054 (Si–O–Si), 804.

12-MNPs: UV-Vis (DMSO): FT-IR [KBr disc ($\nu_{\max}/\text{cm}^{-1}$): 1653, 1575 (N–H bend), 1388, 1060 (C–O–C), 795.

2.5.4 Conjugation of glutathione-capped CdTe/ZnSe/ZnO to complex 10 (10-QD), Scheme 3.8

Complex **10** and GSH capped CdTe/ZnSe/ZnO QDs were covalently linked by reported procedure [238–240], with slight modification as follows. GSH capped CdTe/ZnSe/ZnO QDs (0.03 g) were dissolved in water (3 mL) followed by addition of EDC (0.1 M, 200 μL) and NHS (0.1M, 200 μL), to convert the carboxylic group (–COOH) of the QDs into an activated carbodiimide ester group [241]. The mixture was allowed to stir for 30 minutes at room temperature, followed by addition of 2 mL of complex **10** (0.02 g, 0.018 mmol) in DMSO, which was slowly added to the reaction mixture followed by continuous stirring for another 24 h. The crude product was precipitated with ethanol and washed several times by centrifugation using ethanol, methanol: water (9:1) and methanol successively as a solvent.

Yield: 0.04 g (80 %). IR [(ATR), $\nu_{\max}/\text{cm}^{-1}$): 3232(–CONH–), 1719, 1656, 1570, 1471, 1378, 1302, 1218 (C–O–C), 1006, 812.

2.5.5 Conjugation of phthalocyanine (11 or 12) to GSH/CdTe/ZnSe/ZnO QDs to form (11-QDs and 12-QDs, respectively), Scheme 3.9

Complexes **11** or **12** were covalently linked to GSH capped CdTe/ZnSe/ZnO QDs in accordance with reported procedures [238–240] with slight modification as follows: A mixture of GSH capped CdTe/ZnSe/ZnO (0.03 g in 3 mL), 0.1 M EDC (200 μ L) and 0.1 M NHS (200 μ L) in water was allowed to stir for 30 min at room temperature to convert the carboxylic group ($-\text{COOH}$) of the QDs into an activated carbodiimide ester group. This was followed by slow addition of 2 mL of complexes **11** (0.02 g, 0.018) or **12** (0.02 g, 0.016 mmol) in DMSO followed by continuous stirring for another 24 h. The crude products were precipitated with ethanol and washed several times by centrifugation using ethanol, methanol: water (9:1) and methanol successively as a solvent.

11-QDs: FT-IR [KBr disc ($v_{\text{max}}/\text{cm}^{-1}$)]: 3301, 3193 (N–H str.), 1574, 1540 (N–H bend), 1385, 1291, 1179, 1093 (C–O–C), 976, 909.

12-QDs: FT-IR [KBr disc ($v_{\text{max}}/\text{cm}^{-1}$)]: 3319, 3189 (N–H str.), 2924, 1575 (N–H bend), 1464, 1385, 1283, 1142, 1093 (C–O–C), 972, 909.

2.5.6 Conjugation of phthalocyanine to gold nanoparticles, Scheme 3.10

Complexes **11** and **12** were conjugated via interaction between the nanoparticle and the amine (or the S) group on the MPc. Briefly as-synthesized 4.5 mL HAD-AuNPs (from section 2.4.2) were mixed with **11** or **12** 100 mM (0.5 mL in DMSO) and allowed to react 80 $^{\circ}\text{C}$ for 48 h under stirring for adsorption of Pcs on the surface of the nanoparticle, by replacing HDA.

2.6 Preparation of Electrospun Nanofibers

A polymer (polystyrene) solution (25% in a mixture of DMF/THF (ratio 4:1)) was prepared. The solution for the modified fiber was prepared by blending phthalocyanine (1.0 g) to the polymer solution. The mixture was homogenized using a magnetic stirrer at room temperature for 24 h, followed by electrospinning of the polymer solutions into the fiber. The process parameters for electrospinning were: tip-to-collector distance (TCD) = 12 cm; applied voltage = 15 kV. The flow rate for polystyrene alone was 0.1 mLh⁻¹. The flow rate was increased to 0.5 mLh⁻¹ of the polystyrene-metallophthalocyanine composite to avoid clogging at the needle tip and jet instability.

2.7 Antimicrobial Studies

2.7.1 Preparation of *E. Coli* Culture

E. coli was grown on a nutrient agar plate prepared according to the manufacturer's specifications to obtain an individual colony. The colony was then inoculated into Luria nutrient broth and then placed on a rotary shaker (~ 200 rpm) overnight at 37 °C. Aliquots of the culture were aseptically transferred to 4 mL of fresh broth and incubated at 37°C to mid-logarithmic phase (absorbance $\approx$ 0.6 at 620 nm). The bacteria culture in the logarithmic phase of growth were harvested through the removal of broth culture by centrifugation (3000g for 15 min), washed once with 10 mM of PBS and re-suspended in 4 mL of PBS. Then the bacteria culture was diluted to 1/1000 in PBS (working stock solution), corresponding to $\approx$ 10⁸ CFU/ml [80].

2.7.2 Photodynamic Antimicrobial Chemotherapy Activity

Photodynamic antimicrobial chemotherapy study of the *E.coli* was performed using methods previously reported [85,242]. In all the experiments, the *E. coli* suspension were incubated in an oven equipped with a shaker for 30 min in the dark at 37°C. Then half (1 mL) of the incubated *E. coli* suspensions were irradiated at the Q-band maximum of the photosensitizers

in 24 well plate, using the set-up described above at different time intervals, while the other half was kept in the dark. After irradiation, 100 μ L samples were serially diluted (10 fold) with PBS and 100 μ L of sample were aseptically spotted on agar plates using micropipette [243]. The plates were incubated inverted at 37°C overnight for 24 h. The absorbance of the cell suspension were measured before and after incubation for 30 min (this has been reported to result in localization of the photosensitizer within the cytoplasm of the bacteria [244]), then finally after 60 min of photoinactivation experiments.

2.8 Photochemical Studies

2.8.1 Preparation of Working Solutions

All the solutions were prepared in phosphate buffer solution, pH 11. Stock solutions of 4-chlorophenol (0.1 mM) were prepared from which the working concentration of 5 μ M was produced. BPA stock solutions (100 mg/l in PBS) were used to make a working solution of 0.02 mM.

2.8.2 Photo-oxidation Experiments

The photochemical transformation of the pollutants was carried out in a magnetically stirred batch reactor (glass vial), using the photolysis set-up described above. The transformation was monitored by observing the absorption bands of 4-chlorophenol and bisphenol A after each photolysis cycle of 30 min using a Shimadzu UV-2550 spectrophotometer. Each sample solution contained 10 mg of functionalized fiber. All the experiments were irradiated under aerobic conditions without bubbling of oxygen. The oxygen in the medium has been proven to be enough to support the degradation of most phenolic compounds below a concentration of 0.1 mM [197].

2.9 Photophysical and Photochemical Parameters

2.9.1 Fluorescence Quantum Yield (Φ_F) and Lifetime (τ_F)

The fluorescence quantum yield (Φ_F) of the MPcs and its conjugates were determined using comparative methods, [199] Equation 1.1 as discussed in the previous chapter. Both the samples and the standard were excited at the same wavelength. The absorbances of the solutions at the excitation wavelength were about 0.05 to avoid any inner filter effects and the lifetimes of the MPcs were measured using TCSPC set-up (**Figure 2.1**) by exciting at the excitation wavelength of the Pcs.

2.9.2 Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T)

The transient curves and decay kinetics of the triplet absorption of phthalocyanines and its conjugates were recorded using a laser flash photolysis set-up (**Figure 2.3**). The absorbance of sample solutions and that of the standard were adjusted to be at approximately 1.5 at their cross-over wavelength. After introducing the solution into a 1 cm quartz cell, argon was bubbled through the solution to remove dissolved oxygen before taking readings. The triplet quantum yields of the samples were determined using Equation 1.8. Triplet lifetimes were determined from the kinetic data obtained, using ORIGIN Pro 8 software.

2.9.3 Singlet Quantum Yield (Φ_Δ) and Photodegradation (Φ_{Pd})

A chemical comparative method was used for Φ_Δ determinations of the phthalocyanines in DMSO, DMF or water using the experimental set-up shown in **Figure 2.2**. The experiments were carried out in the air with 1.5 mL of each Pcs solution with an absorbance of 1 at the Q-band. The Pc was mixed with equal volume of a solution of DPBF or ADMA with the approximate absorbance of 2 at 417 and 380 nm respectively. The resulting solution was irradiated at the Q-band region, using the photolysis system described above. The degradation was monitored by recording the UV-vis spectra of the sample solution at 10 seconds time intervals for DPBF and 10 min for ADMA. The wavelength of the interference filter was chosen (at 700 nm) such that it was close to the Q-band absorption of the MPc. The

concentrations of DPBF were lowered to $\sim 0.3 \mu\text{mol dm}^{-3}$ for all solutions to avoid chain reactions. The initial quencher concentrations were kept the same for both the standard and the MPcs. Absolute methods were used for determination of Φ_{Δ} in fibers using ADMA as a quencher and its degradation was monitored at 380 nm as described in chapter 1. In each case, the modified fibers (10 mg) were suspended in an aqueous solution of ADMA and irradiated using the photolysis set-up, **Figure 2.2**. The quantum yields were estimated using Equation 1.15, the molar extinction coefficient of ADMA in water $\log(\epsilon) = 4.1$ [245] and using the absorbance of the phthalocyanine in the polymer fiber matrix. For photodegradation quantum yield (Φ_{Pd}), the same photochemical set-up is employed, but no quencher are used in the solution.

Results and discussions

Publications

1. **Osifeko, Olawale L.**; Nyokong, Tebello. Applications of lead phthalocyanines embedded in electrospun fibers for the photoinactivation of *Escherichia coli* in water **Dyes and Pigments (2014), 111, 8-15.**
2. **O. Osifeko**, M. Durmuş T. Nyokong. Photophysicochemical Properties of Mono- and Tetra-pyridyloxy substituted Indium (III) phthalocyanines **J. Photochem. Photobiol. A: Chem. 301 (2015) 47-54**
3. **Osifeko, O. L.**, Uddin, I., Mashazi, P. N., Nyokong, T. Physicochemical and Antimicrobial Photodynamic Therapy of unsymmetrical Indium phthalocyanines-Fe₃O₄-Silica core-shell conjugate. **New J. Chem. 1–12 (2016). doi:10.1039/C5NJ01922B**
4. **Olawale L Osifeko** and Tebello Nyokong. A comparative Physicochemical study of unsymmetrical Indium phthalocyanines in the presence of magnetic nanoparticles or quantum dots. **Journal of Coordination Chemistry, 69 (2016) 1050-1065.**
5. **Olawale L Osifeko** and Tebello Nyokong. Synthesis and physicochemical properties of Zinc and Indium phthalocyanines conjugated to quantum dots, Gold, and Magnetic nanoparticles. **Dyes and Pigments (2016), 131, 186-200.**
6. **Olawale L. Osifeko** and Tebello Nyokong. Phototransformation of bisphenol A and 4-chlorophenol using indium phthalocyanines Embedded in Electrospun Fiber. *J. Mol. Cat. Submitted*
7. Owolabi M. Bankole, **Olawale Osifeko**, Jonathan Britton and Tebello Nyokong. Enhanced nonlinear optical responses of zinc diaminopyrimidin-2-ylthio phthalocyanine conjugated to Ag_xAu_y alloy nanoparticles. *J. Photochem. Photobiol. A: Chem.-Submitted*

Chapter 3

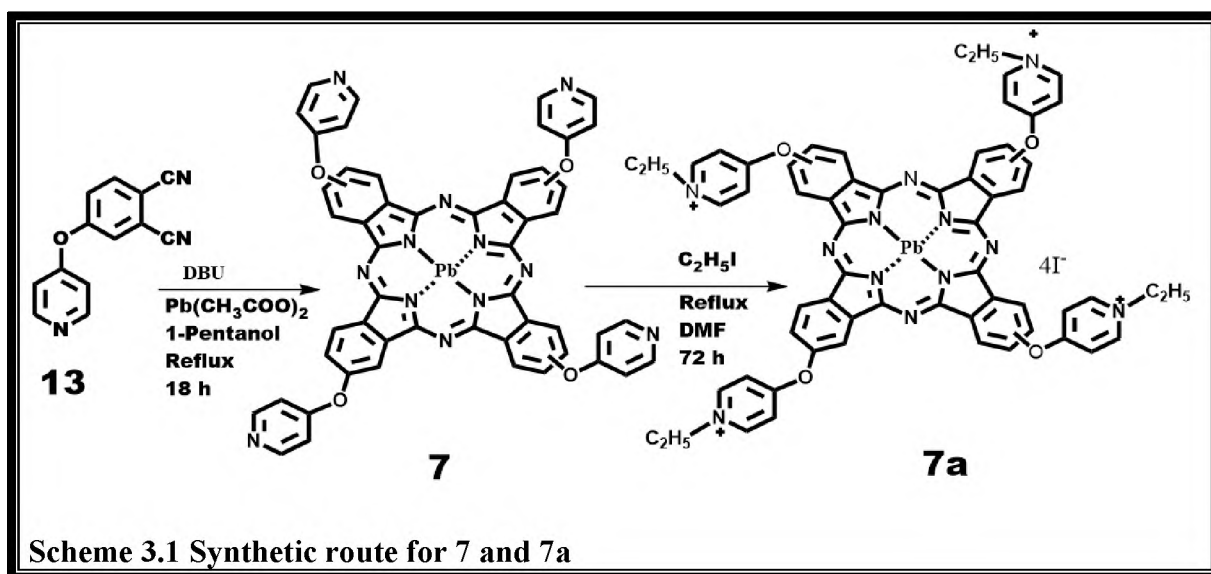
In this chapter, the synthesis and characterization of the MPcs and their conjugates to nanoparticles are discussed. The techniques employed include ^1H -NMR, MALDI-TOF MS, FT-IR, UV–vis spectrophotometry, CHN elemental analysis, XRD, XPS, TEM, and TGA.

3 Synthesis and characterization of Pcs and conjugates

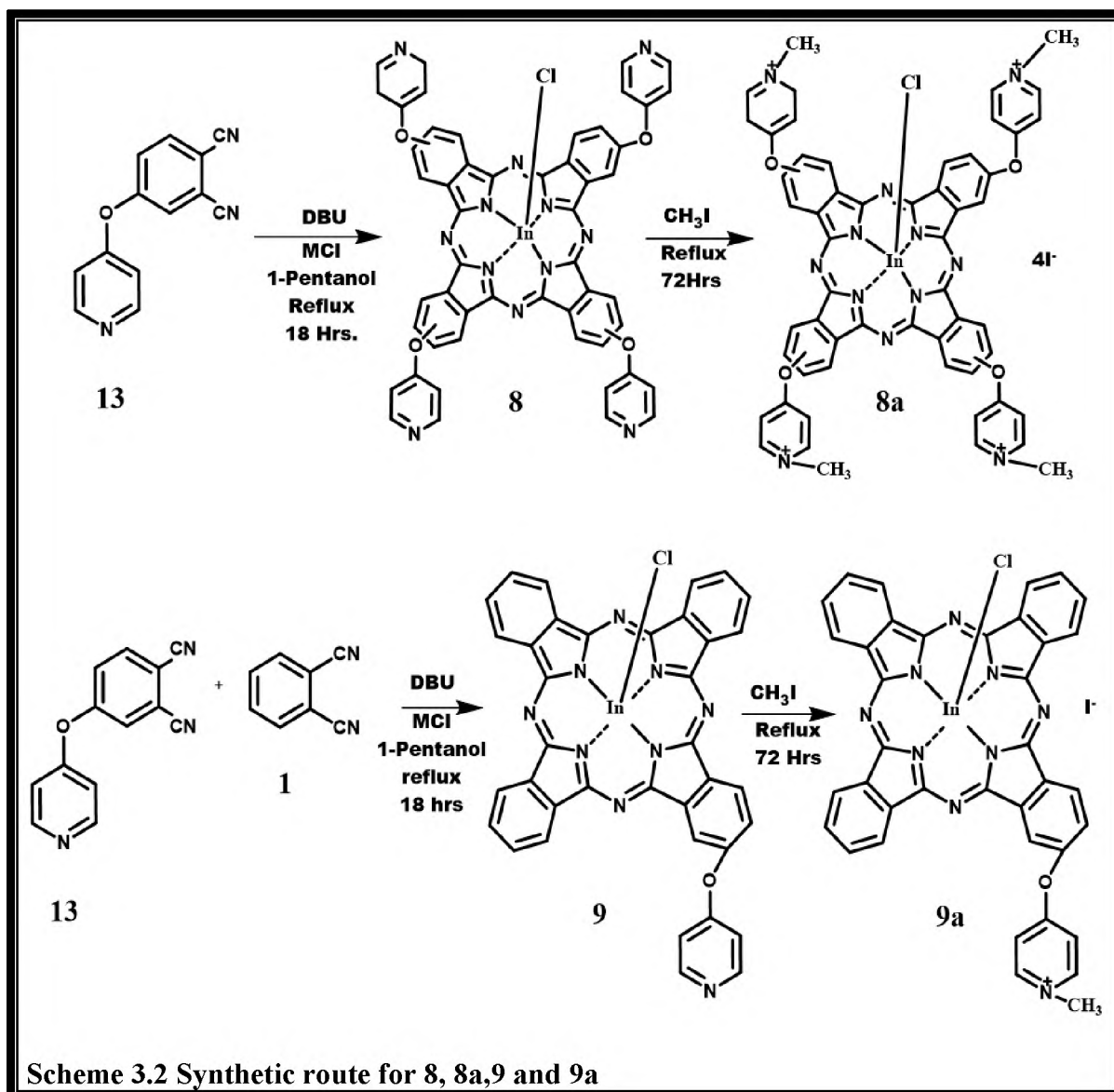
3.1 Characterisation of phthalocyanines alone

3.1.1 Pyridyloxy Substituted Phthalocyanine (7-9, 17, 18)

The tetra-substituted complexes **7** (Scheme 3.1), and **8** (Scheme 3.2) were synthesized by cyclotetramerization of 4-(4-pyridyloxy) phthalonitrile (**13**) (in n-pentanol) in the presence of lead(II) acetate or indium (III) chloride, respectively. The mono-substituted Pc (**9**) was synthesized by statistical condensation of two different phthalonitrile 1, 2-dicyanobenzene (**1**) and 4-(4-pyridyloxy) phthalonitrile (**13**) in the presence of indium (III) chloride in n-pentanol. Subsequently, the purified metallophthalocyanines were quaternized by alkylation process using ethyl iodide for complex **7a** and methyl iodide for complexes **8a** and **9a**.

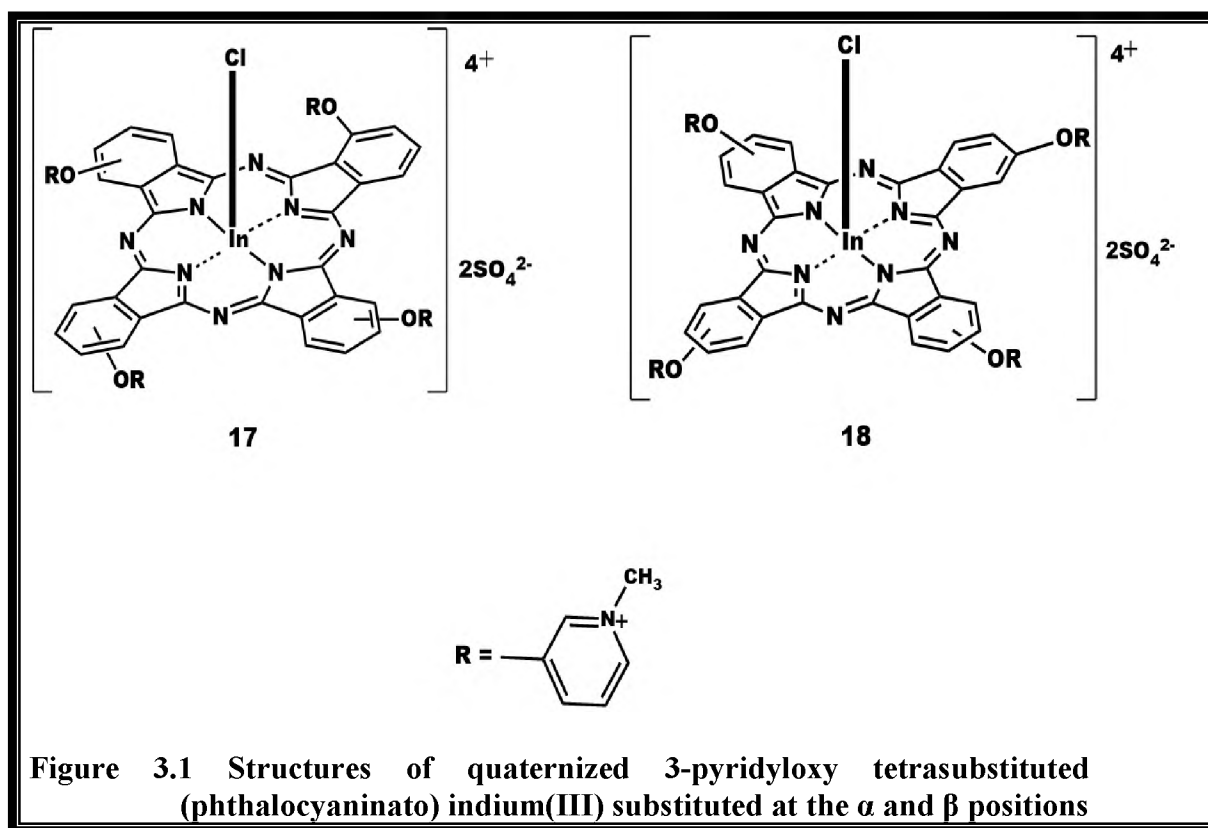


The structures of the compounds were confirmed using UV-Vis, CHN elemental analysis, FTIR, ^1H NMR and MS spectroscopic data. The quaternized metallophthalocyanine complex (**7a**) did not show a molecular ion peak in mass spectra. Pyridyloxy metallophthalocyanine complexes are known for other central metals [246,247]. However, the Pb derivative is reported in this thesis for the first time.

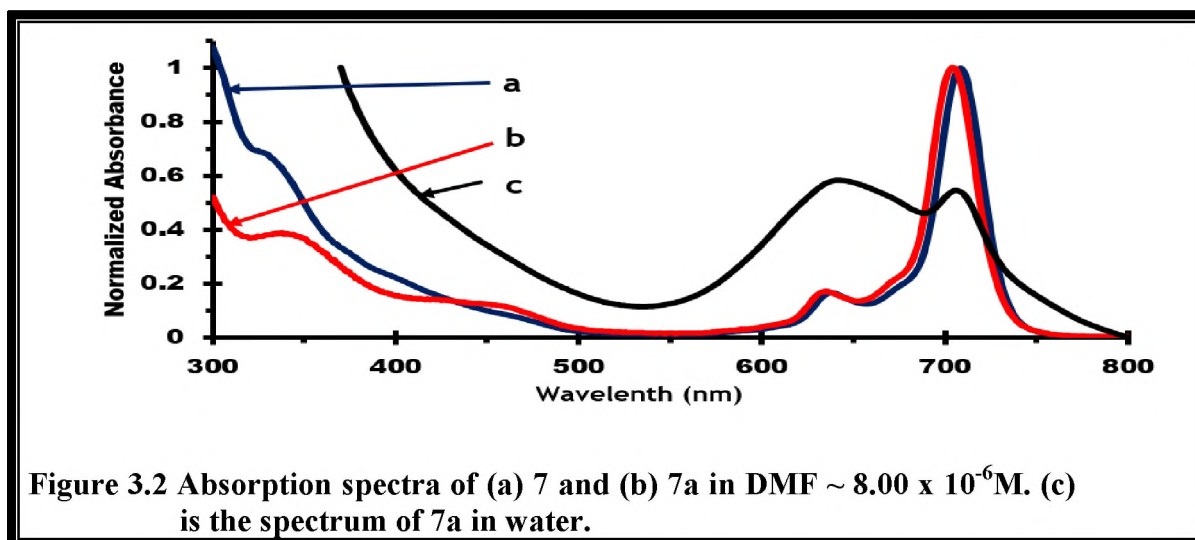


The synthesis of quaternized 3-pyridyloxy tetrasubstituted (phthalocyaninato) indium(III) substituted at the α (**17**) and β (**18**) positions have been previously reported [248], **Figure 3.1** hence, their synthesis and characterization will not be discussed in this thesis. The photophysical behavior of **17** and **18** will be compared to that of **9a** and **10a**. The absorption spectra of complexes (**7**, **8** and **9**) and their quaternized forms (**7a**, **8a** and **9a**, respectively) were studied in DMF, DMSO and aqueous media (the latter only for complexes **7a** and **8a**). Complex **9a** has a single quaternizeable pyridyl substituent as compared to four quaternizeable pyridyl groups on complexes **7a** and **8a**, hence the former is not soluble in

aqueous media. The Q-band for **7a** was observed at 705 nm which is slightly blue shifted compared to **7** which is at 709 nm **Table 3.1** in DMF, **Figure 3.2**.



Nitrogen ligands are known to result in red shifting in phthalocyanines [249], and their engagement due to quaternization may result in the blue shifting in the Q-band as observed in **Figure 3.2(b)**. The blue shift is also observed for **8a** in DMF (**Table 3.1**). For **9a** quaternization of one substituent is not enough to shift the spectra. The Q-band maxima of **17** were observed at 698 nm and **18** at 693 nm, non-peripherally substituted Pcs (e.g **17**) are known to show red shifted Q-band compared to peripheral Pcs (e.g **18**) [248] as shown in **Table 3.1**. Complex **18** with 3-N-methylpyridiniumoxy moieties as compared to **8a** (4-N-methylpyridiniumoxy moieties) shows a red-shifted Q-band, **Table 3.1** in DMSO suggesting that the position of N-group closer to the Pc rings results in red shifting.



Sharp Q-bands for all complexes in DMF or DMSO, (Figure 3.3 DMF used as an example), indicate that there is no aggregation of these photosensitizers in these solvents.

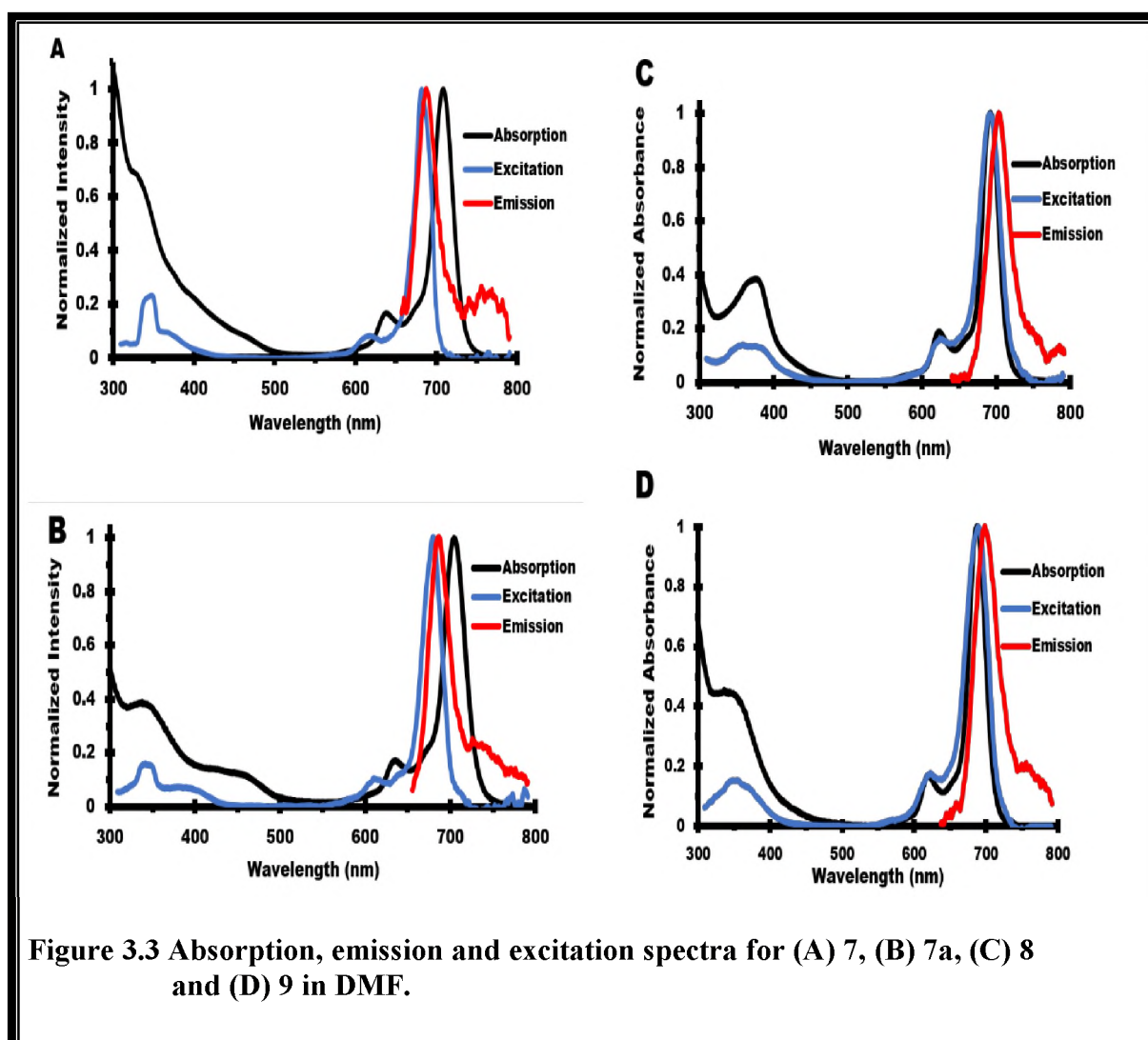


Figure 3.3 shows the emission, absorption and excitation spectra for complexes 7, 7a, 8 and 9 in DMF as examples. For all complexes, the emission spectra were a mirror image of the excitation spectra and the latter were similar to the absorption spectra in DMF or DMSO. Both 7 (Figure 3.3 A) and 7a (Figure 3.3 B) showed blue shifted emission spectra relative to the absorption spectra (Figure 3.3 A and B), a phenomenon that has been reported before for PbPc complexes, and was attributed to the loss of the central lead metal upon excitation [250,251].

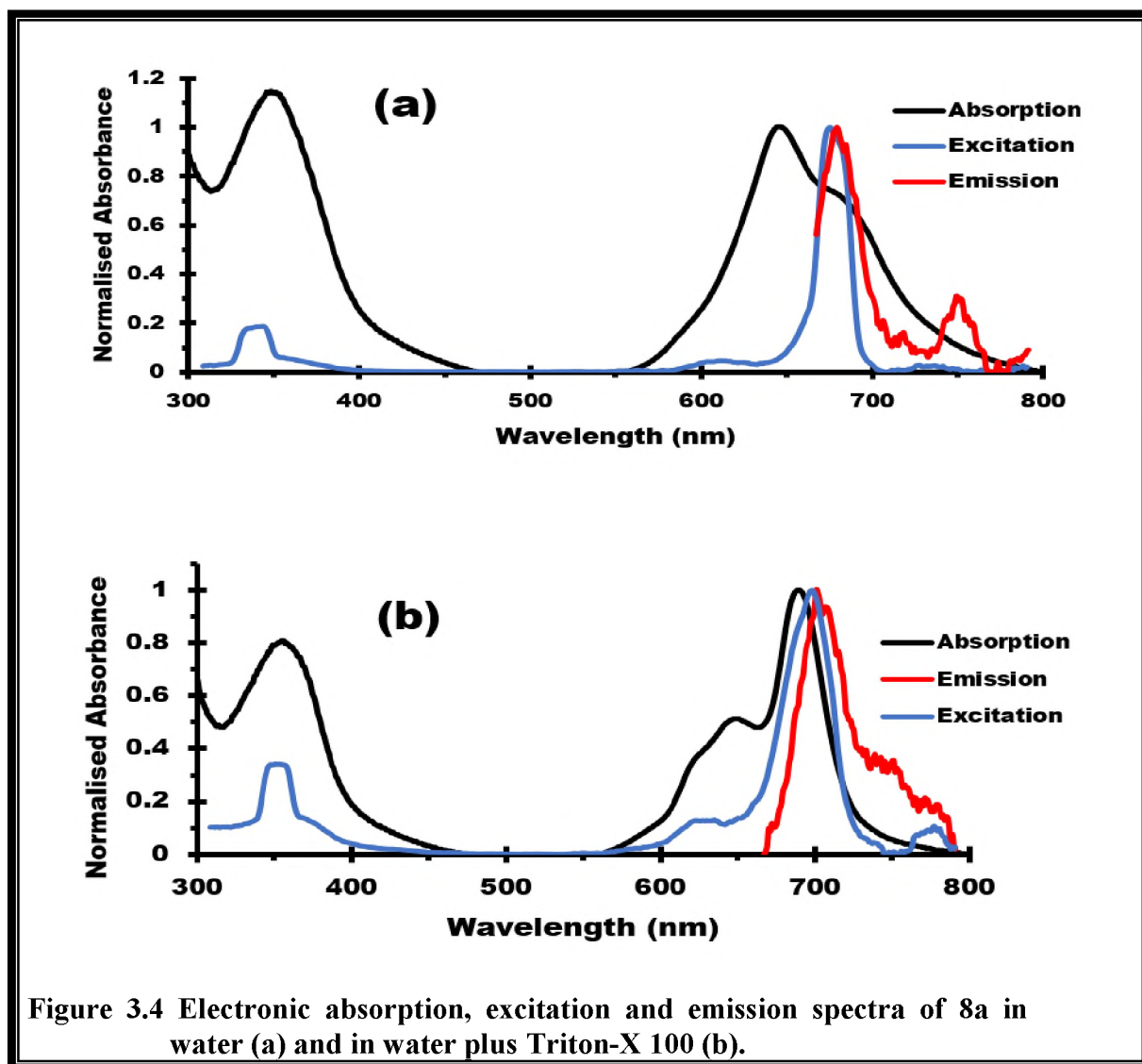


Figure 3.4 Electronic absorption, excitation and emission spectra of 8a in water (a) and in water plus Triton-X 100 (b).

The demetallation of PbPcs is common on excitation because of the “shuttle-cock” configuration, hence emission is from the metal free species. The emission spectra show one Q-band which has been assigned as the 0-0 transition for metal free Pcs [252]. In aqueous media, the absorption spectra were different from the excitation spectra due to aggregation **Figure 3.4**. Aggregation in MPc complexes is judged by broadening or split in the Q-band, with the high energy band being due to the “H” aggregate [253]. Complex **7a** (**Figure 3.2 c**) and **8a** (**Figure 3.4a**) were aggregated in water. Addition of surfactant (Triton X-100) to the aqueous solution of **8a** reduced the aggregation as shown in **Figure 3.4b**. For InPc complexes, **8**, **9** (**Figure 3.3 C and D**), **17** and **18**; absorption and excitations spectra were similar and are mirror images of emission spectra. The absorption, excitation and emission spectra data are listed in Table 3.1

Table 3.1 Electronic absorption and emission properties of the phthalocyanines in DMSO, unless otherwise stated

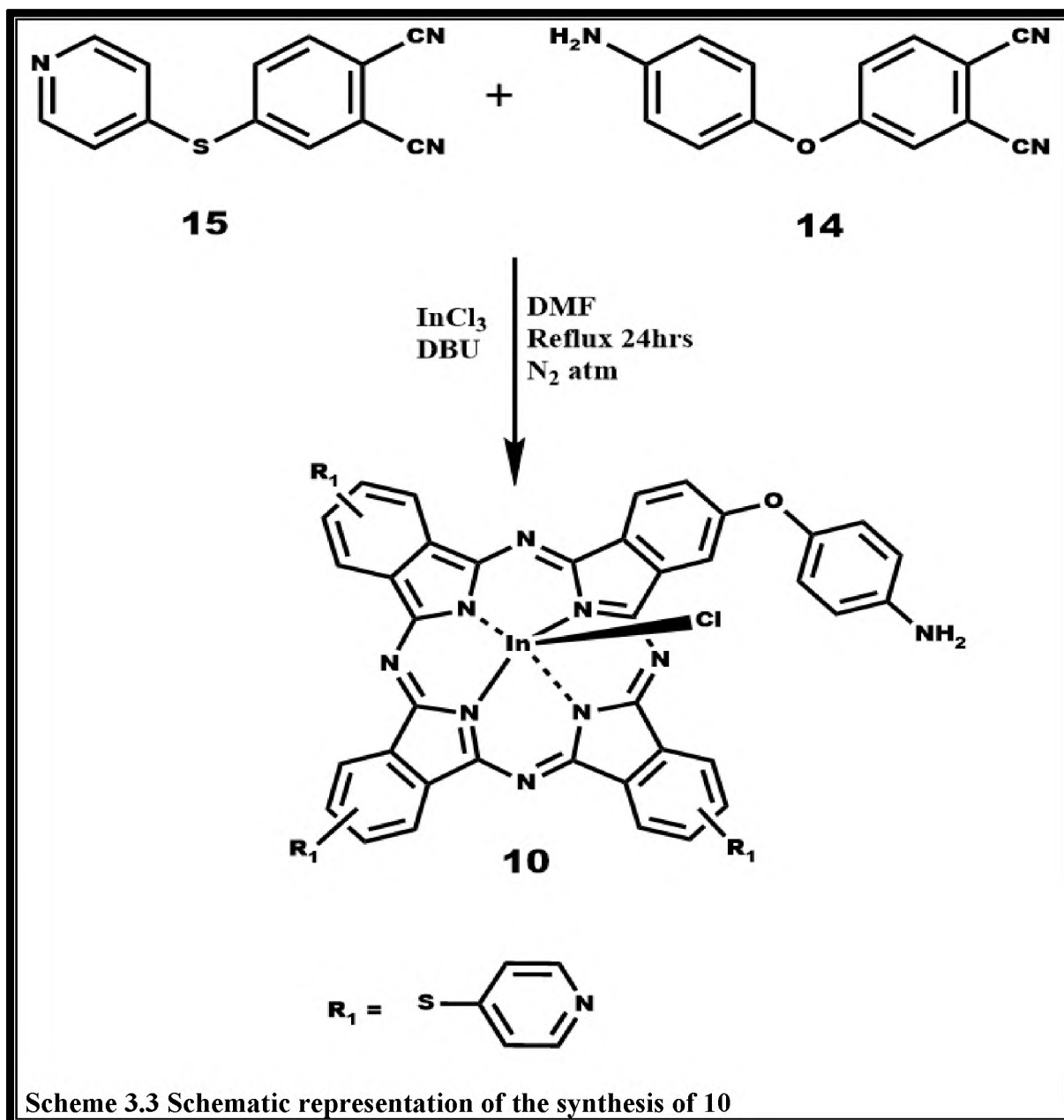
Compounds	Solvent	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{emm}}(\text{nm})$	$\lambda_{\text{exc}}(\text{nm})$
7	DMF	709	687	682
7a	DMF	705	688	680
8	DMF	693	705	695
	DMSO	692	706	694
8a	DMF	689	708	698
	DMSO	691	706	696
	Water	646	676	679
	Water/Triton-X 100	689	701	696
9	DMF	684	698	686
	DMSO	686	695	689
9a	DMF	684	698	686
	DMSO	685	697	687
10	DMSO	698	710	702
10a	DMSO	699	711	703
11	DMSO	689	700	689
12	DMSO	704	711	701
17	DMSO	698	707	718
18	DMSO	693	697	708

λ_{abs} = absorption wavelength, λ_{emm} = emission wavelength, λ_{exc} = excitation wavelength

The Q-band maxima for **17** is red shifted compared to **18**. Also, **8a** is blue shifted compared to **18**, Table 3.1 in DMSO, suggesting that the position of the N group closer to the Pc ring results in red shifting.

3.1.2 Pyridyloxy and aminophenoxy substituted InPc (**10** and **10a**)

Compound **10** was synthesized by template cyclization of 4-(4-aminophenoxy)phthalonitrile (**14**) and 4-(4-pyridylsulfanyl)phthalonitrile (**15**) in the presence of InCl₃ in an inert atmosphere using DMF as the reaction medium (**Scheme 3.3**). Compound **10a** was obtained via quaternization of compound **10** using methyl iodide as the quaternizing agent. Both complexes were characterized by elemental analysis and several spectroscopic techniques. Detailed NMR and mass spectra are provided for **10** and **10a** as an example for other complexes.



3.1.2.1 Nuclear Magnetic Resonance Spectra

^1H NMR spectrum of **10** (Figure 3.5) provided the characteristic chemical shifts for the structure expected. It exhibited the aromatic protons at $\delta = 8.44\text{--}8.48$ ppm and $\delta = 7.26\text{--}7.23$ ppm as a doublet of doublets, and $\delta = 7.91\text{--}7.89$ ppm as a doublet. NH_2 protons were observed as a singlet at $\delta = 6.64\text{--}6.62$ ppm and other aromatic protons were observed at $\delta = 6.88\text{--}6.86$ ppm and $\delta 7.85\text{--}7.83$ ppm respectively.

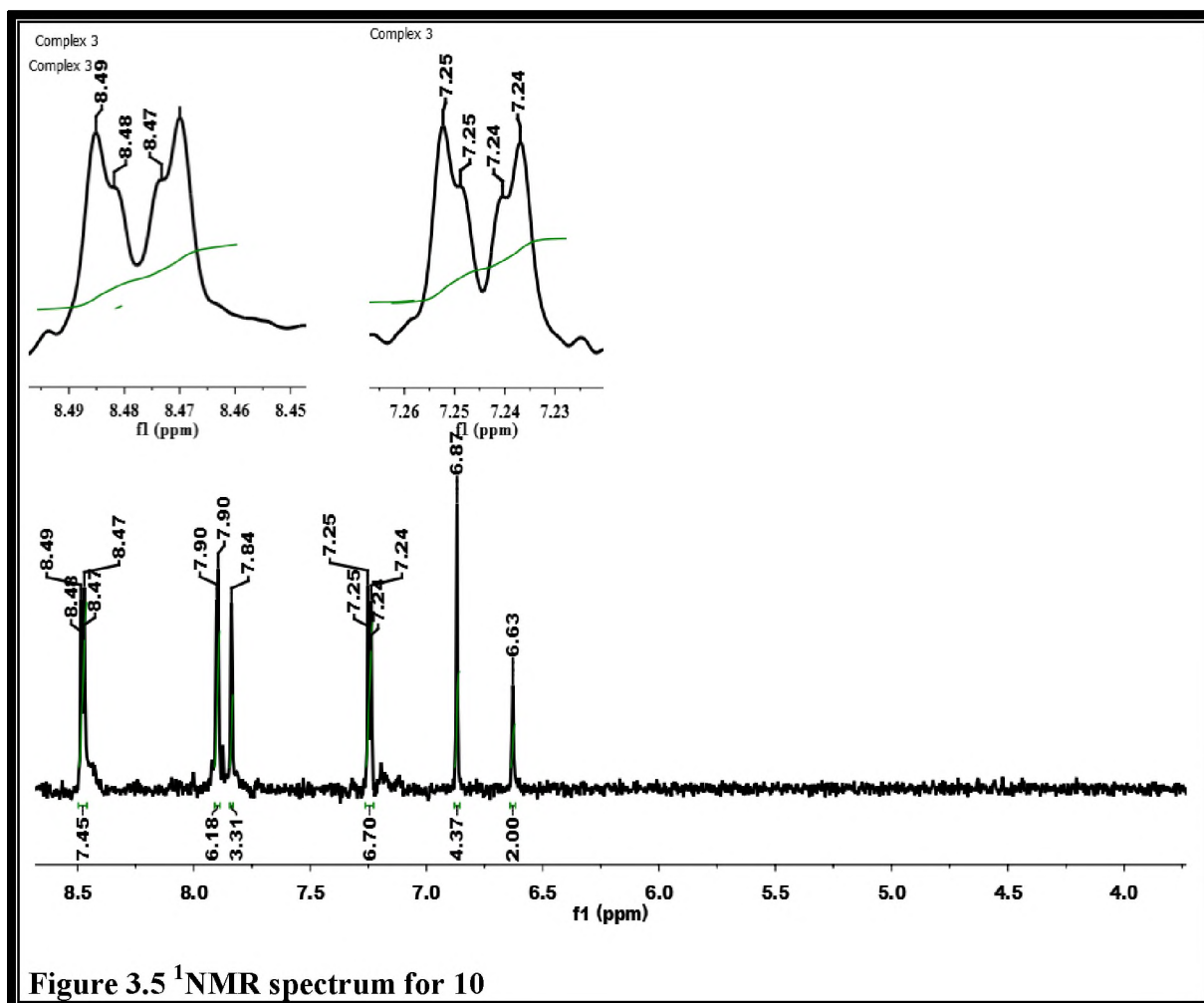
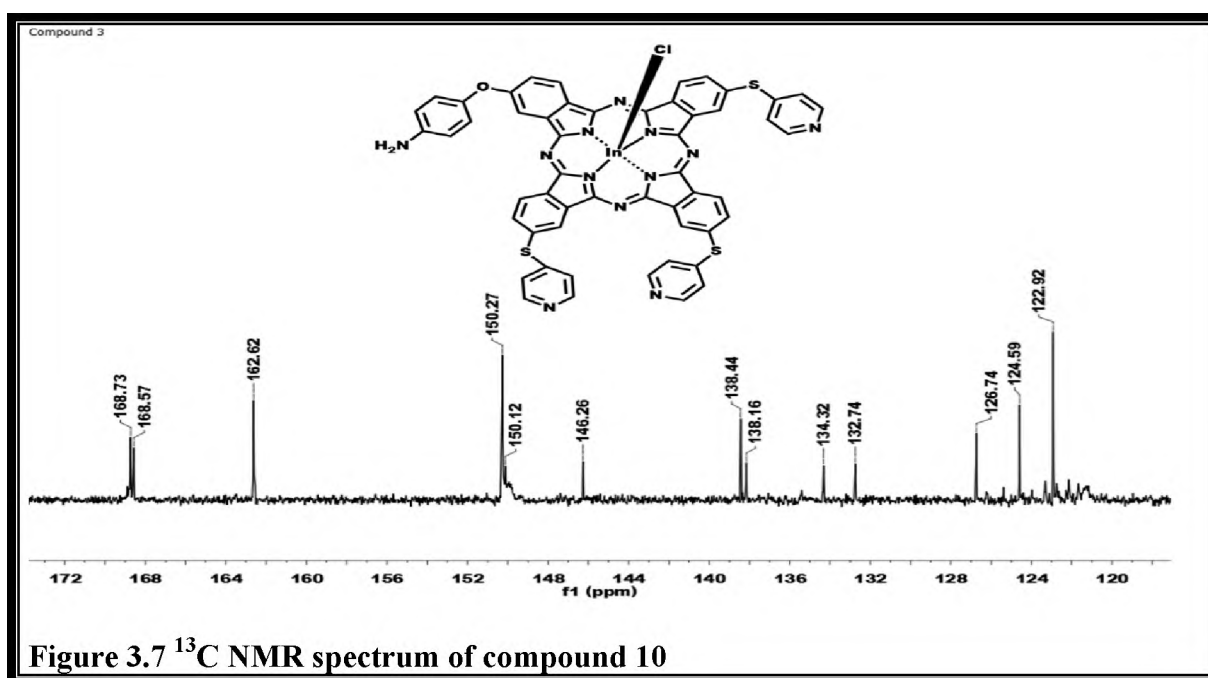
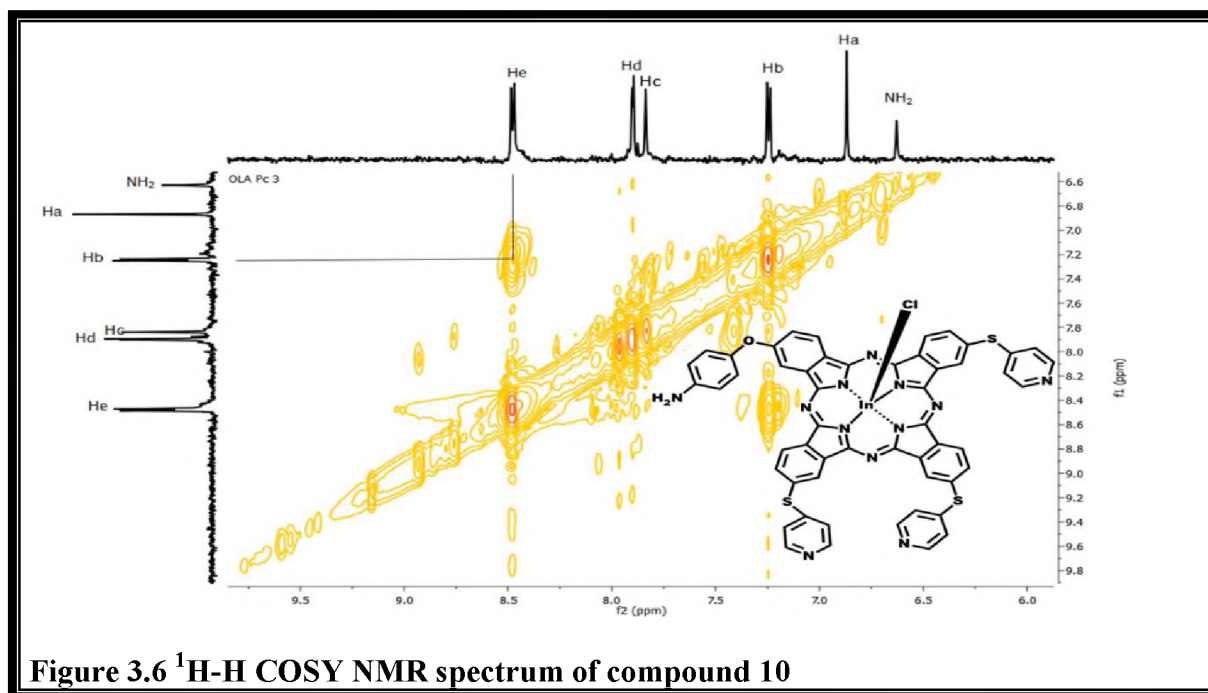
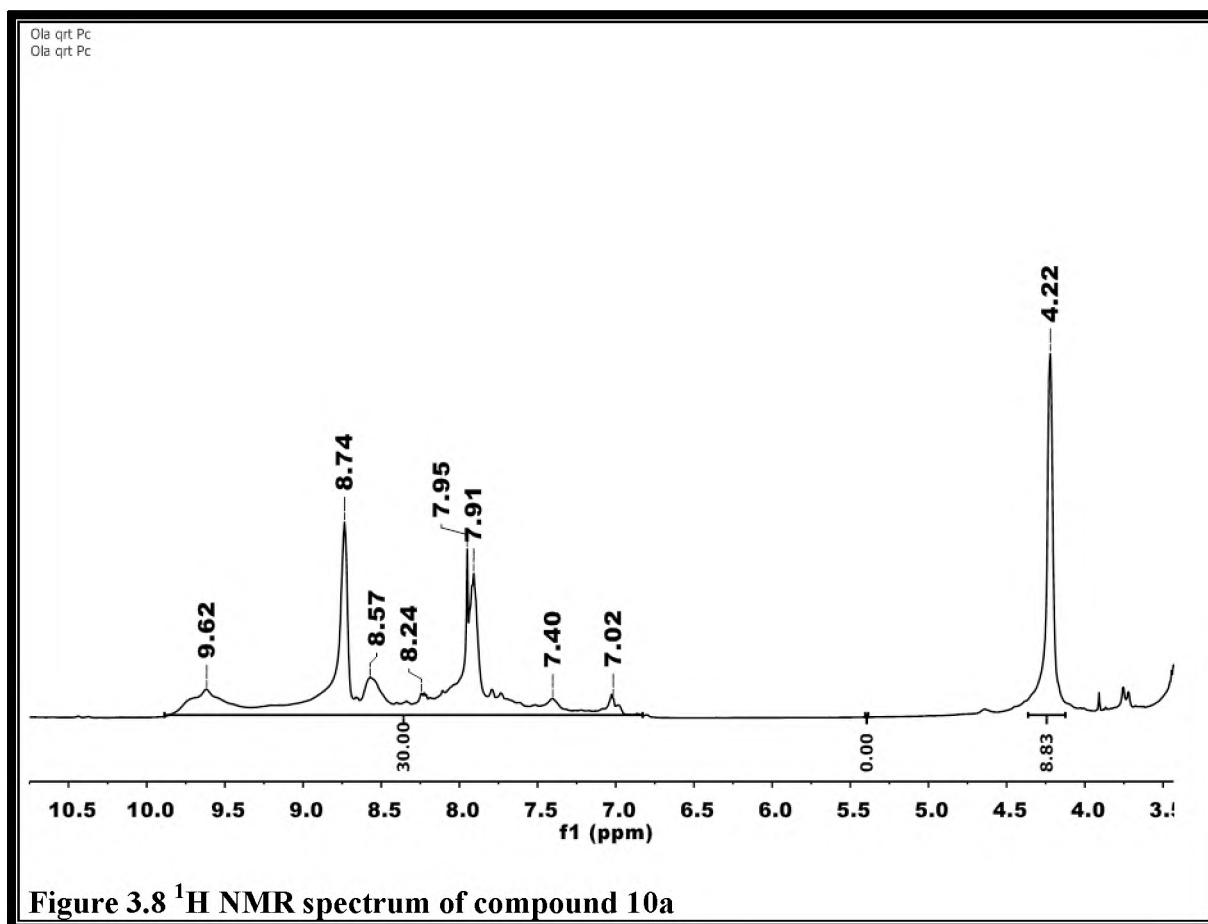


Figure 3.5 ^1H NMR spectrum for 10

Strong COSY correlations (**Figure 3.6**) were observed between the two doublets of doublet; Phenyl-H resonance at 7.26-7.23 (dd, 7H, $J = 4.8, 1.4$ Hz; Phenyl-H and Pc-H) and pyridyl-H at 8.44-8.48 (dd, 8H, $J = 4.7, 1.3$ Hz; pyridyl-H and Pc-H). The signals along the diagonal reflect the normal ^1H - ^1H spectrum. ^{13}C NMR spectrum (**Figure 3.7**) showed typical aromatic carbons between 120-170 ppm.



^1H NMR spectrum for **10a** indicates broad peaks that could not be assigned as was shown in **10** above. There is a clear presence of the alkyl group up the field, **Figure 3.8** confirming that quaternization was successful. The expected number of aromatic is 28, but the observed number of protons in the aromatic area is 30, due to the presence of the overlapping NH_2 peaks.



3.1.2.2 Mass spectroscopy

Mass spectrum for complex **10** is shown in **Figure 3.9(A)** and is consistent with the complex. For complex **10a**, quaternization of the pyridyl nitrogen is well known. It is also possible to methylate the NH_2 groups, with eventual quaternization. XPS (to be discussed below) show the presence of NH for **10a**, hence does not support full quaternization of the NH_2 . There is little or no evidence in the literature for the quaternization of NH_2 substituted Pcs using methyl iodide. There have been reports of the formation of NH_3^+Cl^- when an amino substituted Pc is reacted with hydrochloric acid [254]. The mass spectral data for **10a** showed three prominent peaks which are assigned to (i) removal of 3I^- and 3H^+ (1140 g), (ii) removal of 6H^+ and displacement of Cl^- by CH_4I^+ (1244 g) (iii) removal of Cl^- and 8H^+ (1480), see **Figure 3.9(B)**.

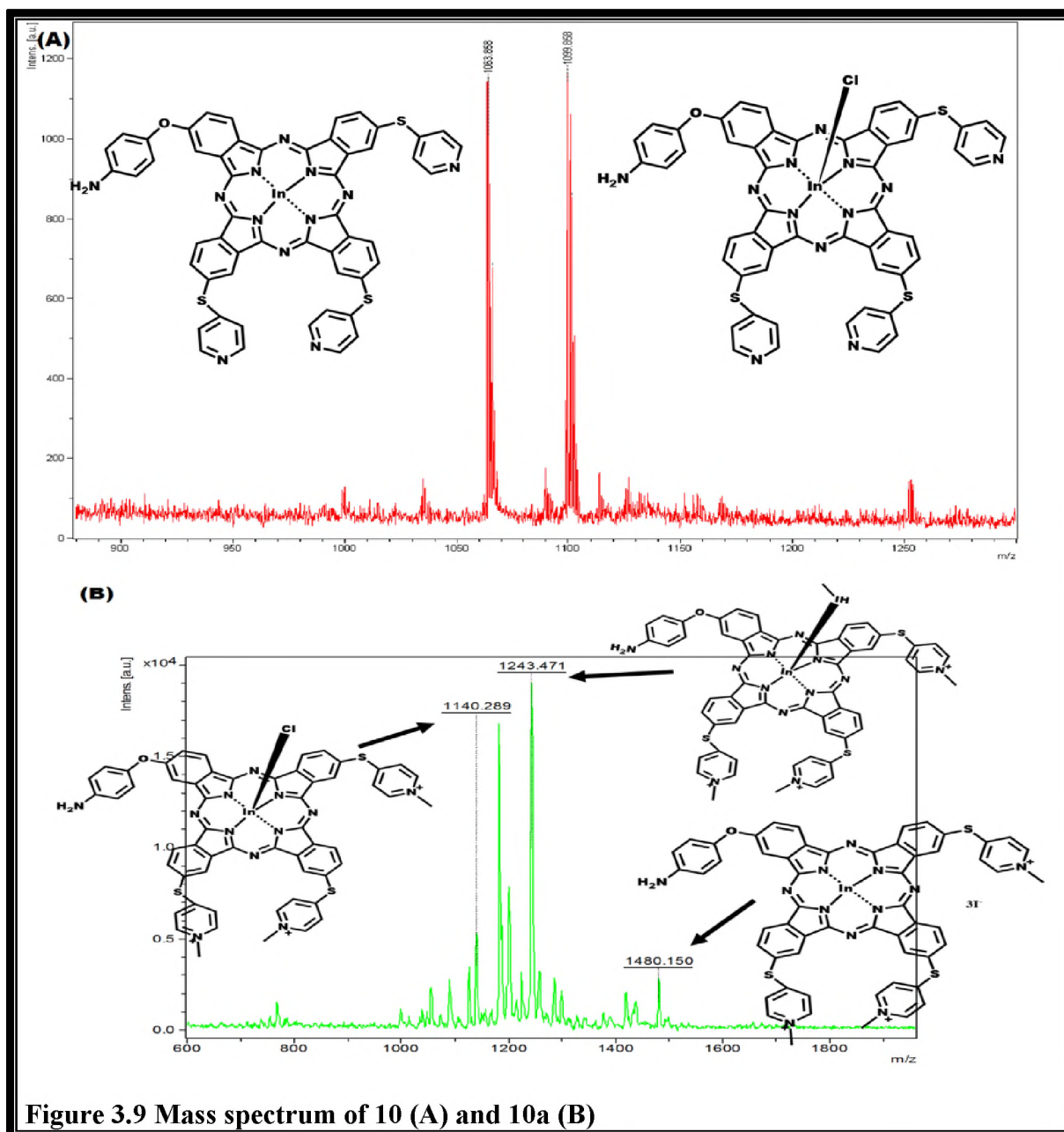
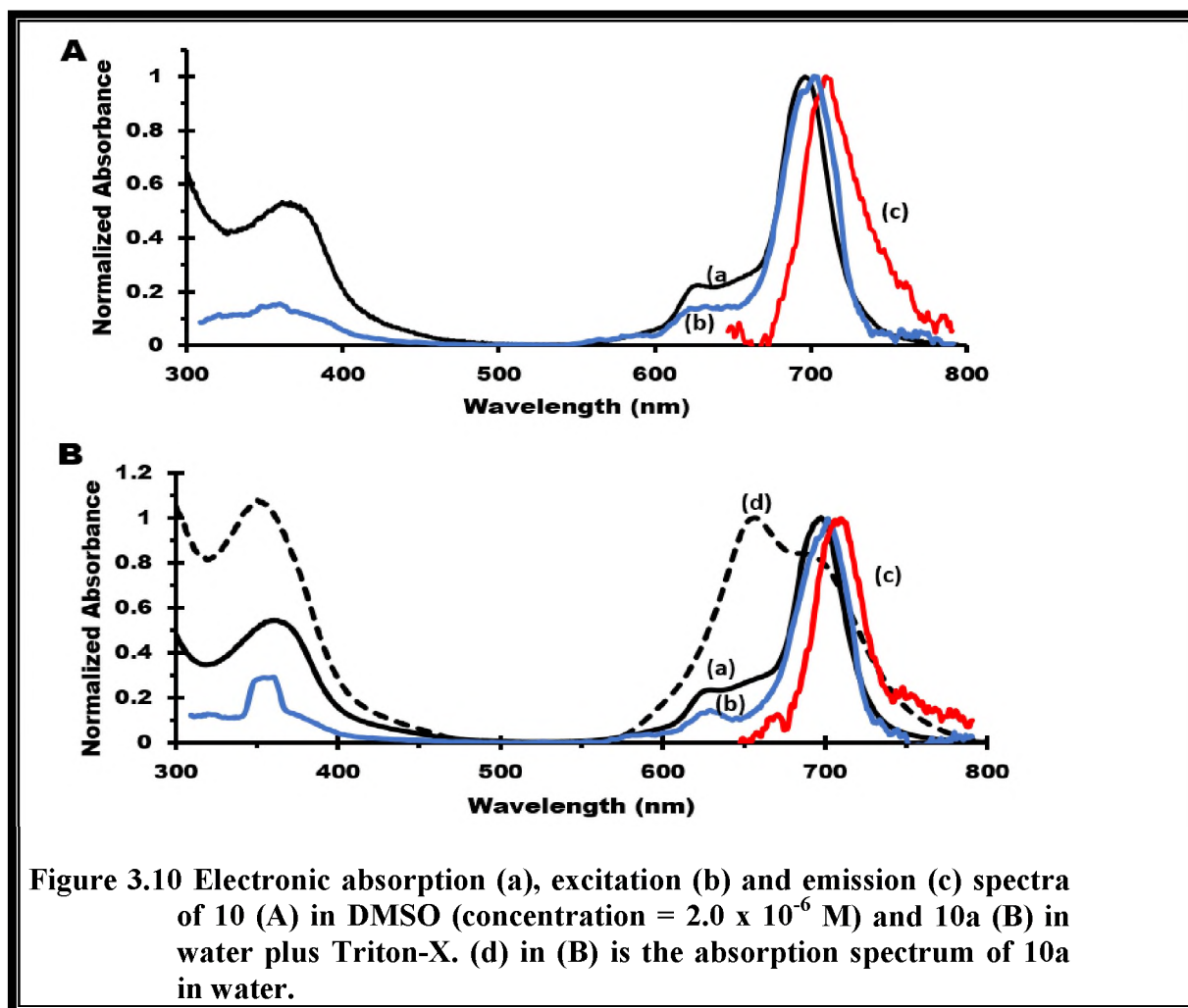


Figure 3.9 Mass spectrum of 10 (A) and 10a (B)

3.1.2.3 UV-Vis Absorption Spectra

The UV-Vis spectra of complexes **10** and **10a** are shown in **Figure 3.10**. The Q-band for **10** is observed at 698 nm Table 3.1 and does not change significantly on quaternization to form **10a**, Table 3.1 (699 nm). Complex **10a** is water soluble, but highly aggregated, **Figure 3.10B** (curve d). Addition of Triton-X-100 reduced the aggregation significantly. The UV absorption of both complexes in DMSO shows monomeric behavior. Emission spectra were mirror images of the excitation spectra in DMSO (for **10** and **10a**) or water plus Triton-X 100

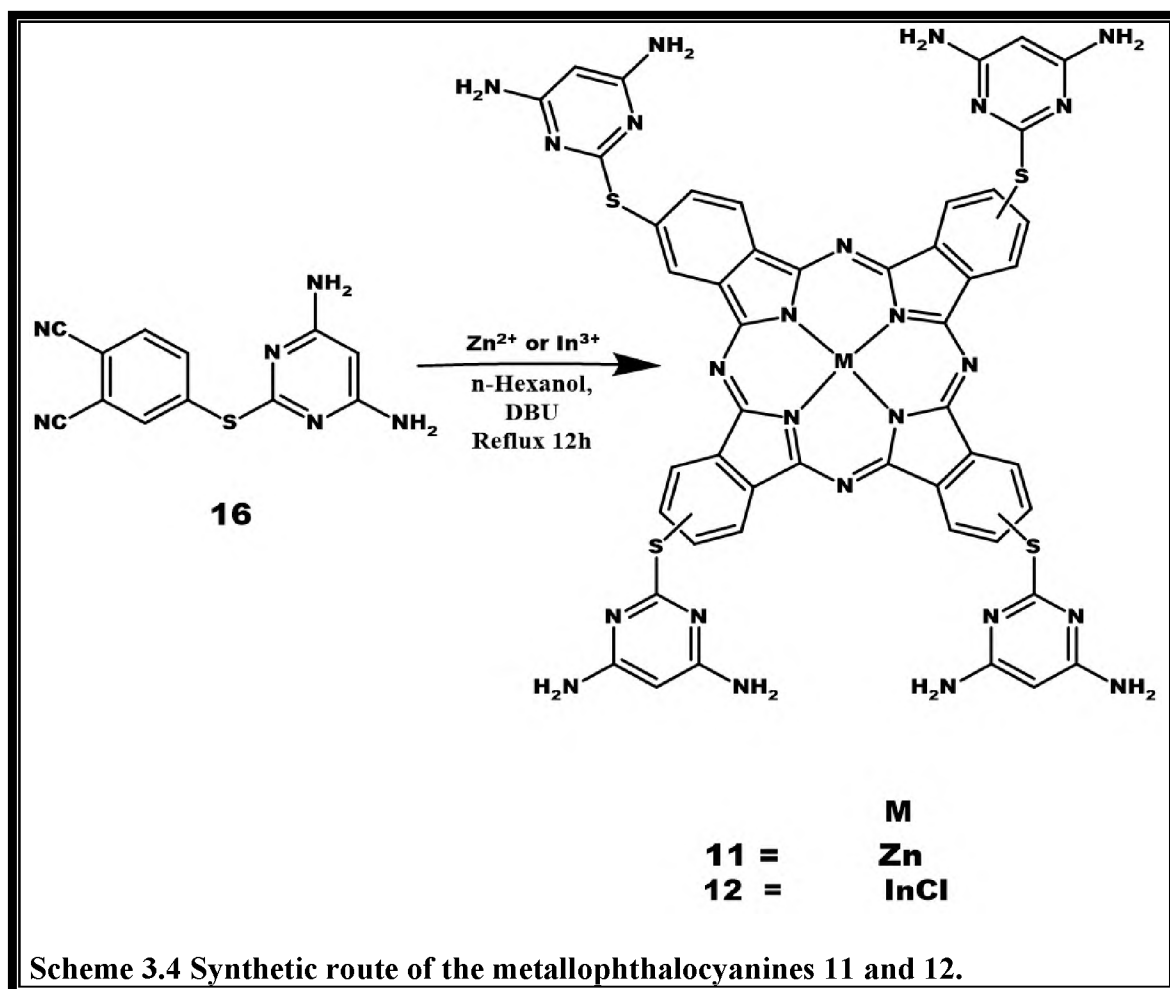
(for complex **10a**), **Figure 3.10**. Slight shifts between the absorption and excitation spectra could be due to the differences in the equipment used. Comparing the spectra of **8a**, **9a** and **10a** shows that **10a** is more red shifted due to presence of S group. The Q-band maximum of complex **8a** containing four pyridyl groups is more red-shifted compared to complex **9a** with one pyridyl group, **Table 3.1**.



3.1.3 Complexes **11** and **12**

Scheme 3.4, represents the pathway for the synthesis of complexes **11** and **12**. A metal-assisted cyclotetramerization process of compound **16** occurred in the presence of catalytic DBU and high-boiling solvent n-hexanol for 12 h to afford peripherally tetra-substituted zinc (**11**) and indium (**12**) phthalocyanines. The synthesized molecules were purified by column

chromatography on SiO₂ as stationary phase, and diethyl ether/DMF as eluents to afford the green solid product. The pure product was obtained in satisfactorily high yield and characterized by FTIR, elemental analysis, UV-Vis, ¹H NMR spectroscopies and MALDI-TOF.



The Q-band maximum for complex **12** is red-shifted compared to that of complex **11**. Large central metals are known to result in the red shifting of the Q-band [255] Table 3.1. **Figure 3.11** shows the absorption, fluorescence excitation and emission spectra of complex **11**. The excitation spectrum is similar to the absorption spectrum, and both are mirror images of the fluorescence emission spectrum. This also applies to complex **12**.

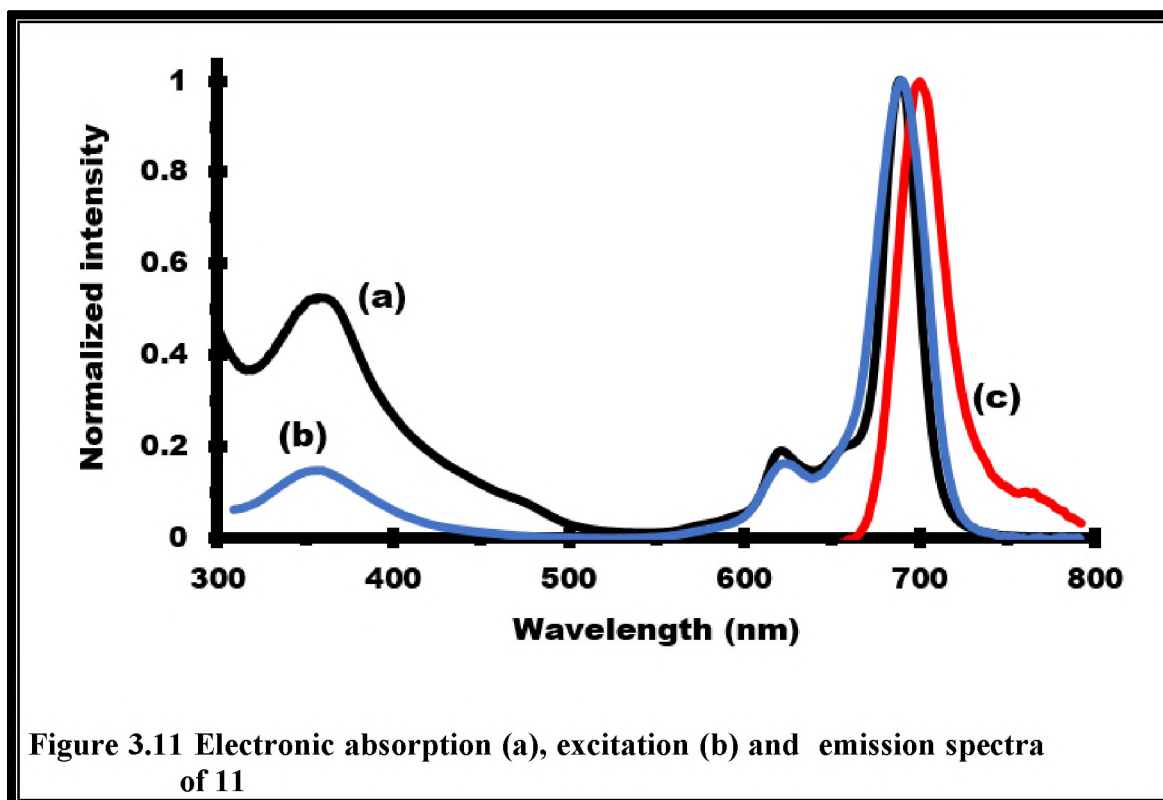


Figure 3.11 Electronic absorption (a), excitation (b) and emission spectra of 11

3.2 Characterization of MNPs and their conjugates to Pcs (10, 11, and 12)

3.2.1 Synthesis

MNP-NH₂ and MNP-COOH were synthesized as reported before [122] except that in the current work, the isolation of the nanoparticles was done by magnetic separation. **Figure 3.12** shows a photograph of the magnetic isolation process of **10**-MNPs as opposed to **10**, showing the effect of magnetic separation. **Scheme 3.5** shows the synthetic route for the MNP-COOH. MNP-COOH was conjugated to complex **10**, **11** and **12** through the formation of the amide bond. **Scheme 3.6** represents a hypothetical representation of the **10** and **10**-MNPs conjugates. **10a**-MNPs is formed by alkylating the pyridyl groups on the Pc of **10**-MNPs with methyl iodide (quaternization) to form **10a**-MNPs. The quaternization was confirmed using XPS below. There is only one amino group on complex **10**, hence only one point of attachment to the MNPs.



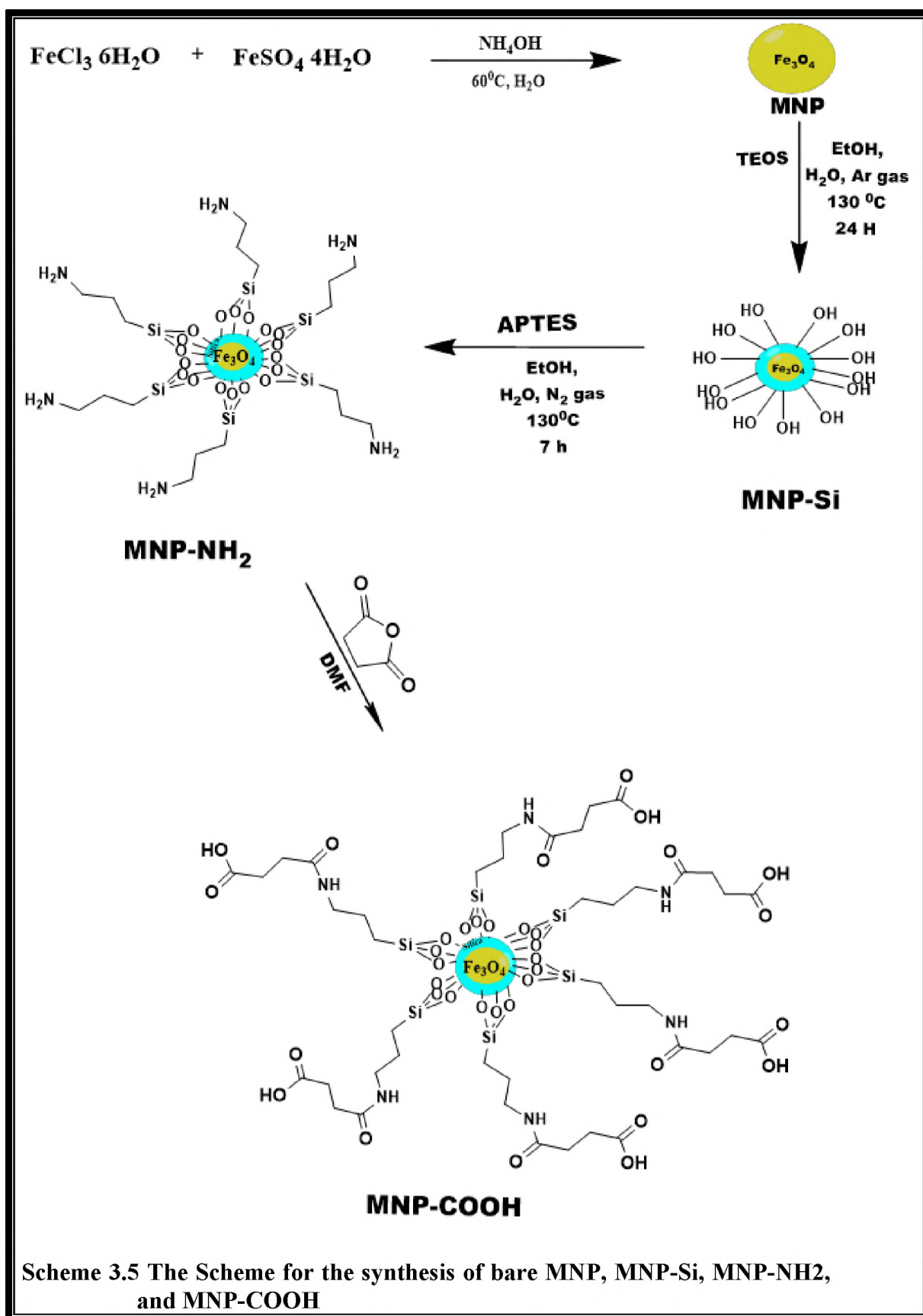
Figure 3.12 Photograph of the 10-MNPs (A) and 10 (B) exhibiting magnetic property of the former

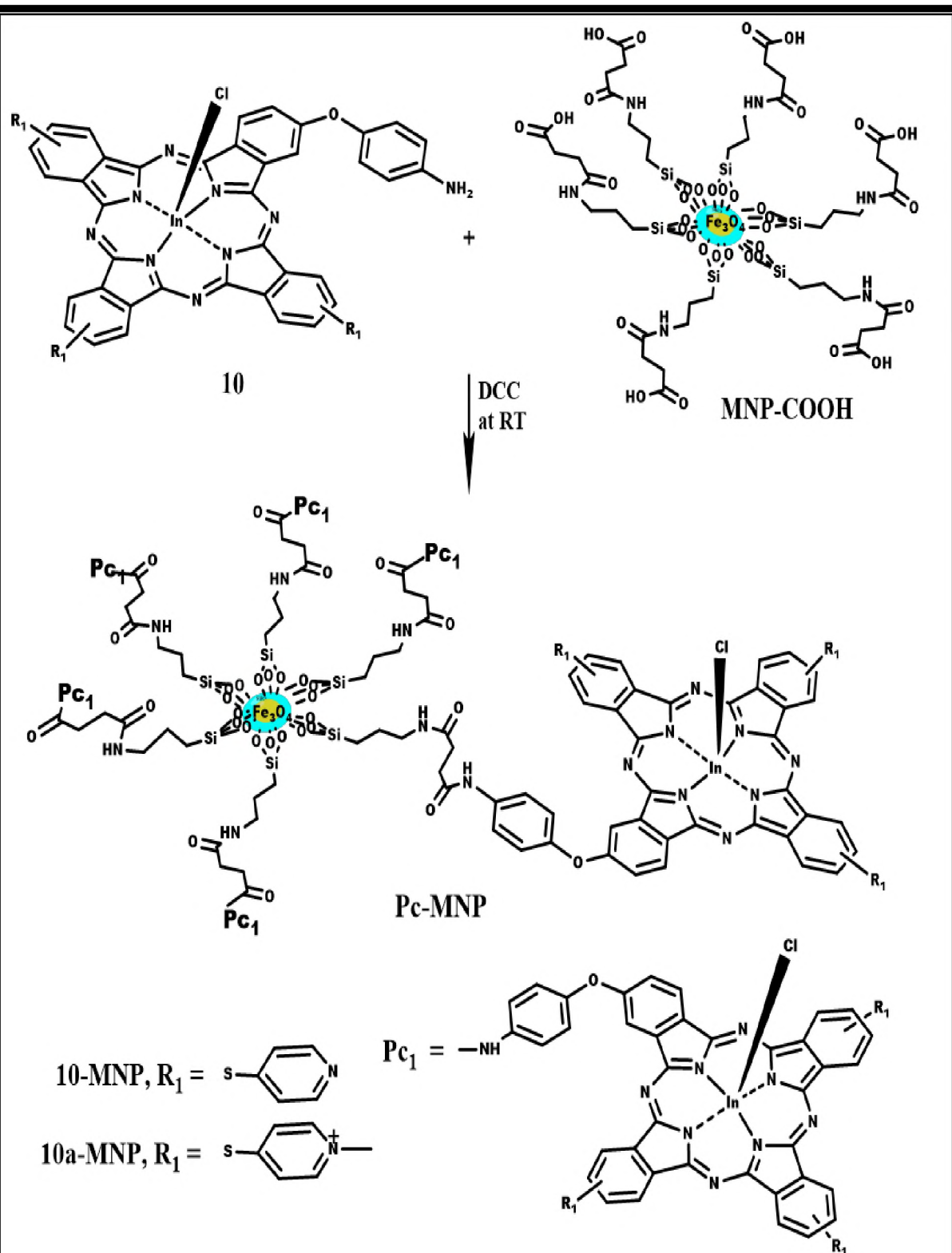
The conjugation of **11** or **12** to MNPs is shown in **Scheme 3.7**. Thus, it is not possible for more than one MNPs to be attached to complex **10**, **11** or **12**. It is possible for more than one Pc to link to the MNPs. The number of complex **10** molecules bonded to the MNPs was determined following literature methods, but using absorption instead of fluorescence [143]. This involves comparing the Q-band absorbance intensity of complex **10** in the conjugate with that of the initial complex **10** before the conjugation. Complex **10a**-MNPs was formed from **10**-MNPs hence the number of Pcs will be the same. The loading of complex **10** to MNPs was found to be 35 $\mu\text{g}/\text{mg}$ while that of **11** and **12** to MNPs are 105 $\mu\text{g}/\text{mg}$ and 72 $\mu\text{g}/\text{mg}$ respectively as shown in Table 3.2. The higher loading estimate for **11** is to be due to lack of axial ligands which is present in **12**, which may prevent interaction with MNPs .

Table 3.2 Electronic absorption and parameters of nanoparticles and MPC/conjugates in DMSO or unless otherwise stated.

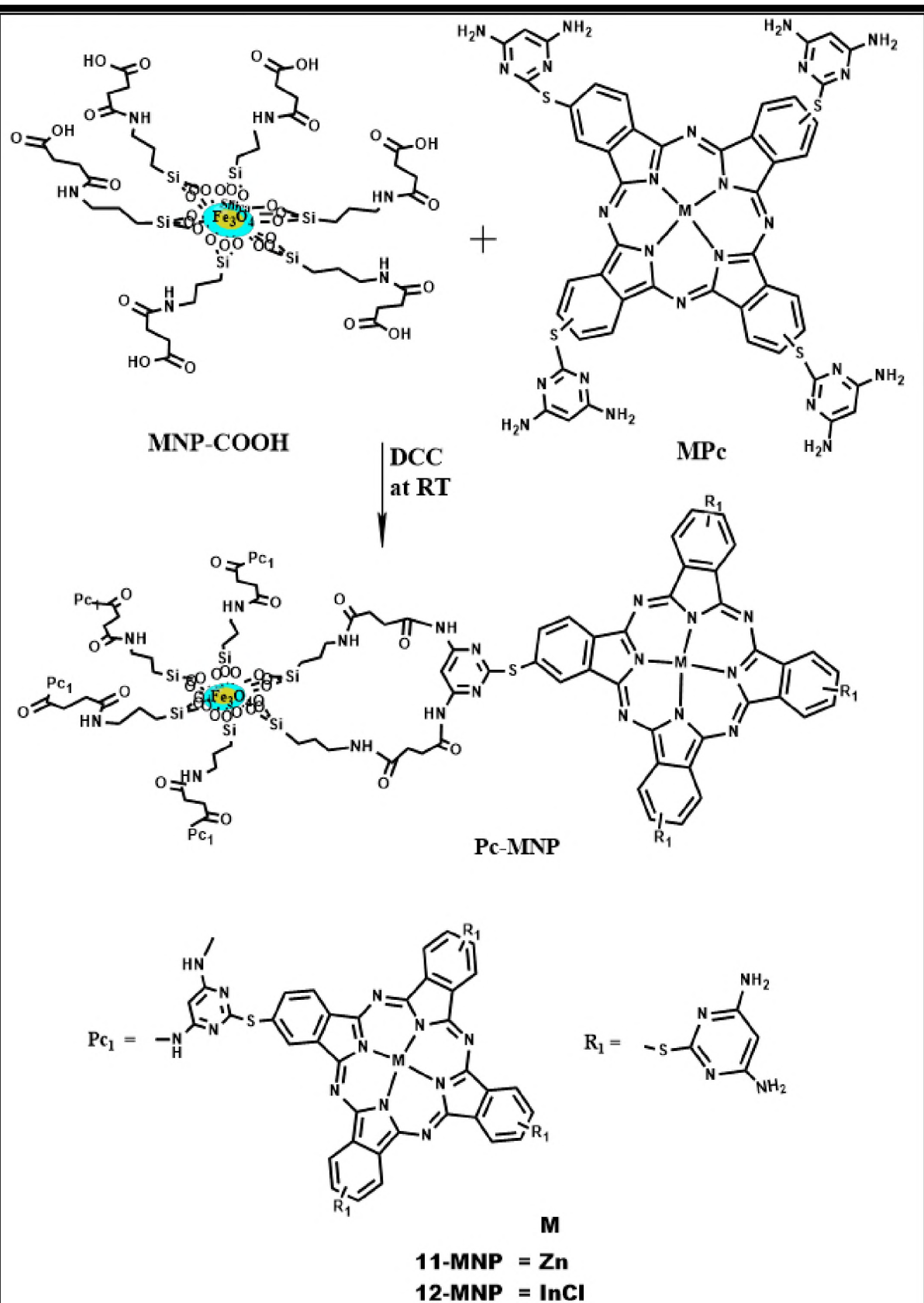
Pc/Nanomaterial	Size (nm)	Pc Loading	^b λ_{abs}
	(from TEM)	($\mu\text{g}/\text{mg}$)	(nm)
10	-	-	698
10a	-	-	699
11	-	-	689
12	-	-	704
10-MNPs	20.90 (20.90) ^a	35	699
10a-MNPs	20.90(20.90) ^a	35	699
11-MNPs	18.39 (17.80) ^a	105	689
12-MNPs	18.46 (17.80) ^a	72	703
10-QDs	8.53 (8.53) ^a	20	701
11-QDs	10.22 (8.53) ^a	72	688
12-QDs	10.45 (8.53) ^a	70	700
11-AuNPs	7.48 (5.35) ^a	60	689
12-AuNPs	7.64 (5.35) ^a	27	700

^a values in brackets are for NPs alone; ^b λ_{abs} = absorption wavelength, ^c values in water





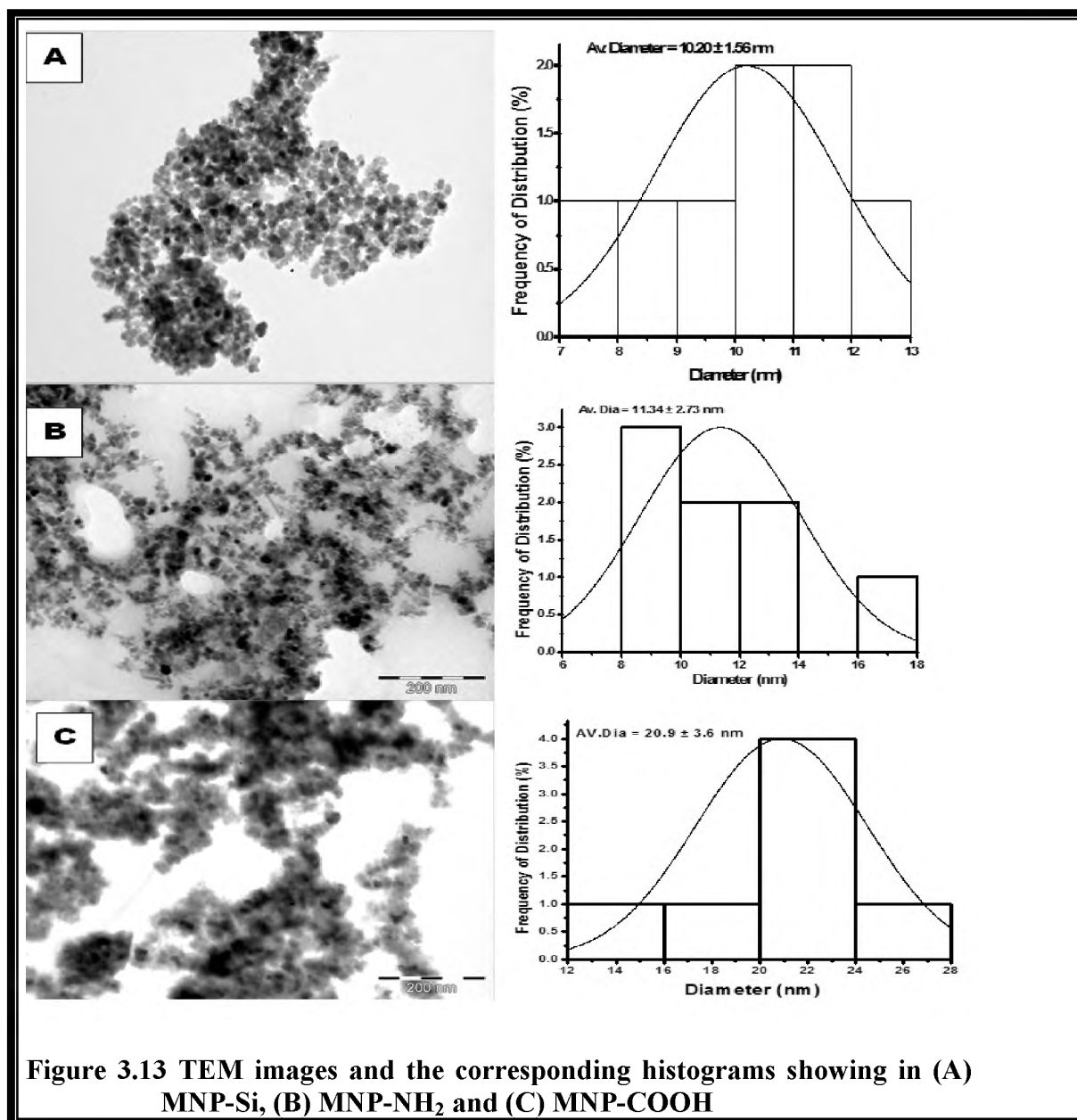
Scheme 3.6 Schematic representation of the conjugation of MNP-COOH and the photosensitizers (10 and 10a)



Scheme 3.7 Schematic representation of conjugation of 11 and 12 to MNPs

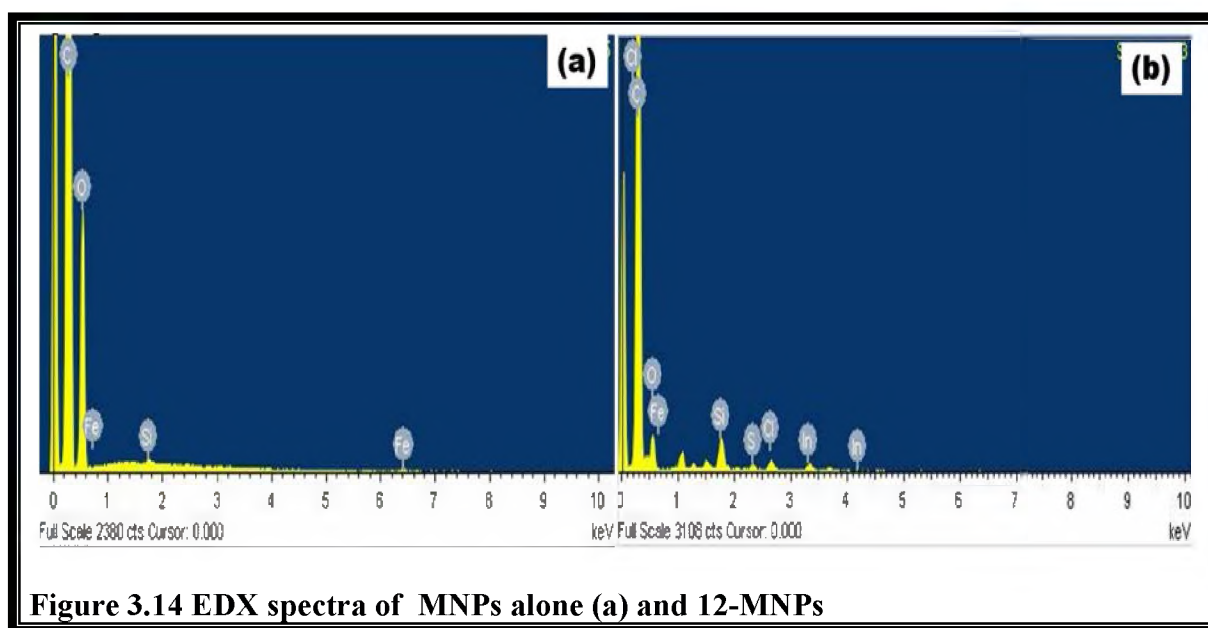
3.2.2 TEM images and EDX spectra of MNP and its Pcs (10, 11 and 12) conjugates

The TEM images of the MNPs (**Figure 3.13**) reveal the morphology of the MNPs at each stage of synthesis.



The size distribution of the nanoparticles is shown in histograms with the diameter of 20.90 nm for MNP-COOH. The size of 20.90 nm MNP-COOH was used for **10** and **10a** while for **11**, **12** a different batch of MNPs was employed, hence the size of 17.80 nm was obtained

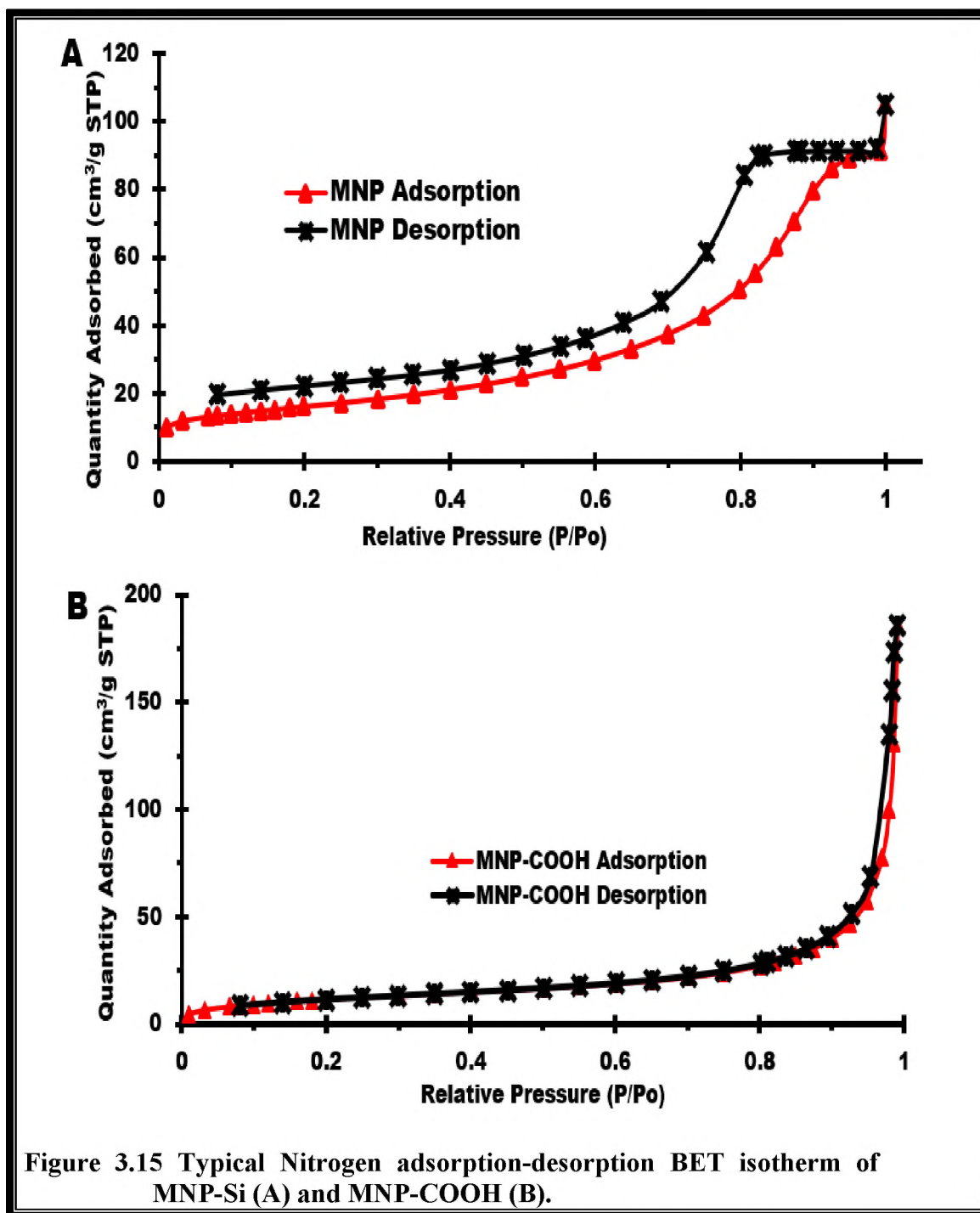
Table 3.2. The MNPs are mostly spherical. The image in **Figure 3.13C** shows increased aggregation upon functionalization with succinic anhydride (**Scheme 3.5**) to form MNP-COOH. Upon conjugation of **10** with first batch MNPs (20.90 nm), size remained the same for both **10**-MNPs and **10a**-MNPs, there is a relative increase on coordinations of **11** and **12** to the second batch of MNPs (17.80 nm), Table 3.2. There is a decrease in the size of MNPs used for **11** and **12** (17.80 nm) against that of **10** (20.90 nm) hence the loading pattern variations as seen in Table 3.2. The qualitative determination of the elemental compositions of the complexes with or without nanoparticles was evaluated using energy dispersive X-ray spectrometer (EDX) **Figure 3.14**. The EDX of the NPs alone show the expected atoms. On conjugation of **12** to MNPs (as examples) additional peaks (In, Cl and S) due to the former are observed when comparing to NPs alone. The Cl is the axial ligand on the In central metal.



3.2.3 Surface Area and Porosity Analyses of MNPs alone

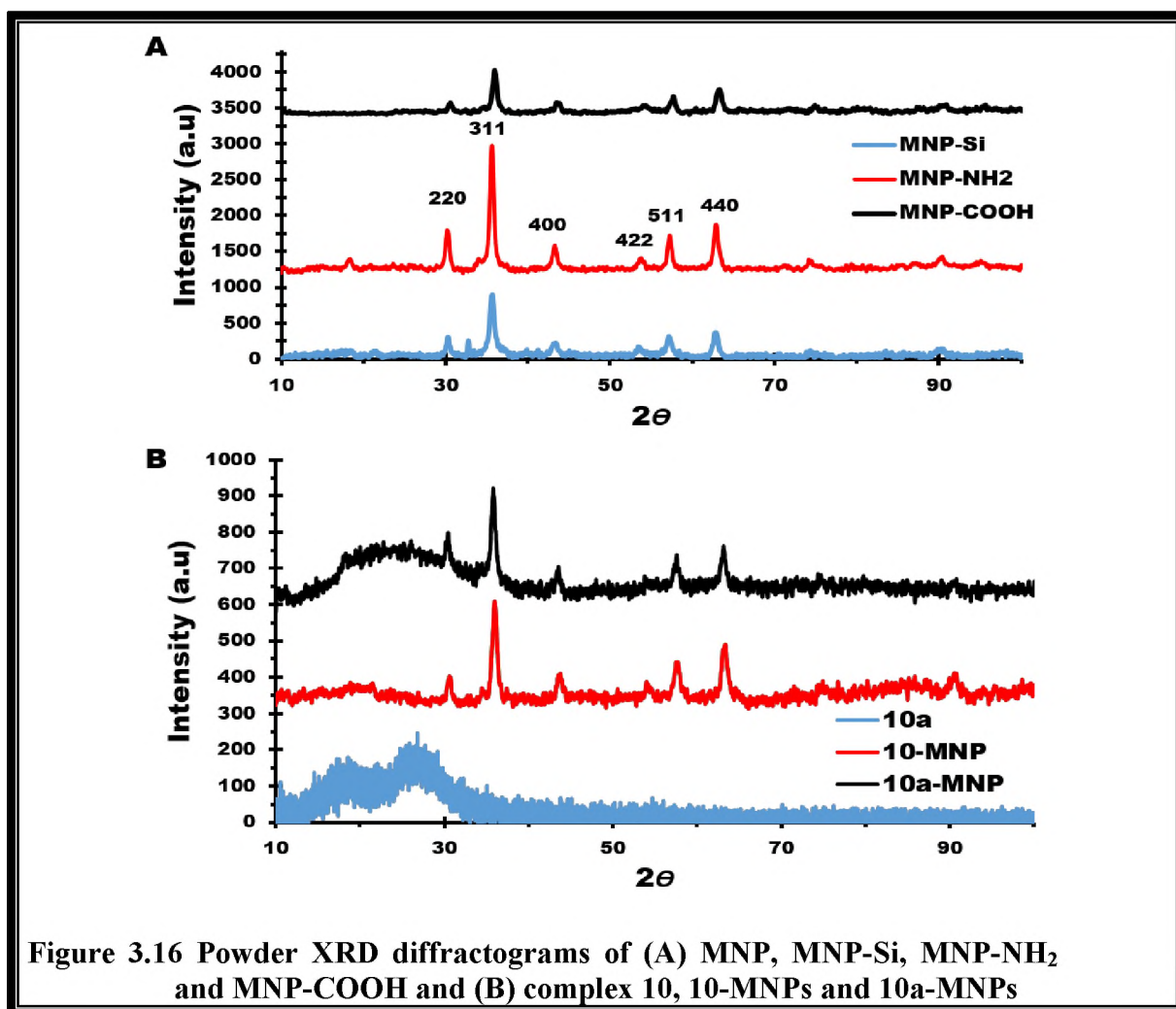
BET surface area and pore volumes of the silica and carboxylic acid coated MNPs were determined. Nitrogen adsorption-desorption isotherms for the MNP-Si and carboxylic acid functionalized MNPs are shown in **Figure 3.15**. BET characterization show type IV sorption

isotherms with surface area $56.49 \text{ m}^2/\text{g}$ and pore size $99.99 \text{ \AA}$ for MNP-Si. There is a reduction in surface area and an increase in pore size for MNP-COOH to $25.77 \text{ m}^2/\text{g}$ and $284.24 \text{ \AA}$, respectively. It has been documented that rough surface results in larger surface area than a smooth one [256]. Thus BET studies confirm that MNP-Si is rougher than MNP-COOH.



3.2.4 XRD Patterns

The XRD diffractograms (**Figure 3.16A**), show peaks characteristic of magnetite at (220), (311), (400), (422), (511) and (440), this revealed that the magnetic particles were pure Fe_3O_4 with spinel structure. The XRD peaks in **Figure 3.16B**, show that MNPs still retain their crystallinity in the conjugates upon formation of an amide bond between the amino group on the photosensitizer and the carboxylic acid group on the nanoparticles, though there is a broadening of the peaks, (complex **10**, and **10a** is used as an example for the conjugates).



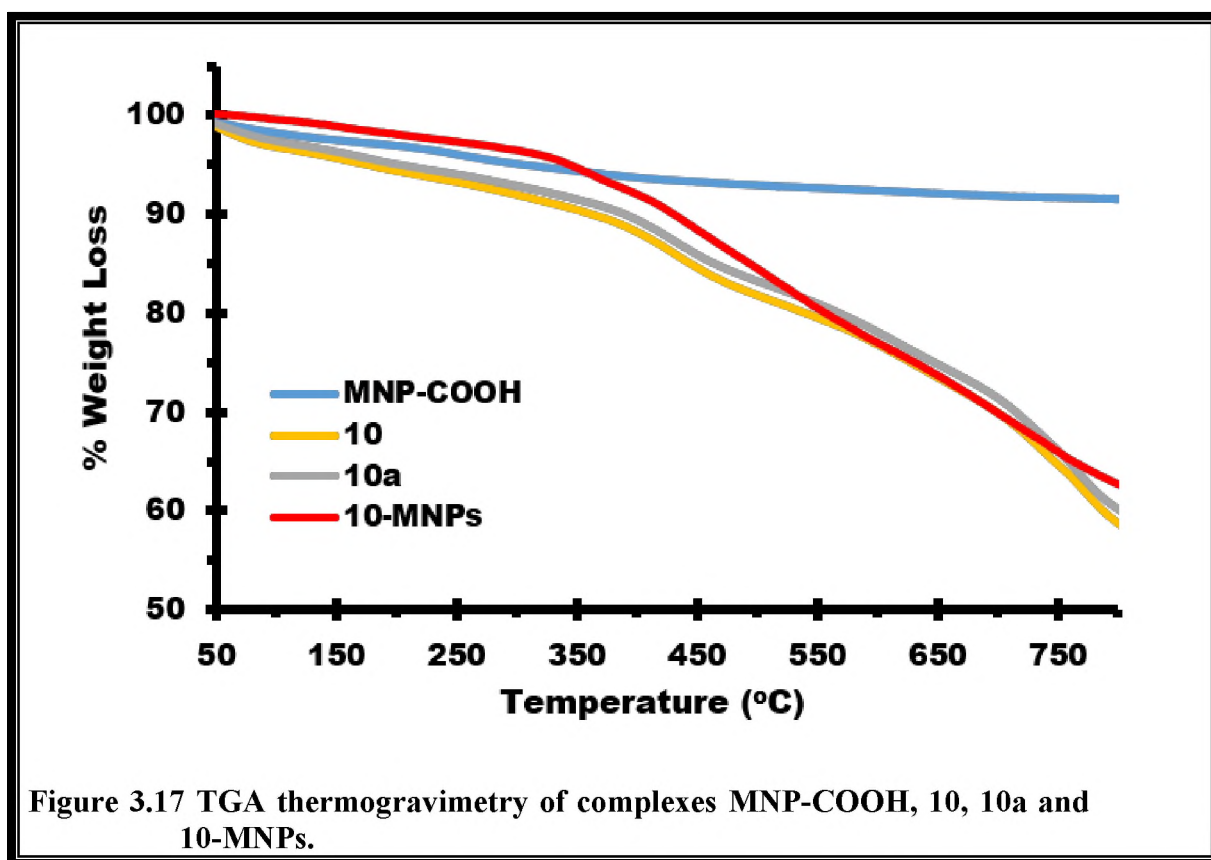
The NPs sizes were calculated based on the Debye-Scherrer Equation (3.1) [257]:

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

where λ is the wavelength of the X-ray source (1.5405 Å), k is an empirical constant equal to 0.9, β is the full width at half-maximum (FWHM) of the diffraction peak and θ is the angular position. The size estimates were obtained by focusing on the peak (300) for MNP-COOH; this was found to be ~15 nm which is in the same range as TEM values, for the MNPs used for **10** or **10a** (1st batch).

3.2.5 Thermal Analysis

The thermographs (**Figure 3.17**) show weight loss as a function of temperature from 50 to 800 °C. MNP-COOH is more stable than complexes **10** and **10a** at all temperatures. Complexes **10** and **10a** are less stable than the conjugate (**10**-MNPs) at temperatures less than 500 °C, suggesting that MNPs improve the stability of Pcs below this temperature. The loss in weight could be due to the elimination of adsorbed water, oxidation of any remaining residual organics and relaxation of the silica matrix as the temperature increases.



3.2.6 XPS Spectra

The surface wide scan XPS spectra of the nanoparticles and its conjugation with phthalocyanines (**10** and **10a** as examples) was carried out using XPS. The core level spectra were background corrected using the Shirley algorithm, and the chemically distinct species were deconvoluted using a nonlinear least-squares curve fitting procedure. The core level binding energies were aligned with respect to the C 1s binding energy (BE) of 285 eV.

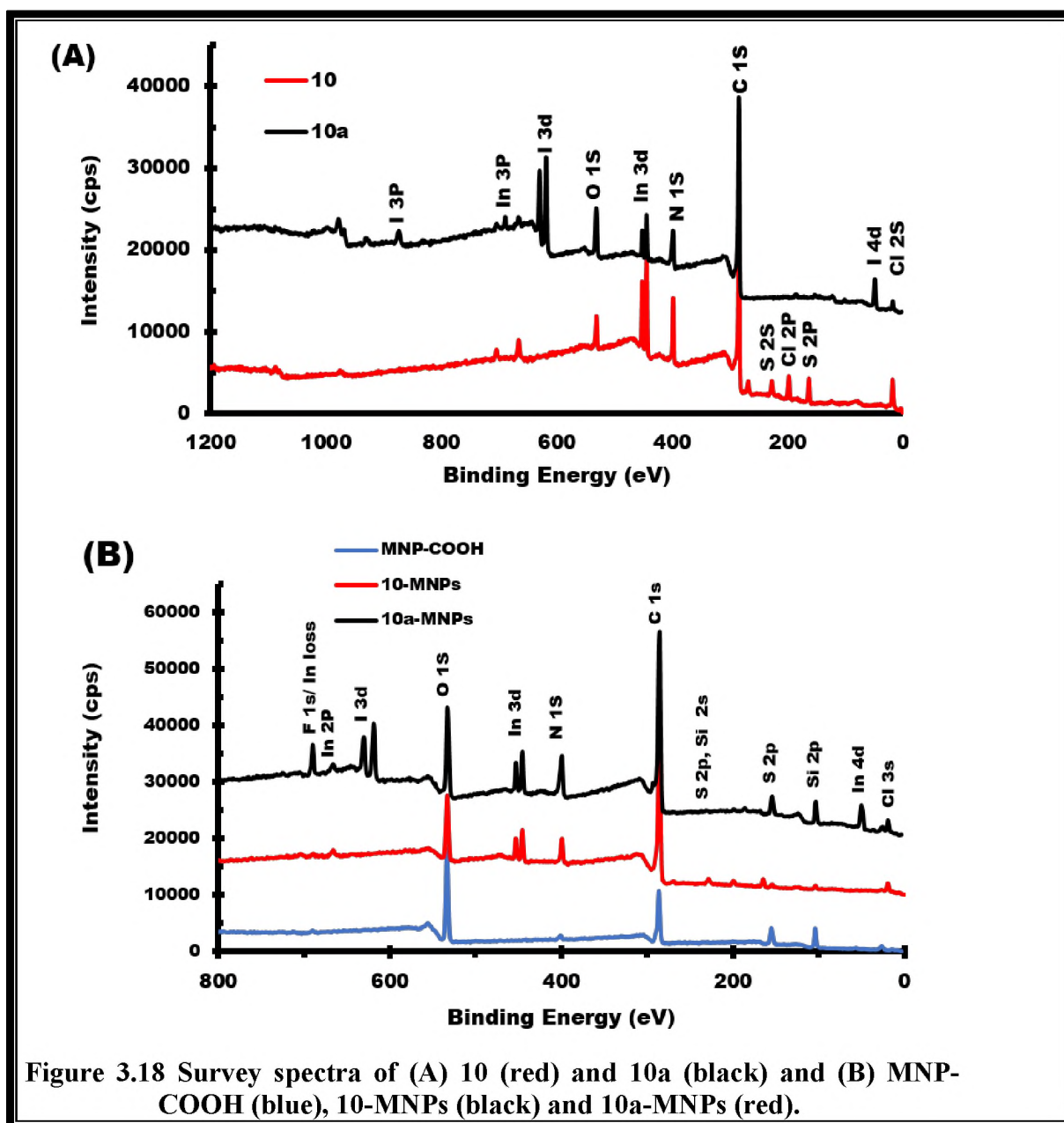


Figure 3.18 Survey spectra of (A) **10** (red) and **10a** (black) and (B) MNP-COOH (blue), **10**-MNPs (black) and **10a**-MNPs (red).

The survey spectra **Figure 3.18(A)** showed all the expected peaks corresponding to the elements found in Pcs. The expected difference between **10** and **10a** is based on the fact that **10a** is quaternized (that is the pyridine substituents are positively charged with additional methyl groups) hence the C 1s peak is higher in intensity for **10a**. Also, complex **10a** shows the presence iodide peaks. The chloride peaks are less intense for complex **10a**, but they are still present. **Figure 3.18(B)** also shows the spectra of MNP-COOH (blue) and its conjugates with **10** (**10**-MNPs, red) and **10a** (**10a**-MNPs, black). O 1s, N 1s, C 1s and Si 2p and 2s are from the capping and the core of the NP.

The survey spectra of the conjugates showed (in addition to the MNP-COOH) peaks due to the Pcs (**10** and **10a**). The peaks due to Pcs observed in **Figure 3.18(A)** were all prominent in the conjugate. The increase in the relative intensity of N atoms for **10**-MNPs compared to MNP-COOH alone is a result of the presence of N atoms from the Pc. Again, for **10a**-MNPs, there is an increase in C peaks due to the presence of the methyl groups. Also, the iodide peaks are evident for **10a**-MNPs.

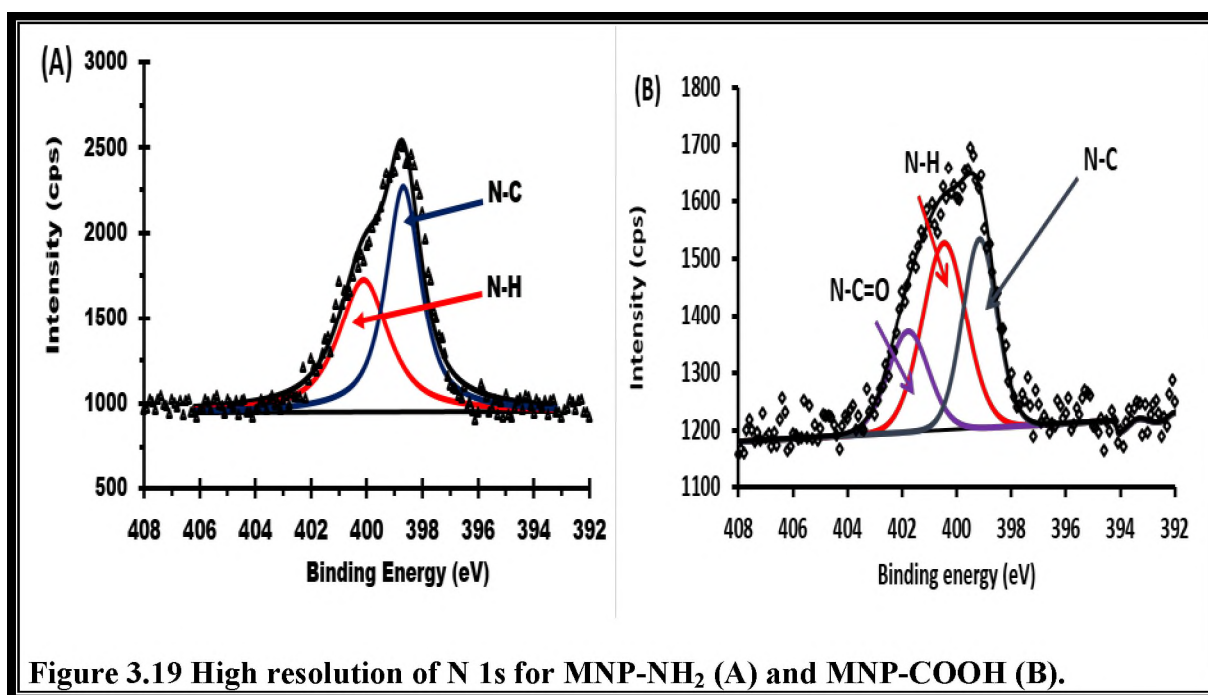


Figure 3.19 High resolution of N 1s for MNP-NH₂ (A) and MNP-COOH (B).

The N1s high-resolution peak for the MNP-COOH (**Figure 3.19B**), was deconvoluted to yield three components at 398.9 eV, 400.5 eV and 401.9 eV corresponding to N-C, N-H, and

N-C=O, respectively. The component at high binding energy 401.9 eV due to N-C=O (is an amide bond) between the amino functionalized nanoparticle and the succinic anhydride. This peak is not present in MNP-NH₂ (**Figure 3.19A**).

The high resolution of N 1s XPS analysis was undertaken to prove that the nanoparticles are conjugated with Pc by an amide linkage. **Figure 3.20** shows the high-resolution N 1s for compound (A) **10**, (B) **10a**. **Figure 3.20(A)** shows the N 1s core level spectrum for **10** could be deconvoluted to show two chemically distinct components centered at 398.7 eV and 400.5 eV and are attributed to N-C and N-H (from NH₂). Upon quaternization of **10** to form **10a** the additional peak at 401.6 eV was obtained due to the quaternary nitrogen (N⁺), **Figure 3.20(B)**. The presence of NH peaks in **10a** proves that the NH₂ group was not quaternized as discussed above. The N 1s core level spectra for **10**-MNPs (**Figure 3.20C**) could be fitted into three chemically distinct components with binding energies 398.6 eV, 399.9 eV and 401.7 eV due to (N-C), (N-H) and (N-C=O) bonds, respectively. The higher binding energy component at 401.7 eV corresponds to the amide bond [237], which further proves that conjugation took place between the MNP-COOH nanoparticles and complex **10**. The amide bond peak is also present in MNP-COOH alone (but at different energies, 401.9eV). The intensity of the N-C=O peak in **Figure 3.20C** (for the conjugate containing two amide bonds) is larger than that for MNP-COOH (**Figure 3.19B**, compare the magnitude of the y-axis units). In **Figure 3.20(D)**, the N 1s core level spectra for **10a**-MNPs could be deconvoluted into three chemically distinct components which correspond (N-C), (N-H) and (N-C=O and N⁺) groups with binding energies 398.5 eV, 399.9 eV, and 401.6 eV; respectively.

Figure 3.21 is the deconvoluted N 1s for **11** and **11**-MNPs. Two distinct peaks were obtained for **11**. N1s spectra of **11**- MNPs revealed three components between 399.87 and 401.06 eV as opposed to the two peaks of the unconjugated Pc at 399.24 and 400.56 eV. The

higher binding energy component at 401.6 eV corresponds to the amide linkage [258]. This confirms successful quaternization of **10**-MNPs to **10a**-MNPs.

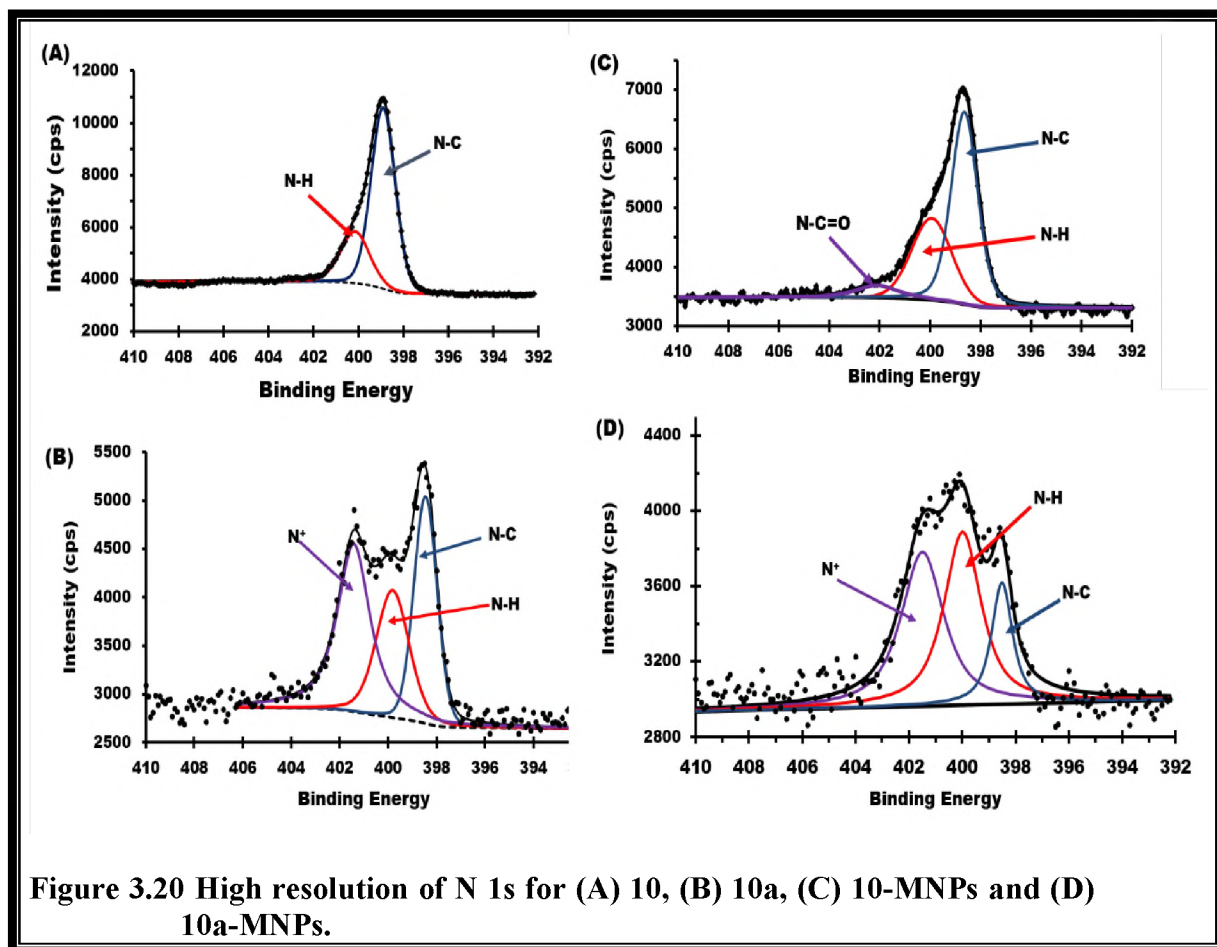


Figure 3.20 High resolution of N 1s for (A) **10**, (B) **10a**, (C) **10**-MNPs and (D) **10a**-MNPs.

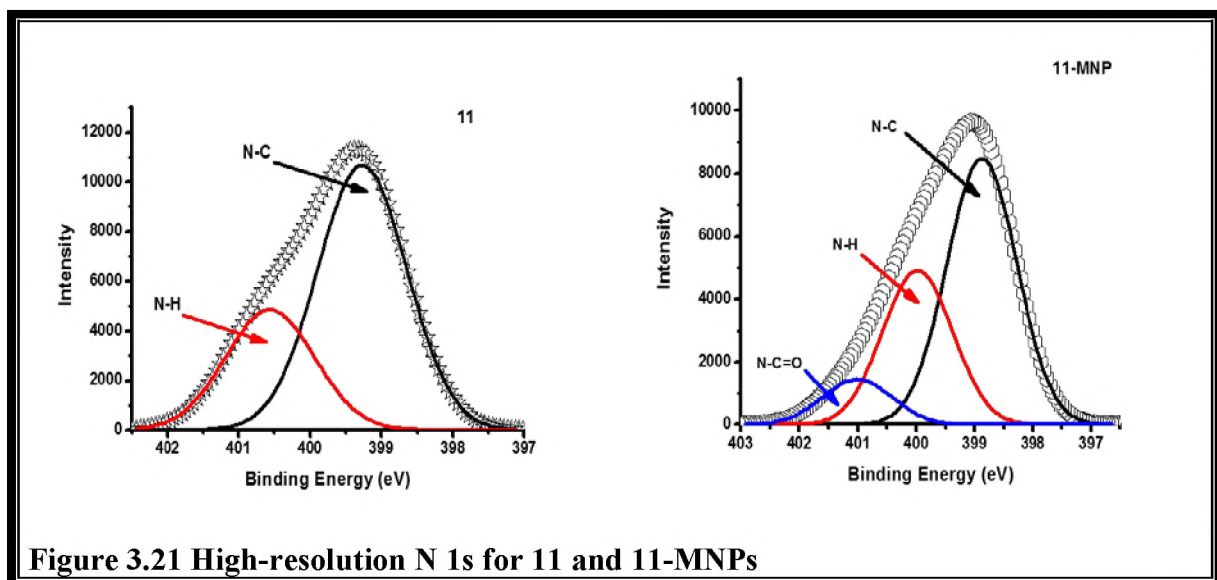


Figure 3.21 High-resolution N 1s for **11** and **11**-MNPs

The high-resolution XPS spectra (for **10a**-MNPs) of I 3d was deconvoluted to produce three peaks for I 3d_{5/2} and I 3d_{3/2} (**Figure 3.22**). The I 3d_{5/2} three peaks were observed at 618.79, 620.99 and 622.29 eV while the corresponding split orbit coupling peaks for I 3d_{3/2} were observed at higher binding energies 630.49, 632.49 and 633.99 eV. The split orbit component separation (ΔE) ranged between 11.2 to 11.5 eV for all the identified components. The three components are due to different iodine chemical binding on the Pc. The first peak at 618.79 eV for I 3d_{5/2}, is due to the counter anion Γ^- for quarternized substituents, the second peak at 620.99 eV is due to displacement of Cl^- axial ligand by Γ^- [259,260]. The small component at higher binding energies 622.69 eV is due to the IO_4^- possibly due to iodine reacting with oxides in solution. The presence of several species of iodine confirmed the successful quaternization of the MPc (**10a**).

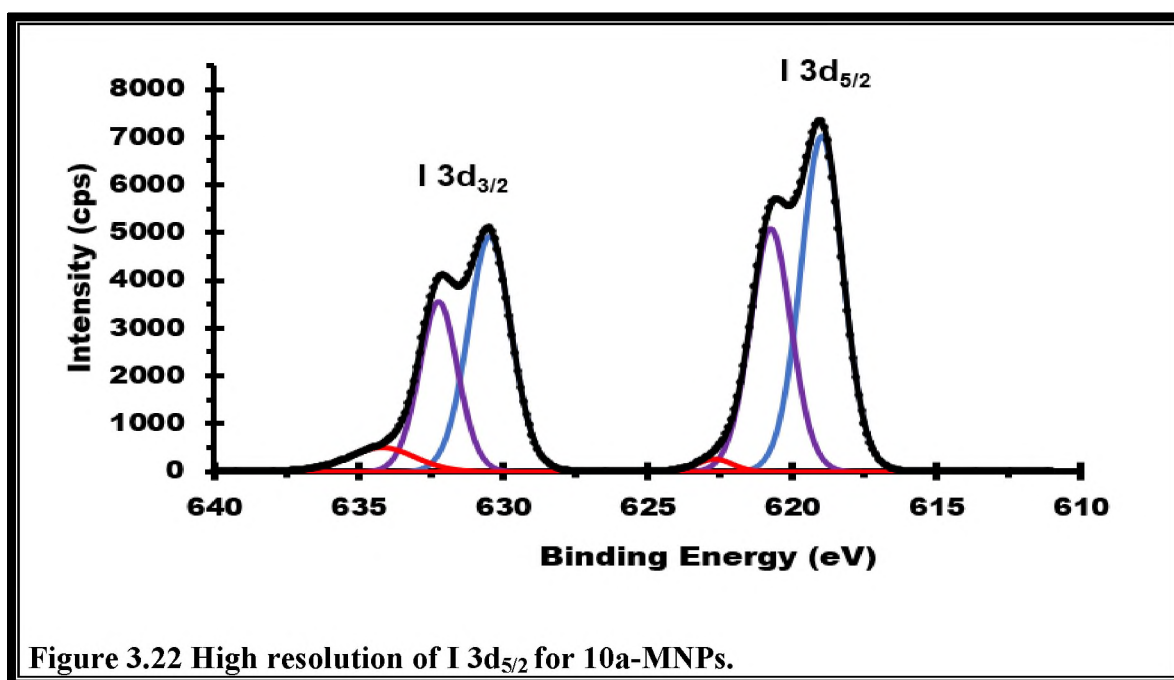


Figure 3.23A and **B** shows the In 3d spectra of **10**, **10**-MNPs and **10a**, **10a**-MNPs; respectively. In 3d components could be resolved into two peaks with binding energies of 443.10 and 450.60 eV for **10**-MNPs and 444.41 and 451.99 for **10a**-MNPs, which are

attributed to In 3d_{5/2} and 3d_{3/2}, respectively in trivalent indium ion. This further confirms the presence of In³⁺ within the phthalocyanine rings [261].

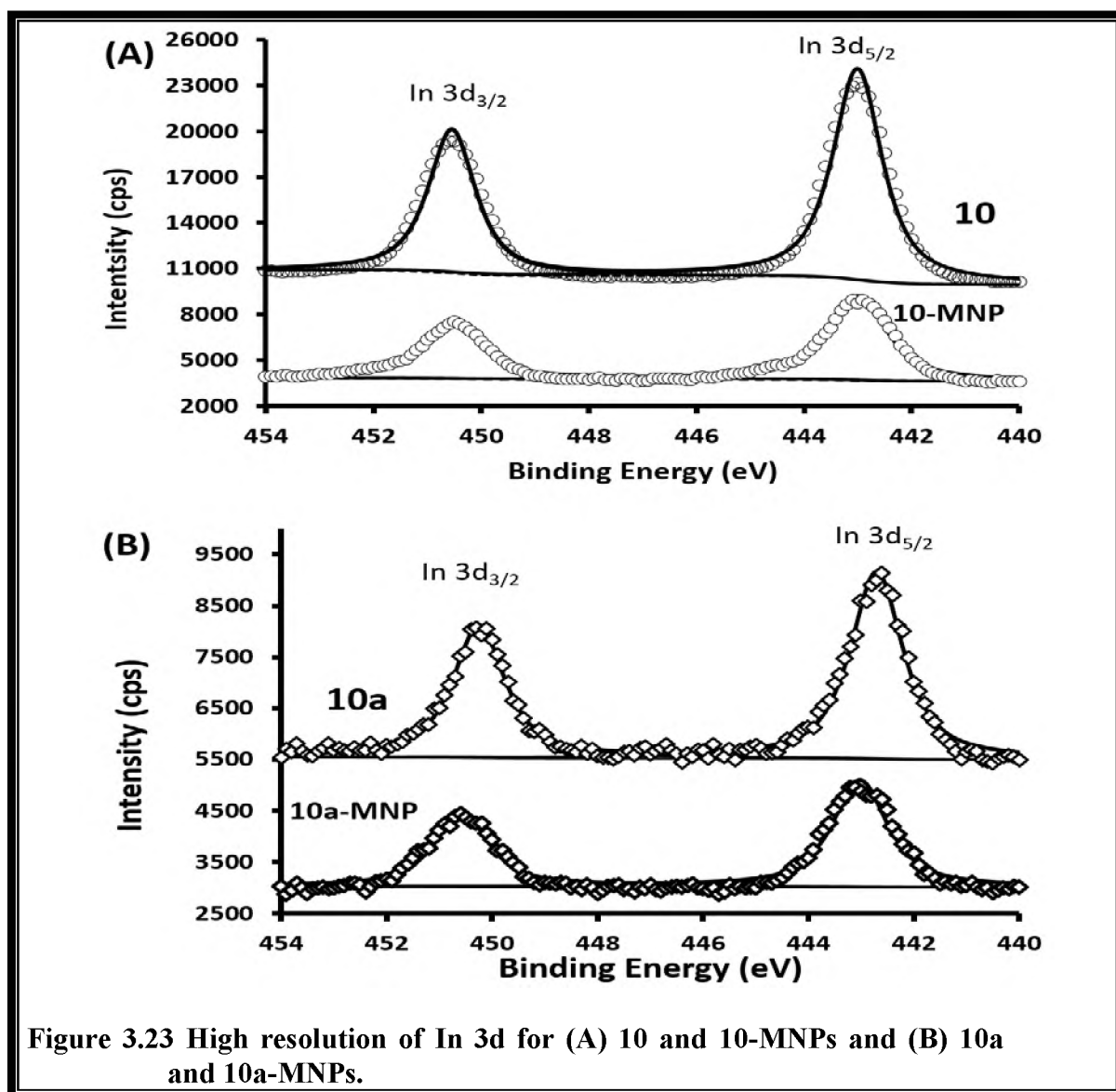


Figure 3.23 High resolution of In 3d for (A) 10 and 10-MNPs and (B) 10a and 10a-MNPs.

3.2.7 FT-IR spectra

The presence of carbodiimide on the FTIR spectrum implies the successive formation of an amide bond between the MPcs and the nanoparticle. **Figure 3.24** shows the FTIR spectrum of MNPs, **12** and its conjugates. The characteristic peak for carbodiimide was observed around 1653 cm⁻¹ for **12**-MNPs and at 1643 cm⁻¹ in MNPs, and the siloxane band at 1060 cm⁻¹ for the conjugates. The shift of carbodiimide in MNPs to a higher wavenumber upon

conjugation to **12** affirmed that the conjugation was successful. The MNP-COOH have amide bonds hence, FTIR cannot prove definitely that amide bonds were formed between the complexes **10**, **11**, **12** and MNPs.

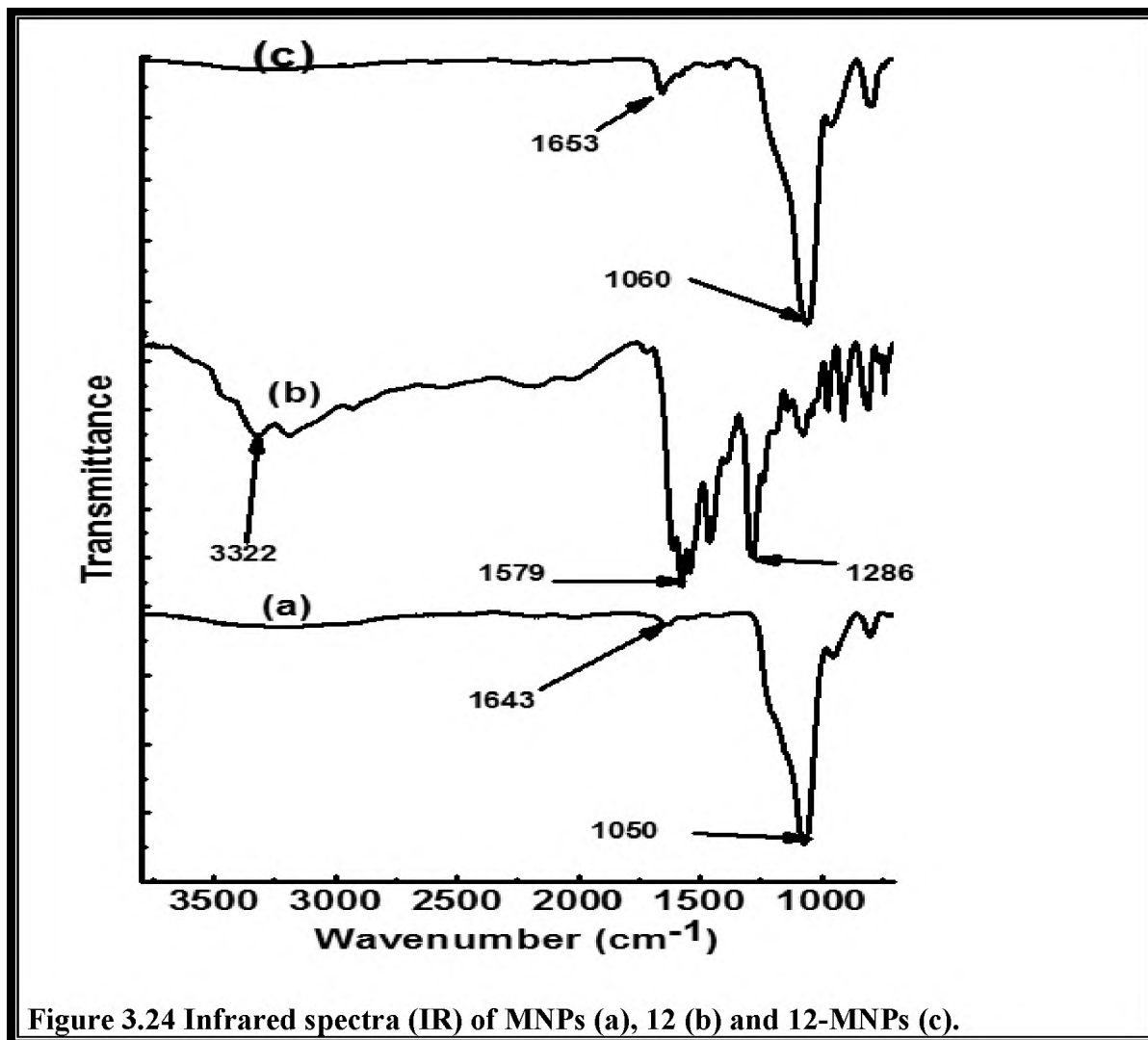
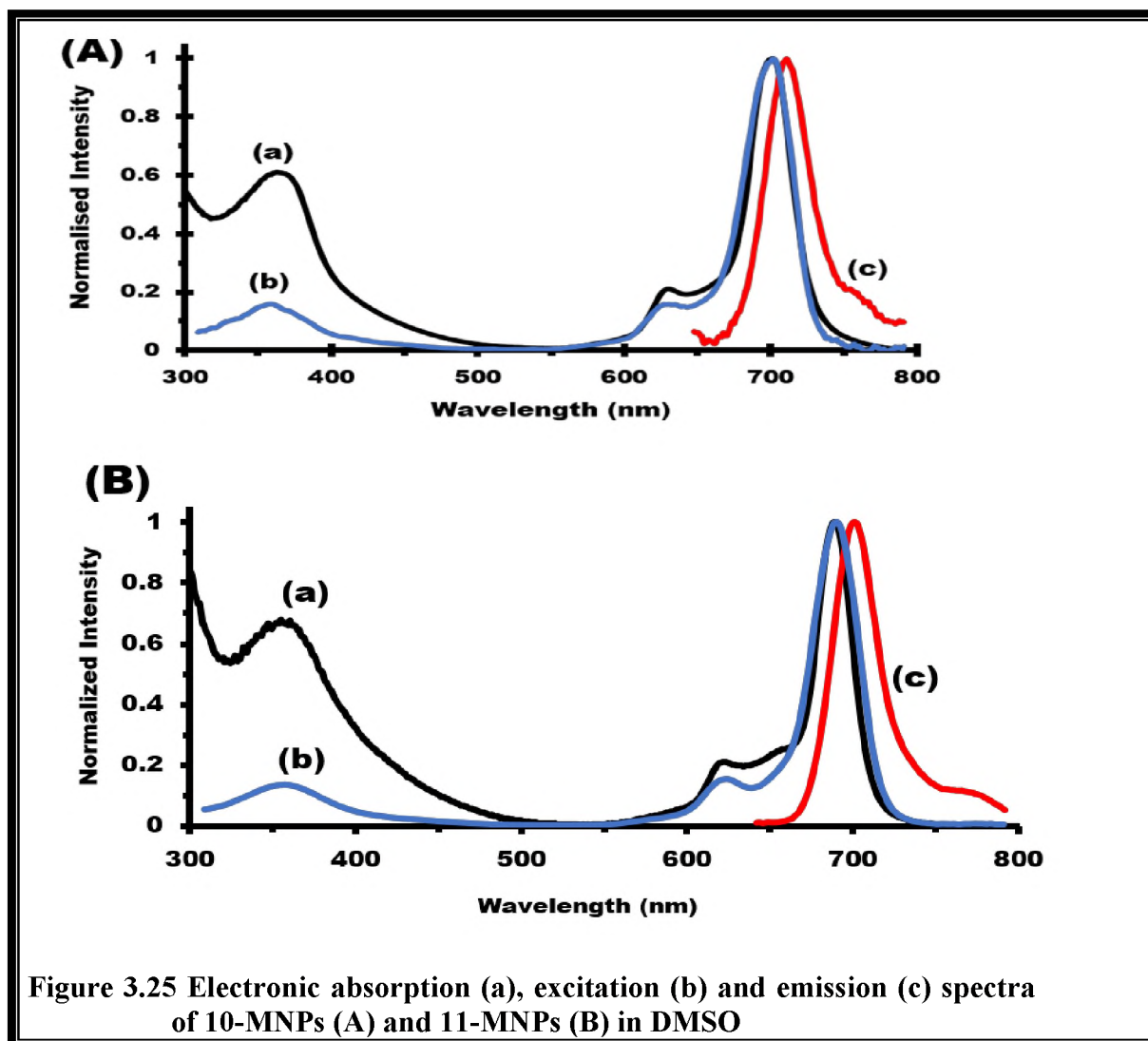


Figure 3.24 Infrared spectra (IR) of MNPs (a), 12 (b) and 12-MNPs (c).

3.2.8 UV-Vis Absorption Spectra

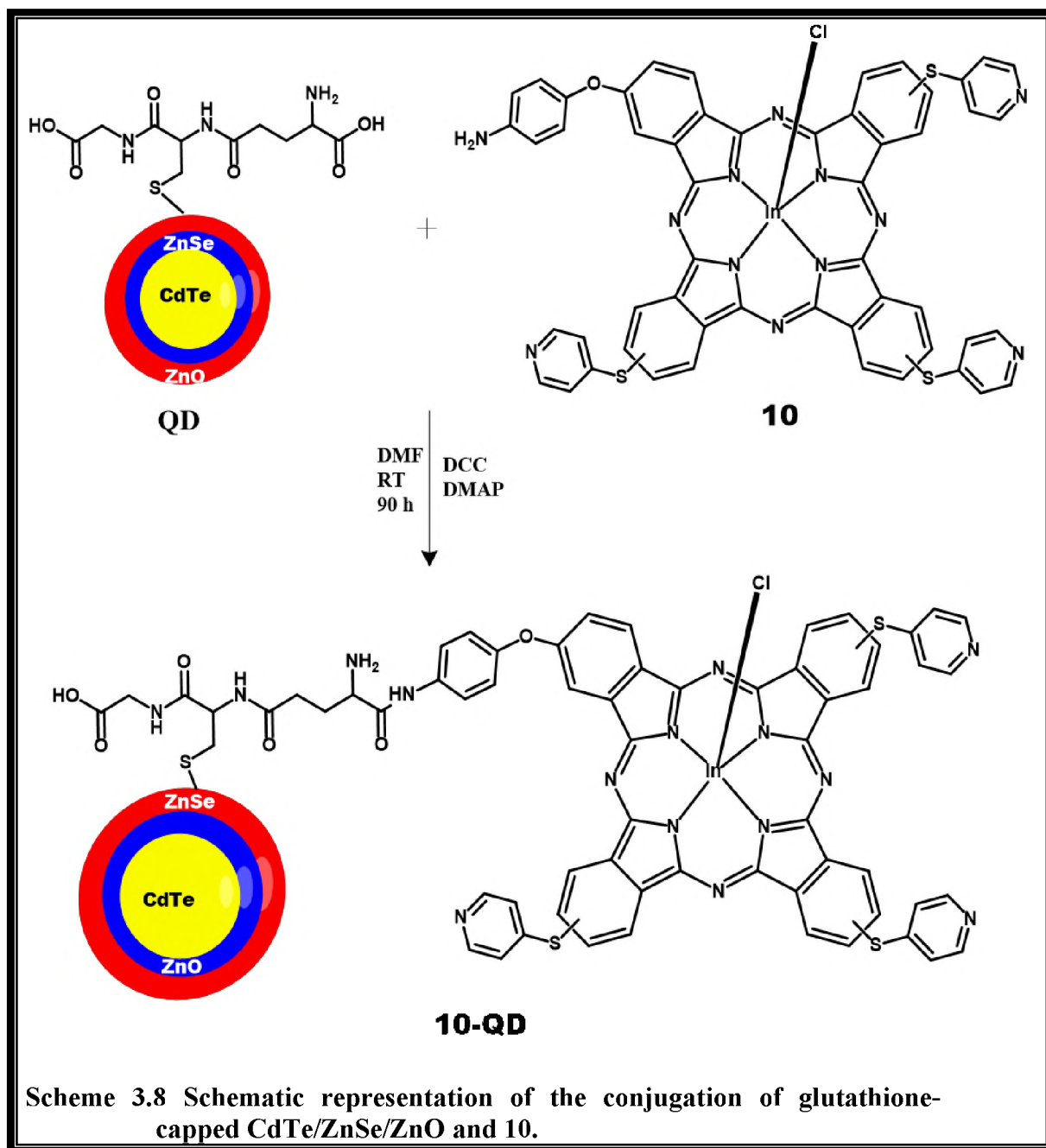
The UV-visible spectrum of the complexes (using **10**-MNPs and **11**-MNPs as examples) are shown in **Figure 3.25**. The absorption maxima of the complexes show the monomeric characteristic of the phthalocyanine. No shift in Q-band on coordinations to MNPs, Table 3.2 for **10**, **11** and **12**. The emission spectra are mirror images of the absorption spectra and excitation spectra.



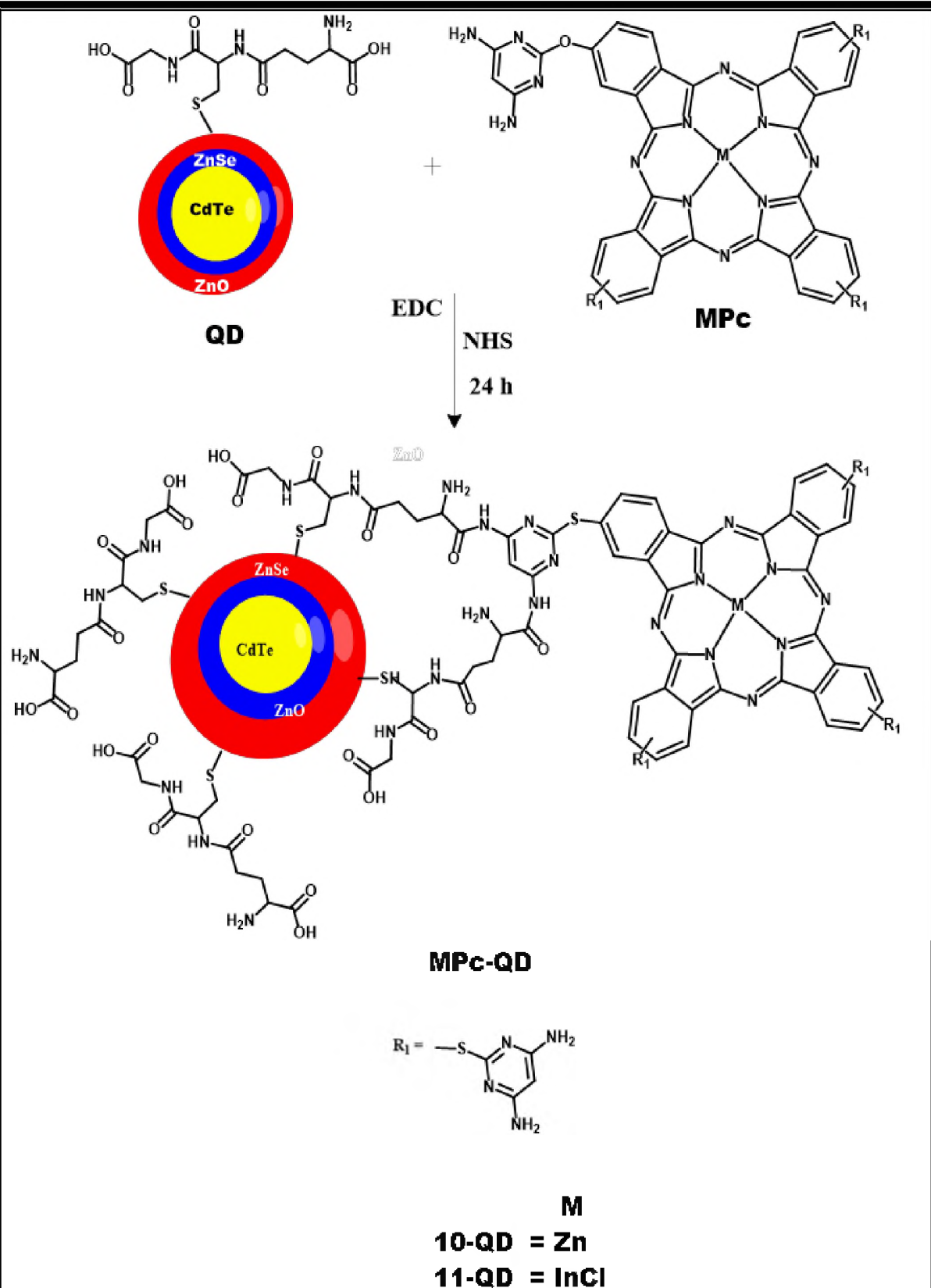
3.3 Conjugates of QDs and with Pcs (10, 11 and 12)

3.3.1 Synthesis

GSH capped CdTe/ZnSe/ZnO QD [145] were synthesized according to the procedure reported earlier in our group. Complex **10** was conjugated with the semiconductor QDs as shown in **Scheme 3.8**. Conjugations of **11** and **12** are as shown in **Scheme 3.9**. All complexes were fully characterized, and loading of **10**, **11** and **12** on the QDs surface were estimated as described for MNPs conjugates, values are given in Table 3.2. **10**-QDs was found to 20 $\mu\text{g}/\text{mg}$, **11**-QDS, and **12**-QDS are 72 $\mu\text{g}/\text{mg}$ and 70 $\mu\text{g}/\text{mg}$ respectively.



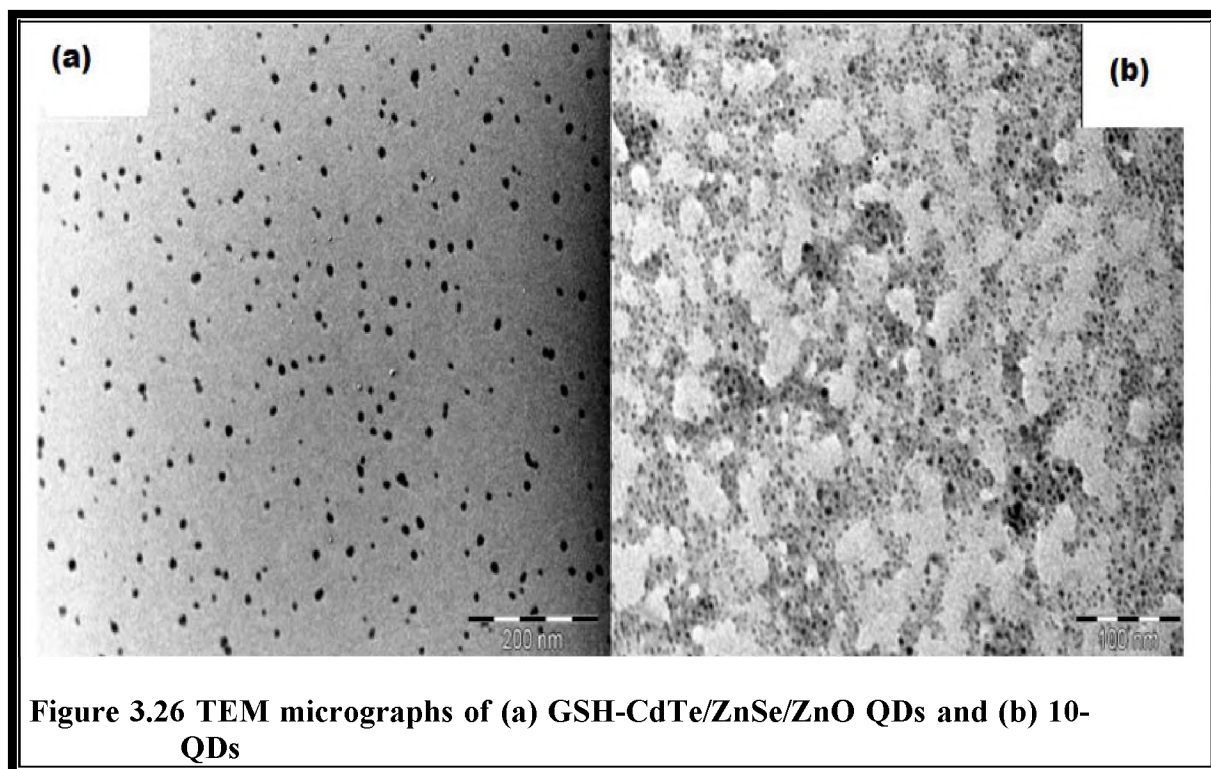
Scheme 3.8 Schematic representation of the conjugation of glutathione-capped CdTe/ZnSe/ZnO and 10.



Scheme 3.9 Synthesis route to MPc-QDs conjugates

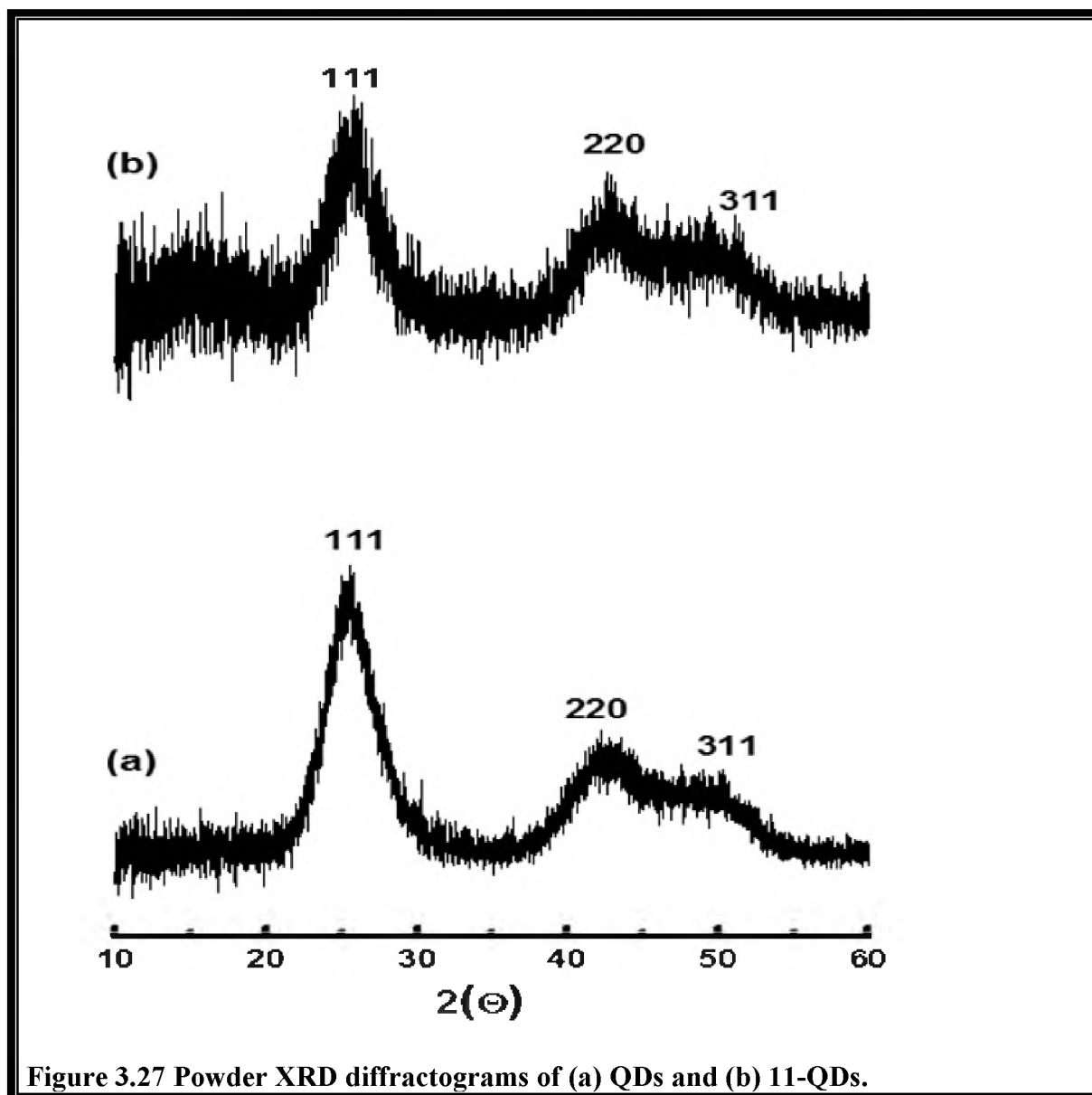
3.3.2 TEM Images

The TEM micrograph of the GSH capped CdTe-ZnSe-ZnO quantum dots shows that they are monodispersed (**Figure 3.26**, using **10** as an example) with an average size of 8.53 nm, and there was no change in size upon conjugation to complex **10**. There was an increase in size for **11**-QDs and **12**-QDs due to aggregation, Table 3.2.



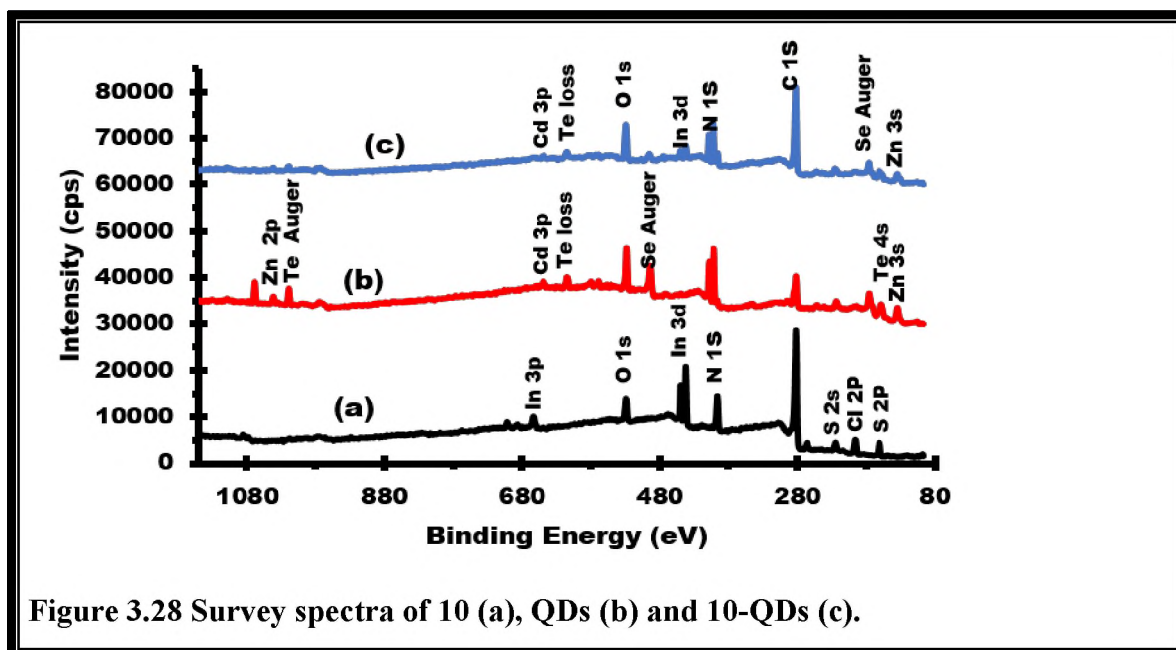
3.3.3 XRD Spectra

For the Pcs, the XRD pattern is typical of phthalocyanines [262] as shown in **Figure 3.16B**. The QDs exhibited three prominent diffraction peaks at $2\theta = 27^\circ, 44^\circ, 52^\circ$ **Figure 3.27(a)**. The 2θ values obtained were in accordance with zinc blend crystal and cubic structure at planes 111, 220 and 311, respectively. The QDs peaks are still present following conjugation, **Figure 3.27(b)**. The size estimate of 7 nm was determined by applying Debye-Scherrer Equation (3.1) [257] on the peak (111), size not too different compared to TEM at 8.53 nm.

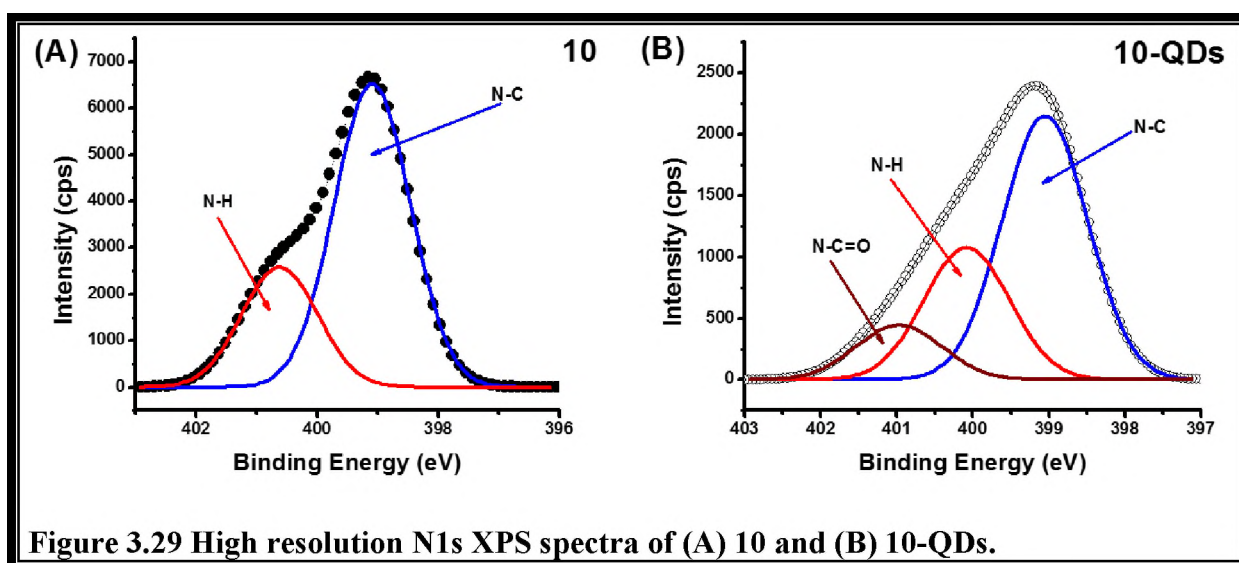


3.3.4 XPS Spectra Characterization of 10-QD

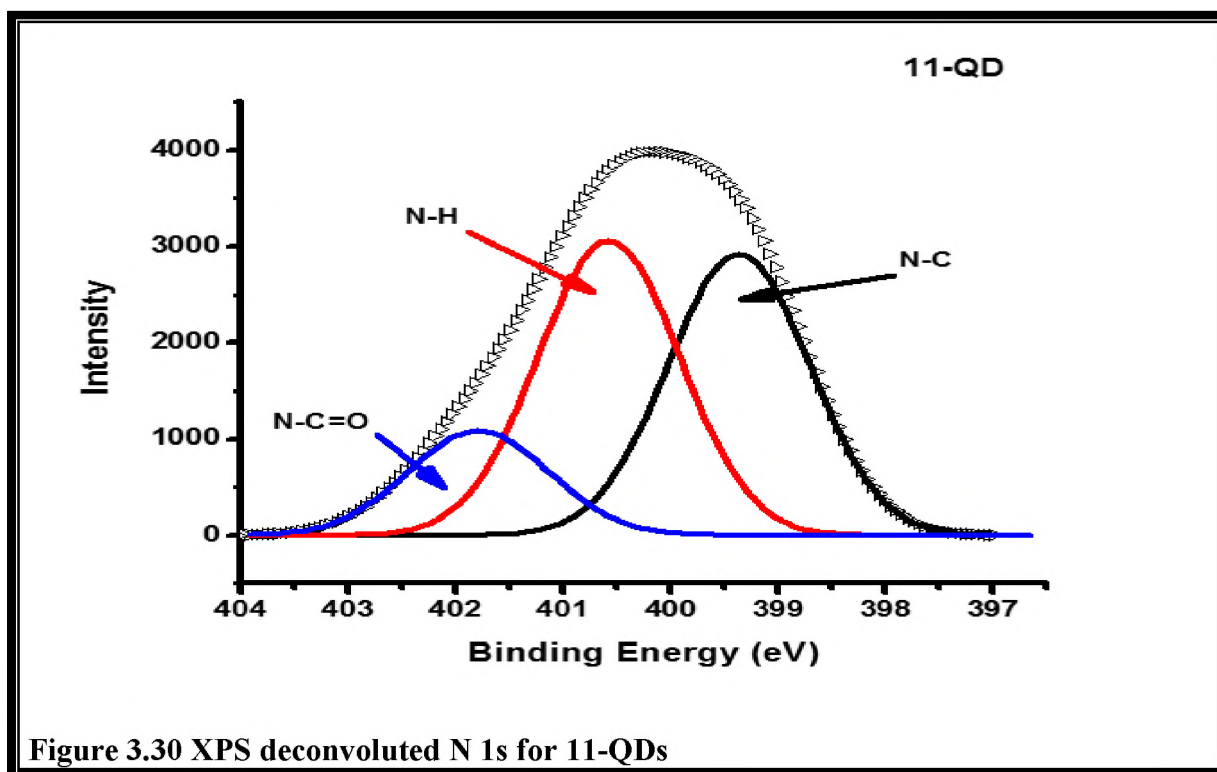
XPS spectra for QDs and its conjugation to **10** (as an example) was carried out to confirm the point of linkage. **Figure 3.28** shows the wide scan XPS spectra of the QDs, **10** and **10-QDs** conjugate. The intense N 1s and O 1s for **10-QDs** is from the GSH capping on quantum dots as well as from the Pc. The presence of characteristic peaks of the QDs and **10** on the corresponding conjugate is an indication of successful conjugation.



High-resolution N 1s XPS analysis was undertaken to prove further that the nanoparticles are conjugated with Pcs by an amide linkage. The N 1s core level spectrum (for **10**, **Figure 3.29A**) is deconvoluted to show two chemically distinct components centered at 399.1 eV and 400.6 eV, attributed to N–C and N–H (from NH₂), respectively. **Figure 3.29B** (for 10-QDs) shows three deconvoluted peaks corresponding to N–C, N–H, and N–C=O at binding energies 399.1, 400.1, and 402.2 eV, respectively.



The presence of the N–C=O bond confirms amide bond formation between the amino group (–NH₂) on the phthalocyanine and the GSH-QDs. N 1s deconvolution of **11-QDs** **Figure 3.30** resolved to three distinct peaks with BE between 399.87 eV and 401.78 eV. The highest BE at 401.78 eV is ascribed as the amide bond (N–C=O).



3.3.5 FT-IR spectra

Figure 3.31 shows the FTIR of **12-QDs** (as an example), the conjugation to the QDs showed the carbodiimide band at 1575 cm⁻¹ (also present in QDs alone) and the characteristic fingerprint peaks of both the QDs and **12** hence does not definitely confirm amide bond between **12** and QDs.

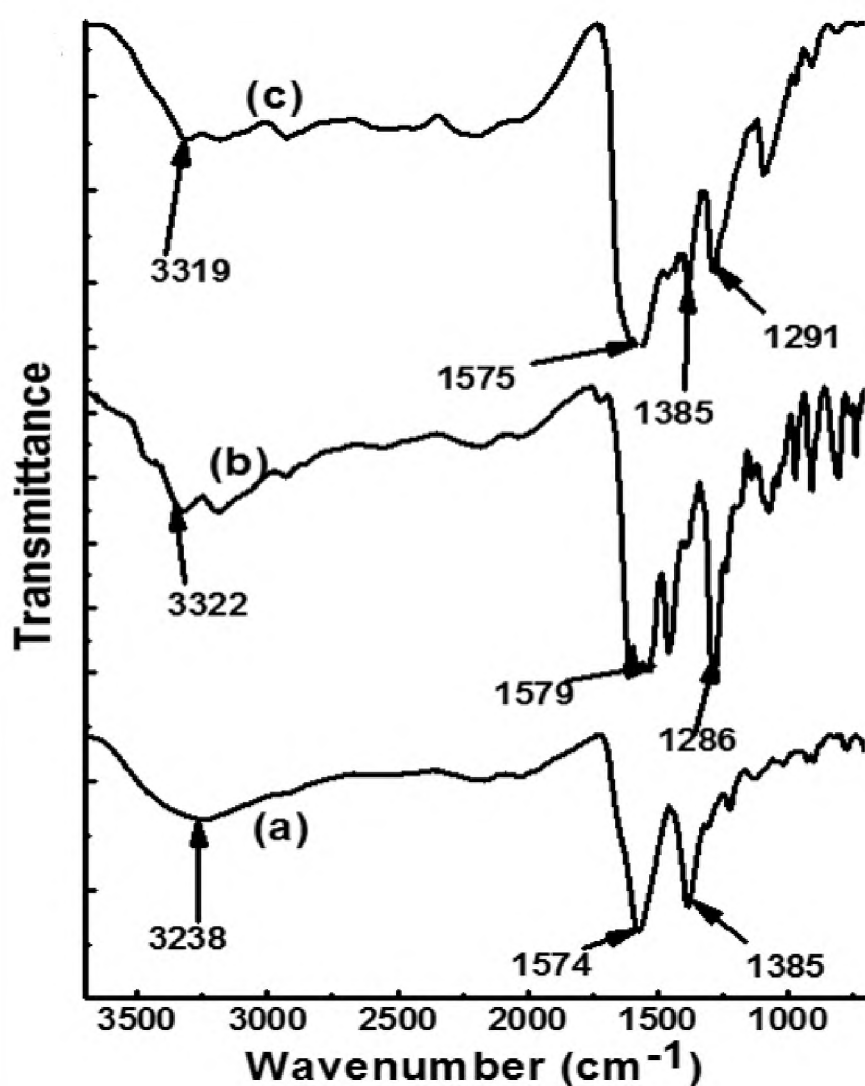


Figure 3.31 Infrared spectra (IR) of QDs (a), 12 (b) and 12-QDs

3.3.6 UV–Vis Spectra

QDs alone show the typical [137] broad absorption and narrow emission spectra, **Figure 3.32A (a and b)**. The overlaid absorption spectra of 10 and 10-QDs are shown in **Figure 3.32(B)**. There is a red shift of 3 nm in the Q-band maximum for 10-QDs, Table 3.2. for 11-QDs and 12-QDs, there is a blue shift compared to Pcs alone, blue or red shifts are due to orientation of Pcs on NPs [263].

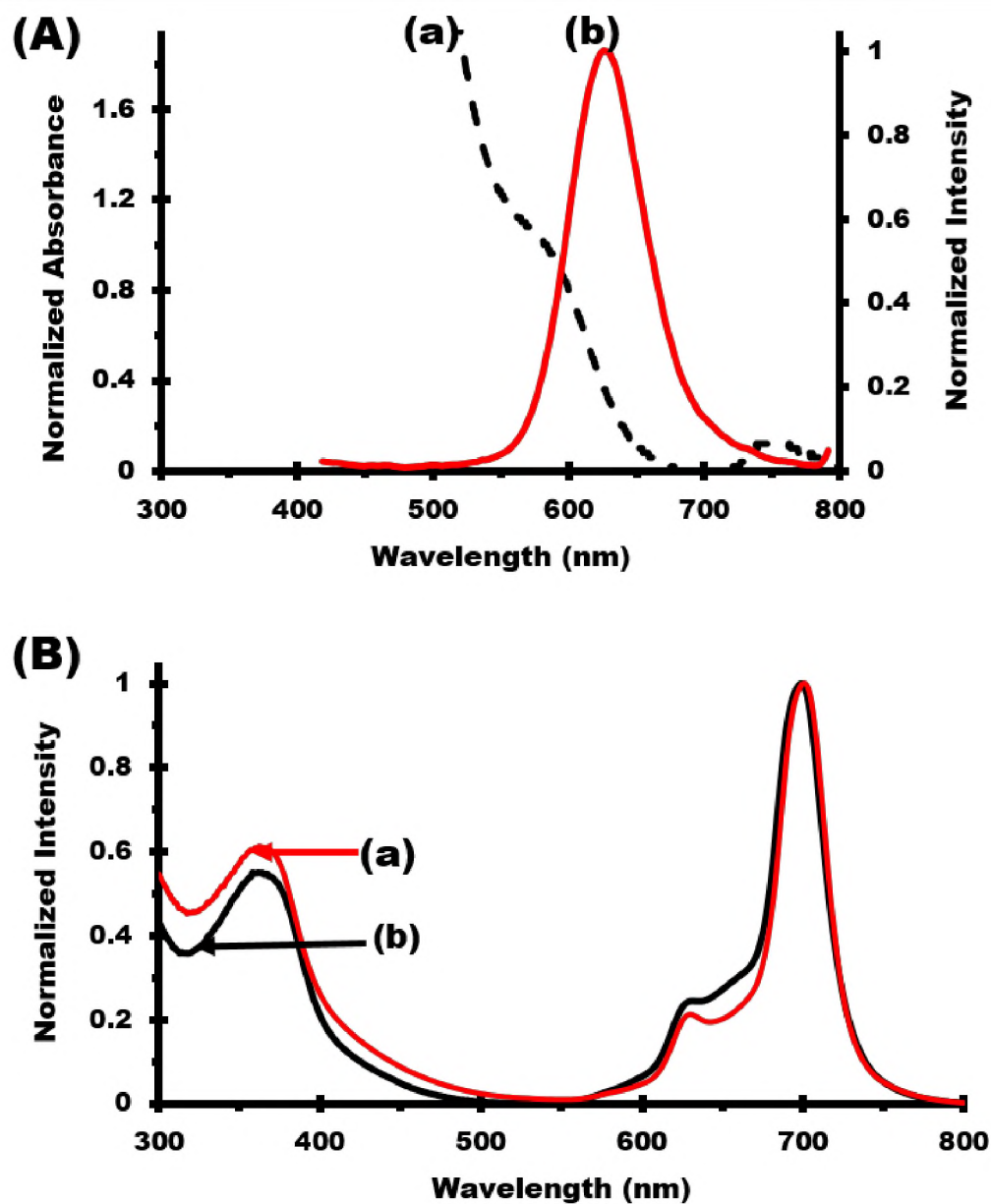
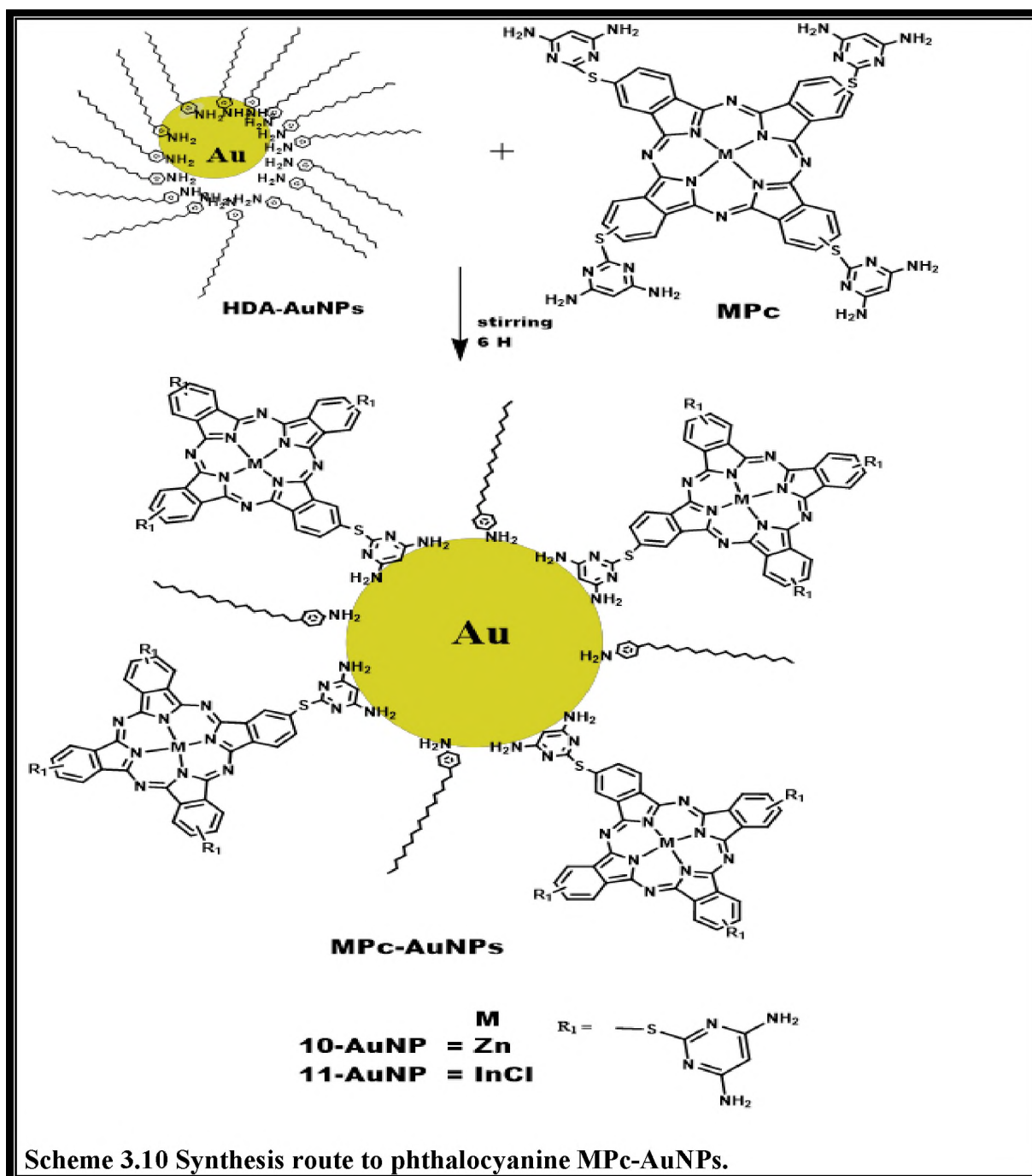


Figure 3.32 (A) the overlap spectra of QDs absorption (a) and QDs emission (excitation at 400 nm) (b) and Electronic absorption spectrum of (A) 10-QDs (a) and 10 (b) in DMSO;

3.4 Synthesis and Conjugation to Gold Nanoparticles (AuNPs)

3.4.1 Synthesis

The formation of conjugates with AuNPs takes advantage of the strong affinity for gold by amine groups. It is also possible that a Au-S bond may form, **Scheme 3.10**. The point of coordination will be confirmed by XPS below.



Scheme 3.10 Synthesis route to phthalocyanine MPC-AuNPs.

The loading of Pc onto nanoparticles was as follows ($\mu\text{g Pc/mg AuNPs}$): 60 $\mu\text{g/mg}$ for **11**-AuNPs and 27 $\mu\text{g/mg}$ for **12**-AuNPs Table 3.2. Thus, there is a higher loading of complex **11** onto NPs compared to **12**. This could be related to the fact that complex **12** has an axial ligand, which might course steric hindrance.

3.4.2 TEM Images

TEM micrograph of AuNPs alone (**Figure 3.33(a)**) show monodispersed patterns with an average size of 5.35 nm. Upon conjugation, there is increased aggregation for all NPs with estimated sizes presented in Table 3.2. Aggregation may occur by π - π interaction of MPcs on adjacent NP.

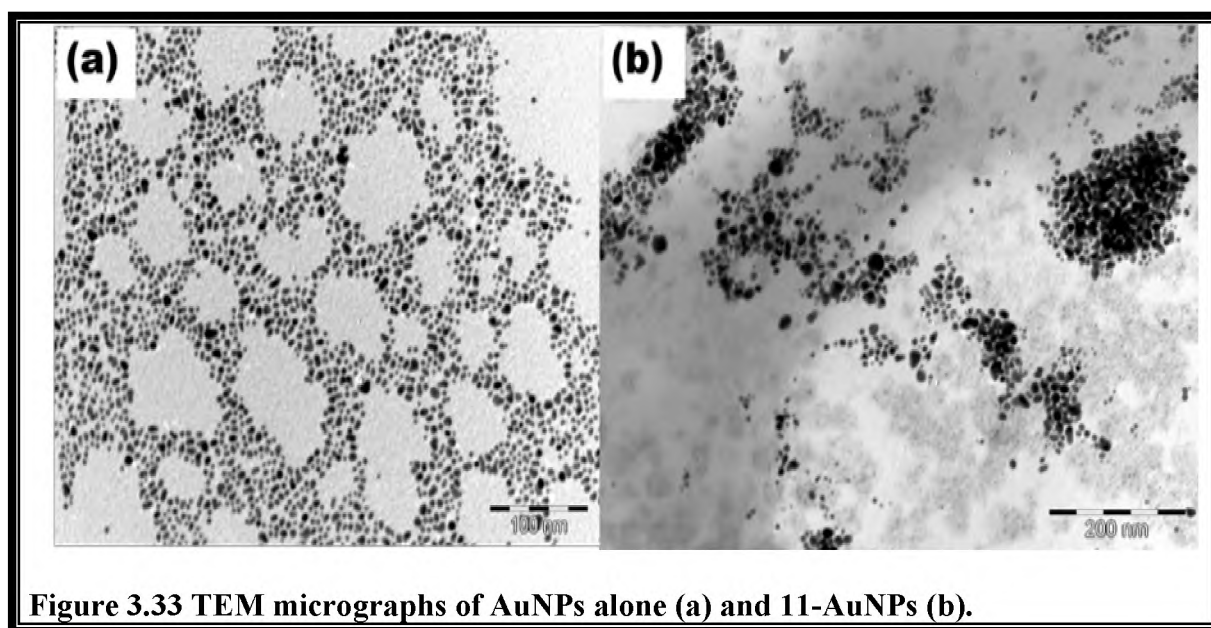


Figure 3.33 TEM micrographs of AuNPs alone (a) and 11-AuNPs (b).

3.4.3 XRD Patterns

AuNPs showed well-defined patterns with experimental 2θ values at 38.5° (111), 44.1° (200), 65.1° (220), 78.0° (311) and 82.3° (222). The powder diffraction pattern corresponds to a face-centered cubic crystal structure, which is typical of gold **Figure 3.34**. The conjugates show the presence of the Pc as judged by the enhancement of peaks near $2\theta = 25^\circ$. The estimated

size of 4 nm was obtained by applying Debye-Scherrer equation on the (111) peaks which is smaller than 5.35 nm by TEM.

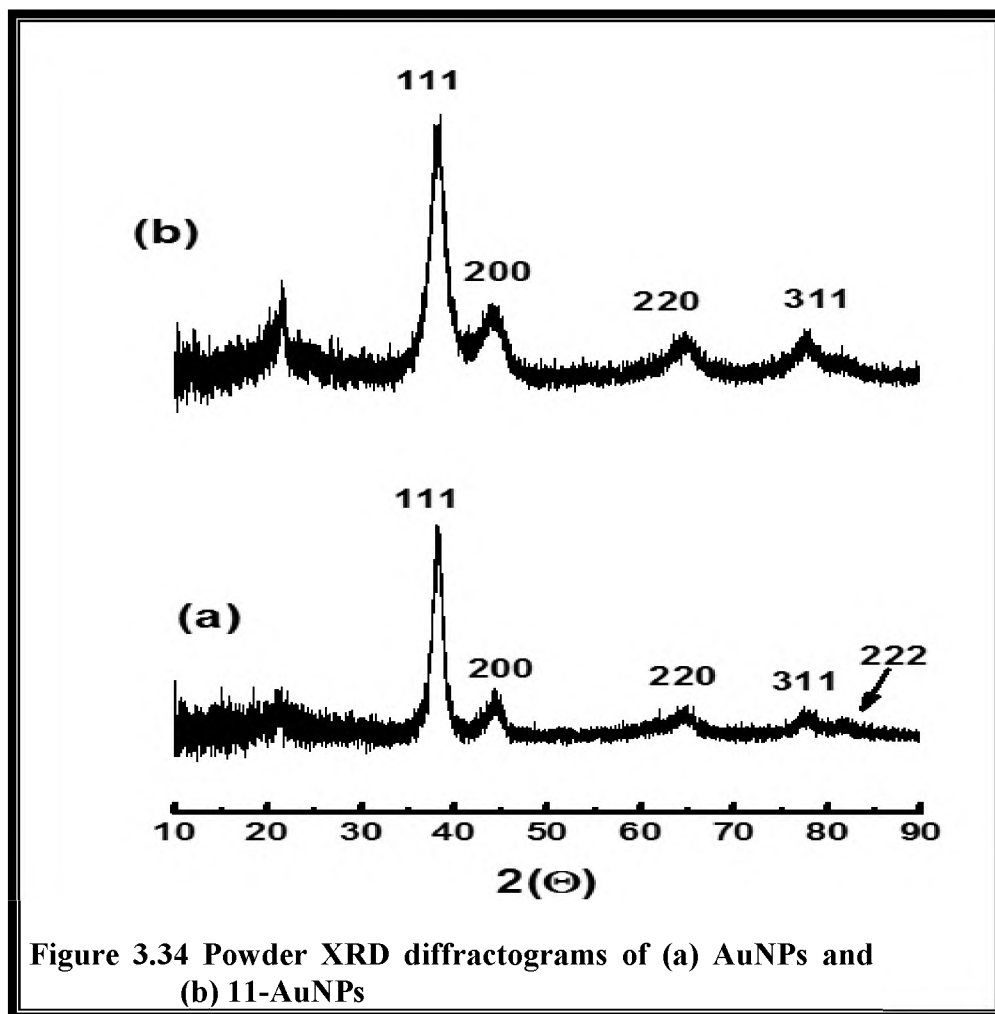


Figure 3.34 Powder XRD diffractograms of (a) AuNPs and (b) 11-AuNPs

3.4.4 XPS Spectra

The C 1s peaks in the survey spectra for the AuNPs (**Figure 3.35**) and 11-AuNPs show the highest intensity compared to AuNPs or 11 alone. The C 1s peak for AuNPs alone is due to the hexadecylaniline (HDA) is a stabilizing agent. The high resolution of N 1s was deconvoluted to prove the point of attachment of the Pc on the surface of the gold metal (11-AuNPs as an example).

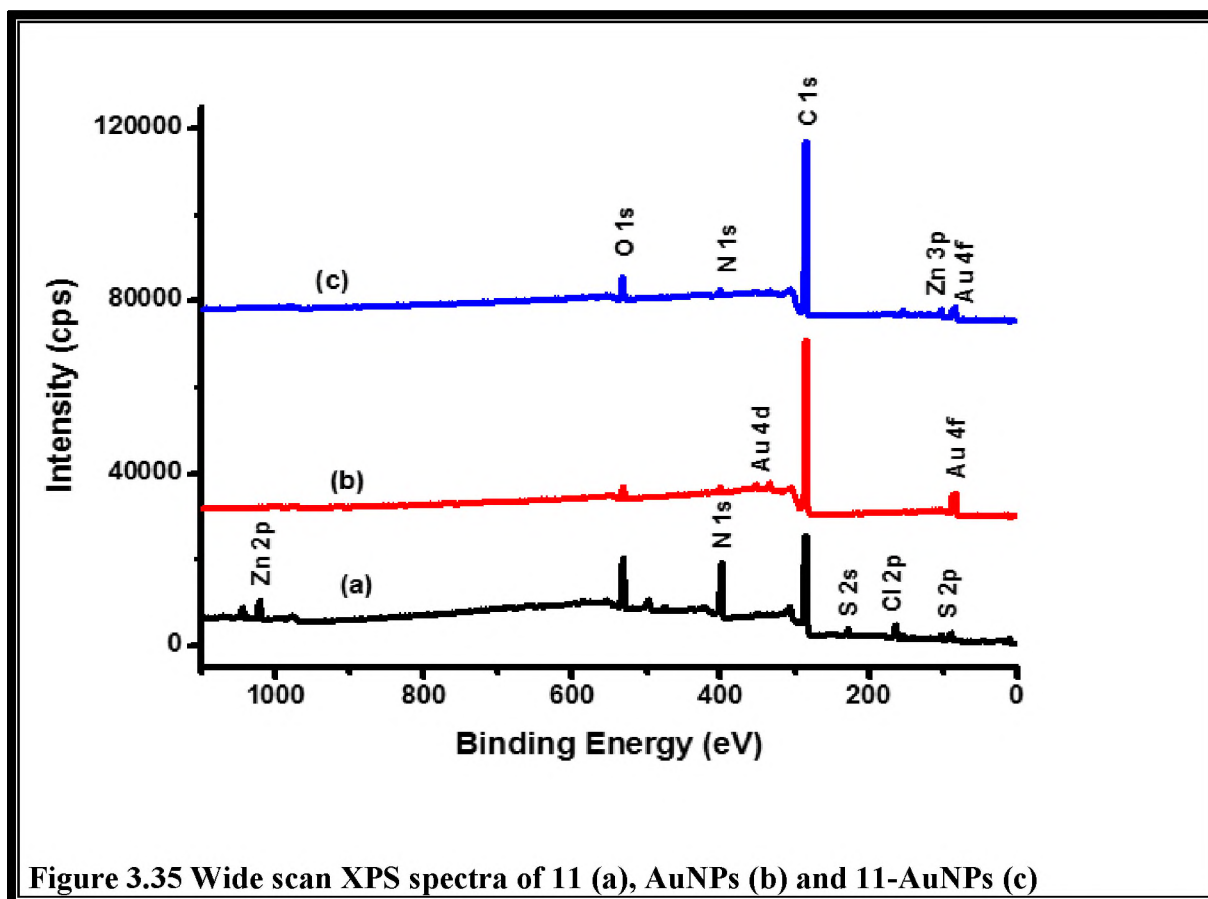
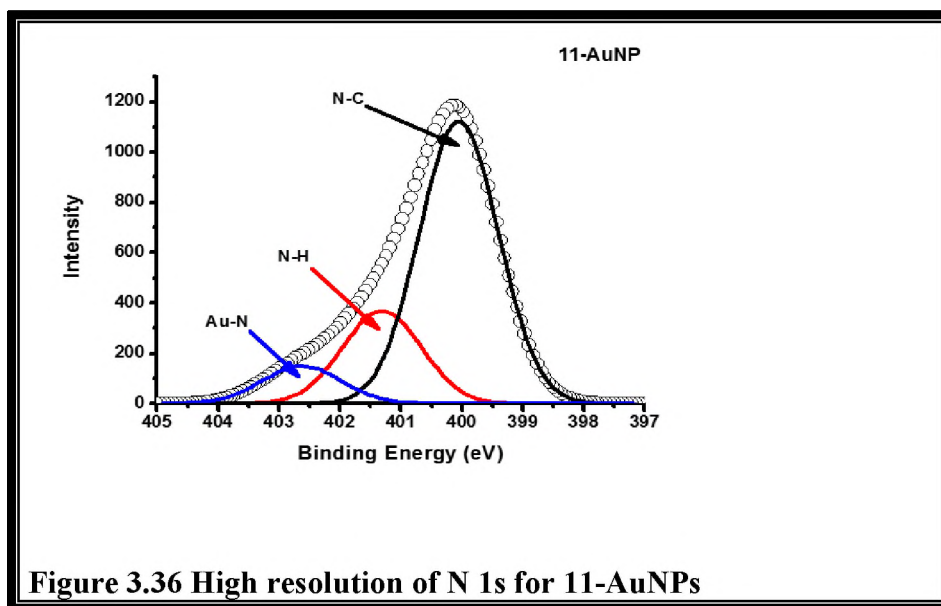


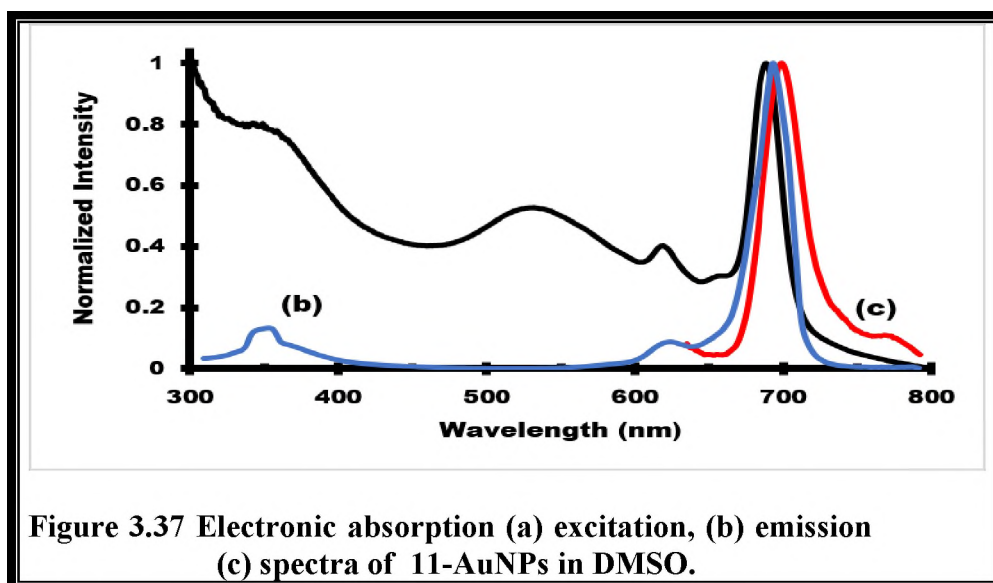
Figure 3.35 Wide scan XPS spectra of 11 (a), AuNPs (b) and 11-AuNPs (c)

N1s spectra of 11-AuNPs (Figure 3.36), revealed three components between 399.87 and 402.65 eV. Au-N is at a highest BE values of 402.65 eV due to chemisorption onto the surface of the AuNPs [264]. This confirms the successful linkage of complexes 11 and 12 with the nanoparticles by chemisorption onto gold nanoparticles via amino groups on the phthalocyanine. XPS could not prove the formation of an Au-S bond. This is possible because the S atom on the Pc is not as exposed as that of the NH₂ groups in complexes 11 and 12.

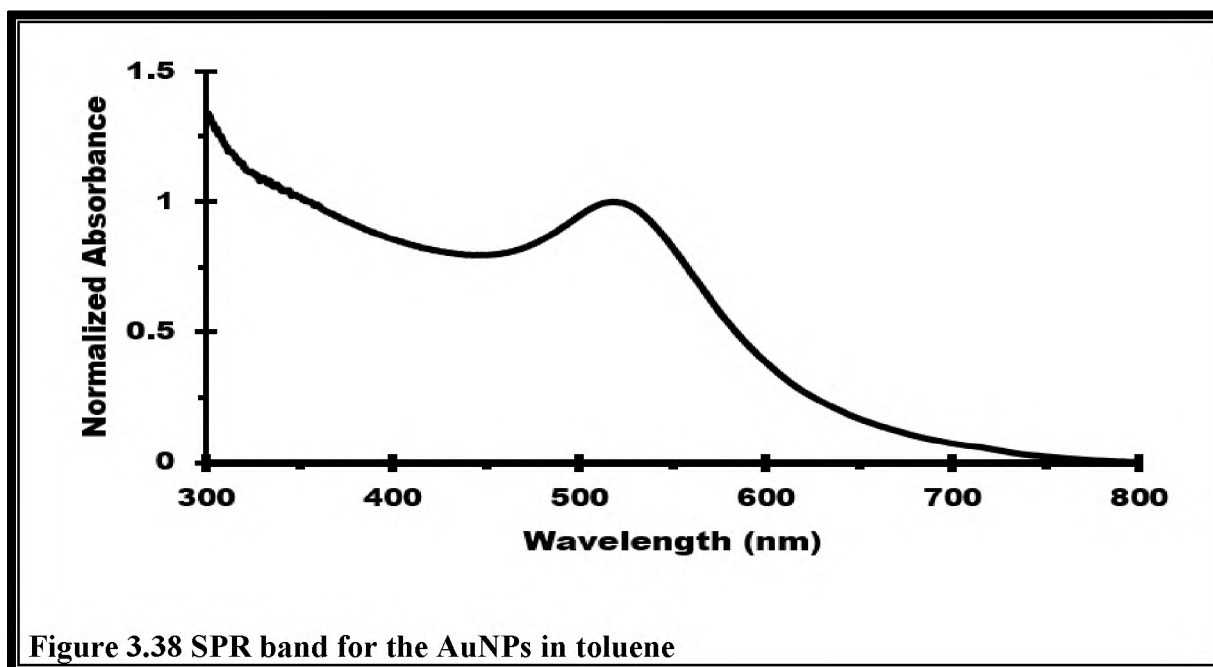


3.4.5 UV-Vis Spectra

Figure 3.37 shows the absorption, fluorescence excitation and emission spectra of 11-AuNP. The excitation spectrum is a mirror image of the fluorescence emission spectrum. The excitation spectrum differs from the absorption spectrum because of the SPR absorption peak. The surface plasmon resonance (SPR) absorption band for AuNPs was observed at 518 nm, Figure 3.38.



There is no change in the Q-band maxima for **11**-AuNPs compared to **11** alone, Table 3.2, but there is blue shifting for **12**-AuNPs compared to **12** alone. The spectral changes in MPC complexes in the presence of nanoparticles such as AuNPs depends on the orientation of the molecular dipole NPs with respect to the MPC-nanoparticle axis as discussed before for other dye systems [263]. There is a red shifting of the AuNPs SPR band from 518 nm to 531 nm and 537 nm upon conjugation with complexes **11** and **12**, respectively probably due to aggregation.



3.5 Characterization of Phthalocyanines When Embedded in Electrospun Fiber

3.5.1 Scanning electron microscope (SEM)

Figure 3.39 shows the SEM images of polystyrene electrospun fiber alone or in the presence of **7**, **7a**, **8a**, **9a** and **10a**. The fiber diameters decreased in the presence of **7**, **8a**, **9a** and **10a** but increased for **7a**. Polymer solution properties such as viscosity and conductivity play a

significant role in the electrospinning process and the resultant fiber diameter and morphology. The modified fibers were uniform and orderly **Figure 3.39**.

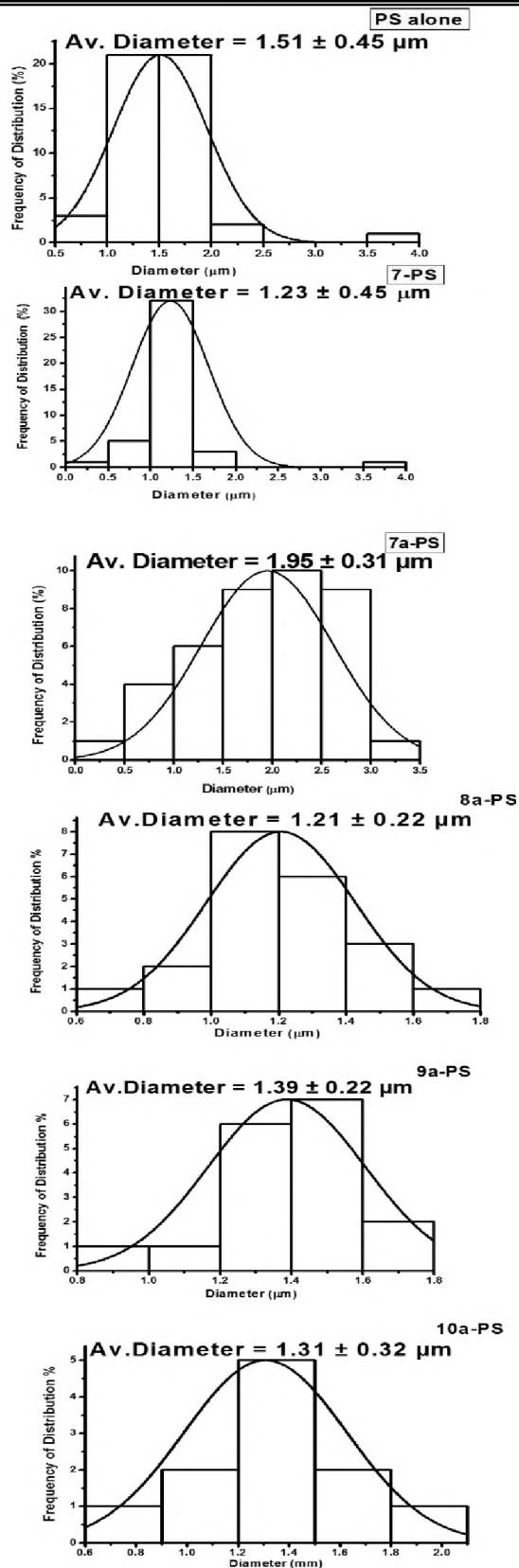
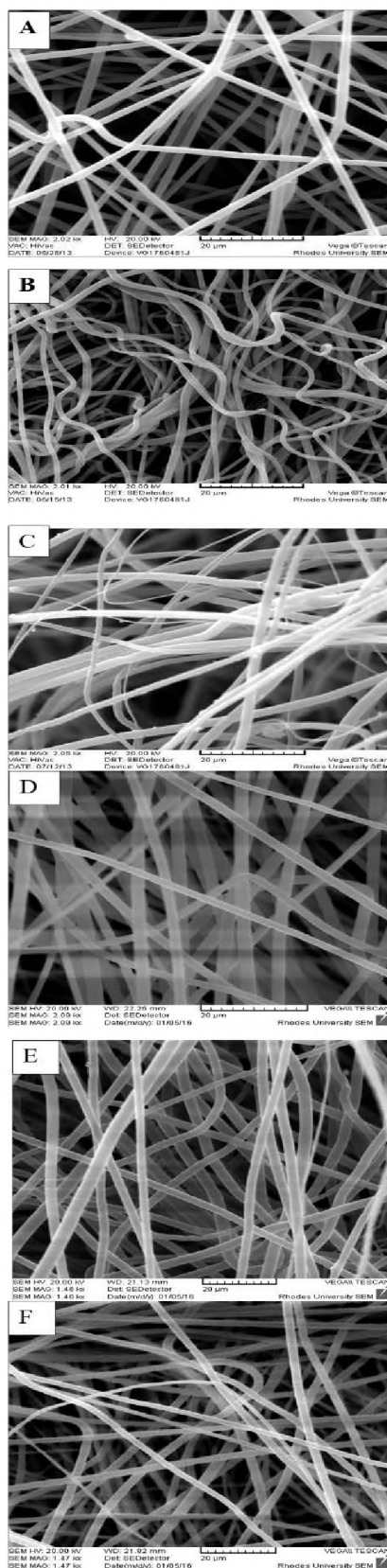
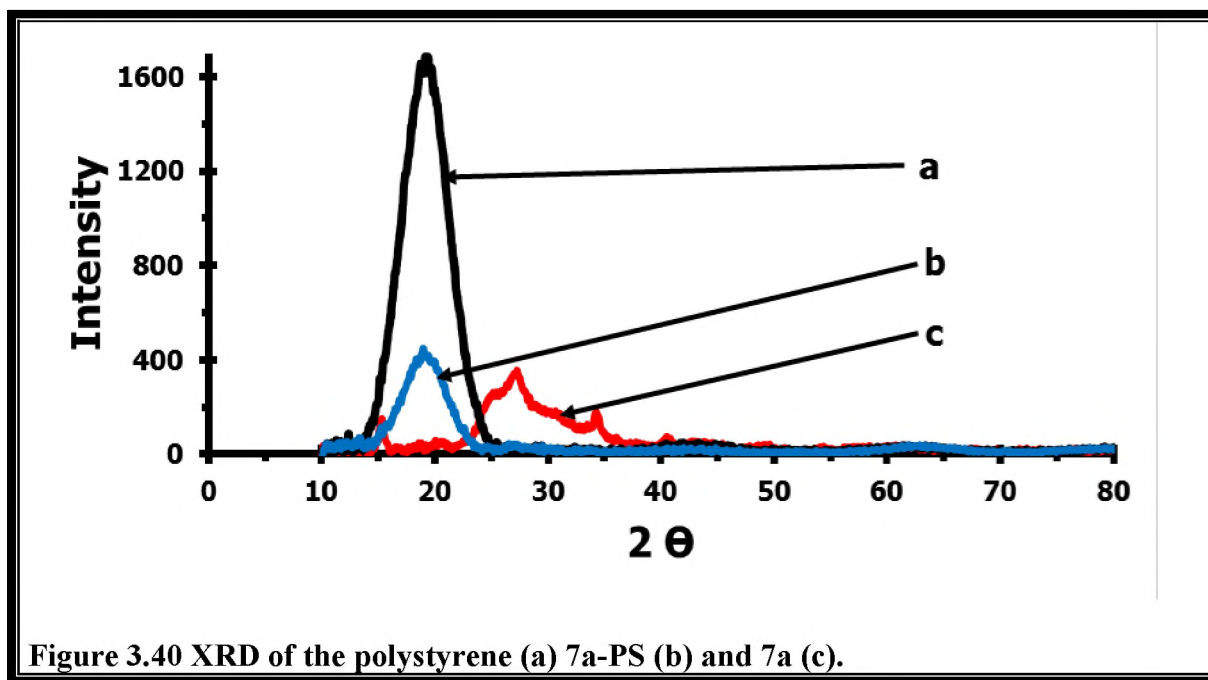


Figure 3.39 The SEM micrographs of electrospun fiber and the histogram showing fiber distribution (A) polystyrene polymer (PS), (B) 7-PS, (C) 7a-PS, (D) 8a-PS, (E) 9a-PS and (F) 10a-PS

3.5.2 XRD Patterns

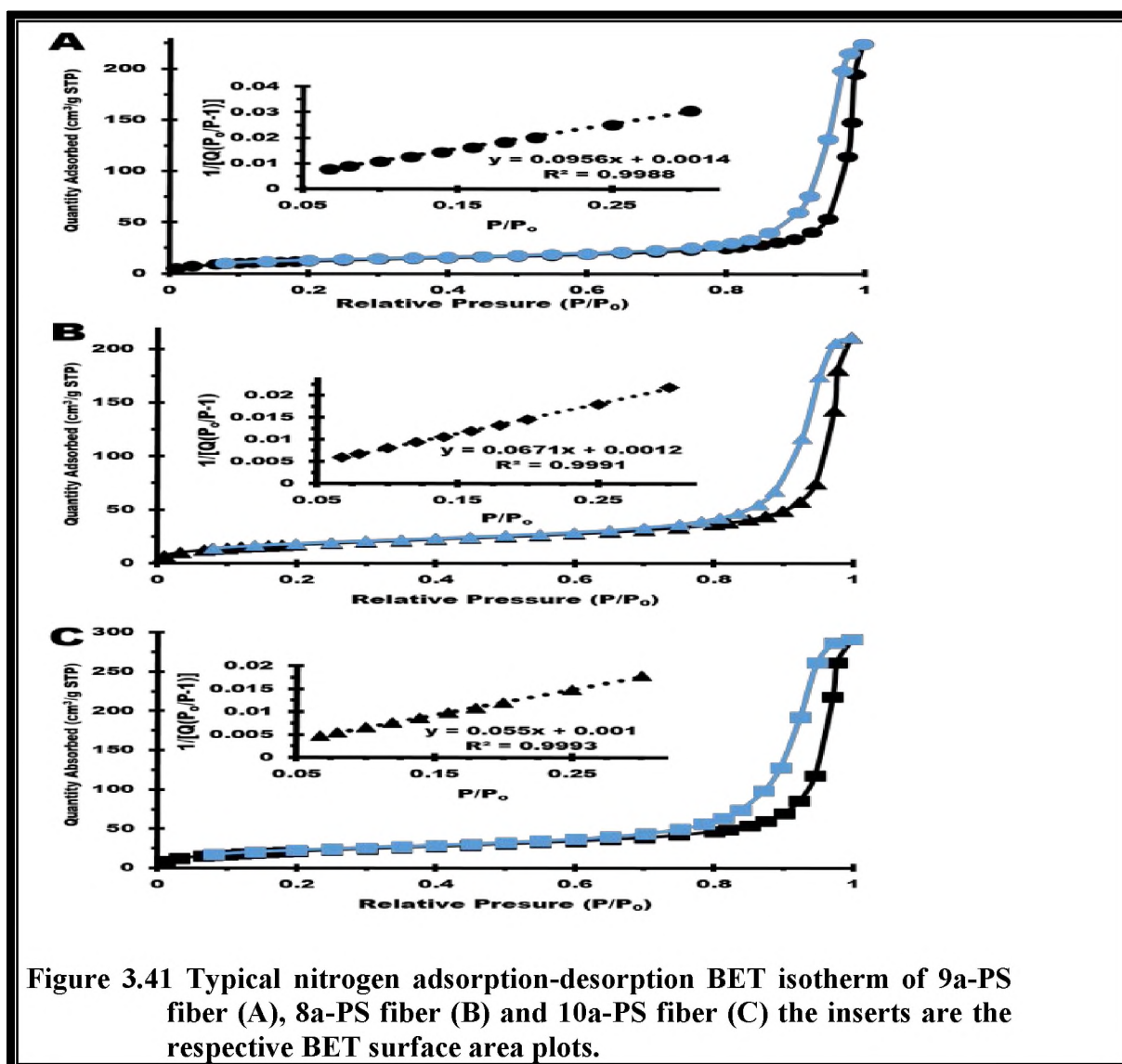
XRD patterns shown in **Figure 3.40** show amorphous PS fibers, consistent with the notion that electrospinning being a rapid process retards crystallite growth [265]. XRD results also confirmed incorporation of the Pc complexes into the PS fibers. This is judged by the absence of the peak due to the Pc (usually very weak) at $\theta = 26^\circ$.



3.5.3 Surface Area and Porosity Analyses

The nitrogen adsorption-desorption isotherms for the modified electrospun fiber are shown in **Figure 3.41**. The BET characterization shows that the modified fibers show type IV sorption isotherms with surface area obtained between 44.87 m²/g and 77.77 m²/g while the surface area of polystyrene alone is 16.15 m²/g. The increase in surface area observed for the modified fibers are expected, since reducing fibre diameter increases the surface area to volume ratio, and vice versa [266], **7a** deviates from this trend since diameter increases but surface area increases compared to PS alone. Surface area and pore volume for **10a**-PS fiber were the highest compared to other modified fibers and PS alone, Table 3.3. Complexes **10a** and **9a** are asymmetrically substituted Pc, but the former (**10a**) consist of pyridylsulfanyl and

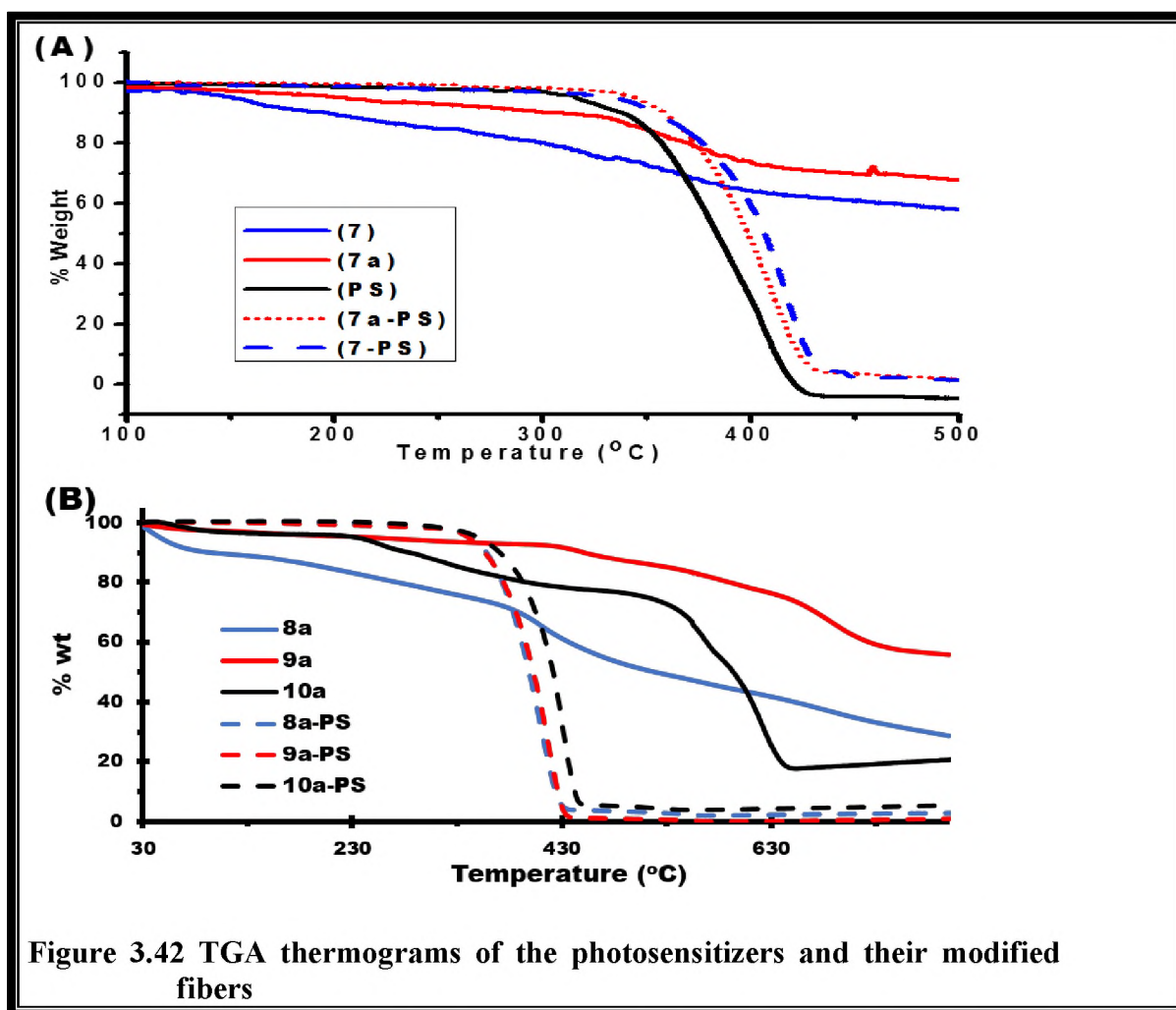
aminophenoxy substituent which might be the cause of the BET observation due to different conductivity.



3.5.4 Thermal stability

Figure 3.42A shows the TGA thermograms for weight loss as a function of temperature from 100 to 500 °C for PS, 7, 7a, 7-PS, and 7a-PS. Figure 3.42B is for cationic Pc modified fibers of 8a, 9a, and 10a. The thermograms show in Figure 3.42A that the functionalized polymer fibers exhibited increased thermal stability compared to polystyrene alone (PS). This result may be attributed to the possible hindrance effect of the Pc complexes on the mobility of the

polymer chains as well as the higher thermal stability of MPcs. The quaternized **7a** show an enhanced thermal stability when compared with un-quaternized **7**; this corroborates the results obtained during photodegradation studies of the phthalocyanines in Chapter 4. Comparing phthalocyanines when not embedded in fiber, lead substituted Pcs (**7** and **7a**) are more stable than In substituted Pcs (**8a**, **9a** and **10a**) while complex **9a** is more stable than complexes **8a** and **10a**. Decomposition may be due to lose of axial ligand and substituents. Complex **9a** with fewer substituents might thus be more stable than **8a** and **10a**.

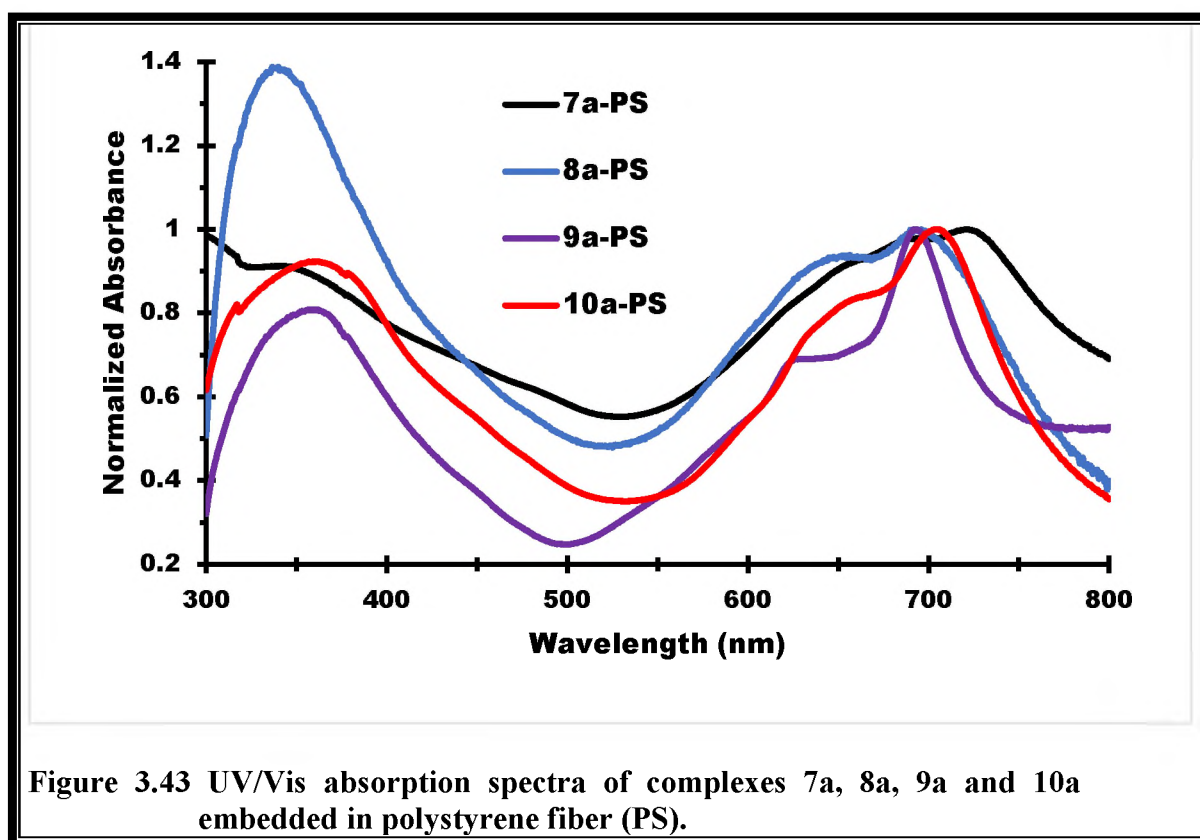


The TGA profiles of the modified fibers; **Figure 3.42A**, for quaternized modified fiber **7a-PS** show an enhanced degradation compared to **7-PS** before 350 °C, and both fibers are less stable beyond 400 °C. Also, modified polymers **8a-PS**, **9a-PS** and **10a-PS** (**Figure 3.42B**)

were relatively stable at a temperature less than 400 °C, but **10a**-PS fiber is slightly more stable beyond 400 °C.

3.5.5 UV/Visible Spectra

The UV/Vis absorption spectra of phthalocyanines (**7a**, **8a**, **9a** and **10a**) embedded in electrospun fibers **Figure 3.43**, shows that the spectra are broad due to aggregation; as is typical of spectra in the solid state [267].



The aggregate peak (high energy) is more intense for complex **7a**-PS and **8a**-PS compared to the other complexes, showing that complex **7a** and **8a** are more aggregated in the solid state than the rest of the complexes. The peaks due to the monomer (low energy) are more red-shifted in embedded fiber when compared to the corresponding peaks in solution, this is typical behavior for phthalocyanines in the solid state [267], Table 3.3.

Table 3.3 Parameters for the modified fibers

Complexes	$\lambda_{\text{abs}}^{\text{a}}$	Av. Diameter (μm)	BET Analysis	
			Surf. Area (m^2/g)	Pore Vol. (cm^3/g)
PS alone	-	1.51 ± 0.45	16.15 ± 1.56	0.20
7	NA (709) ^a	1.23 ± 0.45	49.40 ± 0.79	0.31
7a	722 (705) ^a	1.95 ± 0.31	57.25 ± 0.49	0.31
8a-PS Fiber	694 (691) ^b	1.21 ± 0.22	63.68 ± 0.66	0.33
9a-PS fiber	692 (685) ^b	1.39 ± 0.22	44.87 ± 0.54	0.30
10a-PS	706 (699) ^b	1.31 ± 0.32	77.77 ± 0.71	0.45
Fiber				

^a values in brackets are for phthalocyanines alone in DMF solution;

^b values in brackets are for phthalocyanines alone in DMSO solution;

NA= not applicable because of broadness at the Q-band region

3.6 Conclusion

The complexes (7-12) were fully characterized using various techniques to confirm the as-synthesized metallophthalocyanines. The complexes with amino groups were conjugated to nanomaterials and were also investigated to determine the point of attachment via XPS. MNPs and QDs conjugates form an amide bond between the amino substituents on the Pcs and a carboxylic acid functional moiety of the nanomaterials. The conjugations of the Pcs with AuNPs is via chemisorption onto the surface of the nanoparticles. All the photosensitizers show a monomeric absorbance in DMF and DMSO and the quaternized forms of the photosensitizers exhibit aggregation in water. The absorption of modified fibers were recorded using solid state UV-visible for (7a-PS, 8a-PS, 9a-PS, and 10a-PS).

Chapter 4

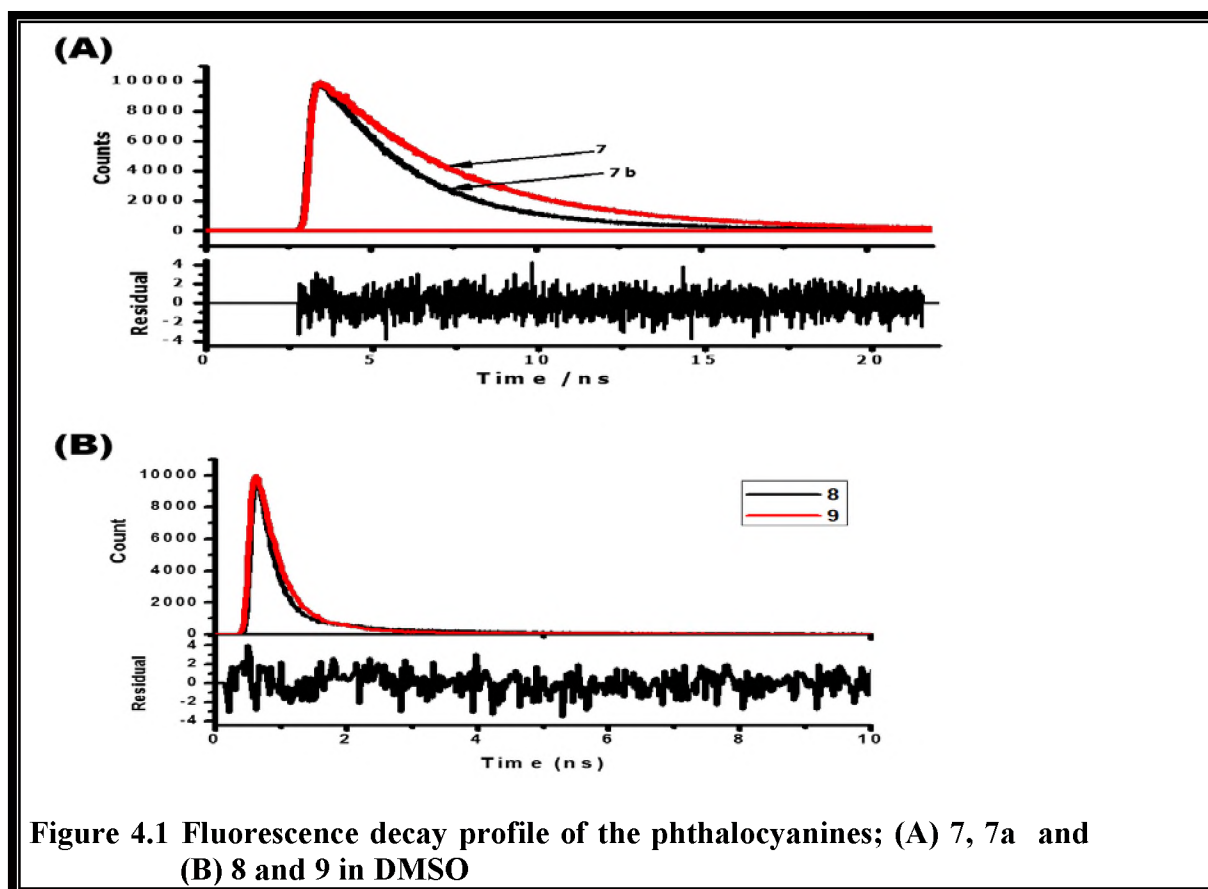
Photophysical and photochemical studies

4 Photophysical and Photochemical Studies of Phthalocyanines and their Conjugates

4.1 Pyridyloxy Substituted Phthalocyanines (7-9, 17, 18)

4.1.1 Fluorescence Quantum Yields and Lifetimes.

The Φ_F values of all complexes are low due to the heavy atom effect of Pb and In metal ions which encourage intersystem crossing to the triplet state (Table 4.1) [99]. However, the values are larger in DMF than in DMSO where both solvents are employed for the same sample. The fluorescence quantum yield (Φ_F) values for **7** and **7a** were 0.02 and 0.01, respectively in DMF, Table 4.1. Φ_F values of **8a** is lower in water than in DMF or DMSO due to the formation of aggregates in water, aggregates do not fluoresce [248,268]. Φ_F for **7a** was not determined in water due to lack of emission as a result of aggregation.



The fluorescence lifetime (τ_F) refers to the average time a molecule stays in its excited state before fluorescing, and its value is directly related to that of Φ_F ; i.e. the longer the lifetime, the higher the quantum yield of fluorescence. Any factors that shorten the fluorescence lifetime of a fluorophore indirectly reduces the value of Φ_F . However the τ_F values are not always low when Φ_F are low [269].

Table 4.1 Photophysical properties of MPcs and their quaternized MPcs

Comp	Solvent	Φ_F	τ_F (ns)	Φ_T	τ_T (μ S)	Φ_Δ	Φ_{IC}	Φ_{pd} (10^{-6})	S_Δ
7	DMF	0.02	3.13	-	-	0.68 0.21 ^a	-	1.75	-
7a	DMF	0.01	2.37	0.69	34	0.60 (<0.01) ^b 0.41 ^a	0.30	0.77	0.87
8	DMF	0.024	1.52	0.78	58	0.44	0.20	10.1	0.56
	DMSO	0.014	1.74	0.83	71	0.62	0.15	3.21	0.75
8a	DMF	0.037	1.42	0.95	60	0.58	0.013	3.73	0.61
	DMSO	0.011	1.68	0.90	61	0.69	0.0	1.09	0.69
	Water	0.006	1.73	-	-	0.31	-	37.8	-
	Water/Triton X 100	0.013	1.30	-	-	-	-	6.26	-
9	DMF	0.032	1.62	0.77	42	0.58	0.20	3.60	0.75
	DMSO	0.020	2.03	0.77	59	0.52	0.21	2.82	0.68
9a	DMF	0.024	1.60	0.80	19	0.66	0.18	4.21	0.83
	DMSO	0.017	1.75	0.82	49	0.56	0.16	4.34	0.68
10	DMSO	0.008	0.26	0.74	55	0.44	0.25	0.12	0.60
10a	DMSO	0.013	0.33	0.48	66	0.26	0.51	0.19	0.51
	Water/Triton X 100	0.018	0.33	-	-	0.31 0.50 ^a	-	1.32	-
11	DMSO	0.11	2.53	0.83	351	0.30	0.06	2.59	0.36
12	DMSO	0.01	0.30	0.88	57	0.33	0.11	4.56	0.38
17	DMSO	0.082 ^c	1.61 ^c	0.81 ^c	50 ^c	0.68 ^c	0.04 ^c	49.0 ^c	0.72 ^c
18	DMSO	0.020 ^c	0.35 ^c	0.94 ^c	70 ^c	0.44 ^c	0.03 ^c	50.0 ^c	0.54 ^c

^a Φ_Δ values (in water) for the modified fiber,

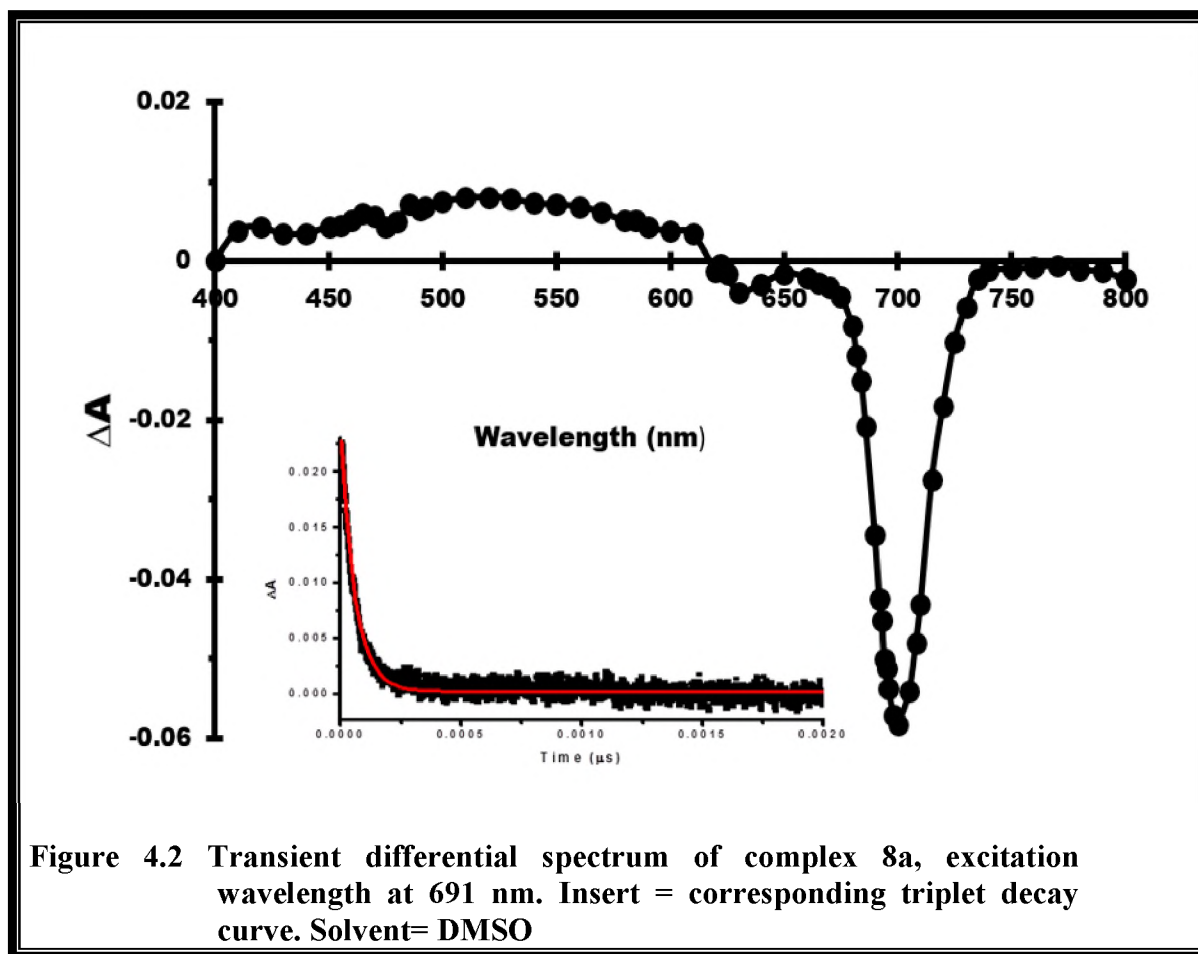
^b Φ_Δ values for 7a in water,

^c Values from reference [248].

The fluorescence decay curves for complexes are shown in **Figure 4.1A** for (**7** and **7a**) and **Figure 4.1B** (**8** and **9** as examples). A biexponential decay process was observed for all compounds. Average lifetimes are shown in Table 4.1. The presence of two fluorescence lifetimes for the phthalocyanine have been explained as being due to the formation of aggregates which are non-fluorescent, but which can quench the monomer [270,271], resulting in quenched and unquenched lifetimes. τ_F values are within those reported for phthalocyanines [201].

4.1.2 Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T).

The transient differential spectrum for complex **8a** in DMSO shown in **Figure 4.2** (as an example) and it shows a triplet absorption maximum at 530 nm. The insert shows the triplet decay curve, the triplet decay curves obeyed second order kinetics which is typical of MPc complexes at high concentration ($>1 \times 10^{-4}$ M) due to the triplet-triplet recombination [272]. Heavy metals result in short lifetimes in metallophthalocyanines [273], hence a weak signal is observed for **7a** and none for **7**. Also, nitrogen containing substituents on the Pc ring have been shown to quench the triplet state [274], resulting in a very short lifetime. This could explain the lack of a triplet decay curve for **7**. The engagement of the nitrogens due to quaternization in **7a** resulted in the observation of a triplet decay curve but with a short lifetime. The triplet quantum yields (Φ_T) were calculated at the absorption maxima using the comparative methods described before [99,275] and ZnPc in DMSO as a standard (Φ_T for the standard = 0.65 [275]). The triplet quantum yield (Φ_T) of **7a** is 0.69 and the corresponding lifetime of 34 μ s, Table 4.1. In general, the Φ_T values are high corresponding to low Φ_F values for **8** only. Φ_T values improve on quaternization (comparing **8** with **8a**, and **9** with **9a**).



The Φ_T values are smaller for the monosubstituted derivatives (**9**, **9a**) when compared to the tetrasubstituted counterparts (**8**, **8a**). This contradicts the reports that asymmetry improves intersystem crossing [40]. Comparing **17** with **8a** shows that 4-pyridyloxy groups (complex **8a**) result in improved Φ_T when compared 3-pyridyloxy groups (complex **17**). However, comparing complex **17** and **18** indicates that peripheral substitution (**18**) resulted in larger Φ_T value compared to non-peripheral substitution (**17**). The triplet lifetimes are short due to the heavy atom effect of In and Pb.

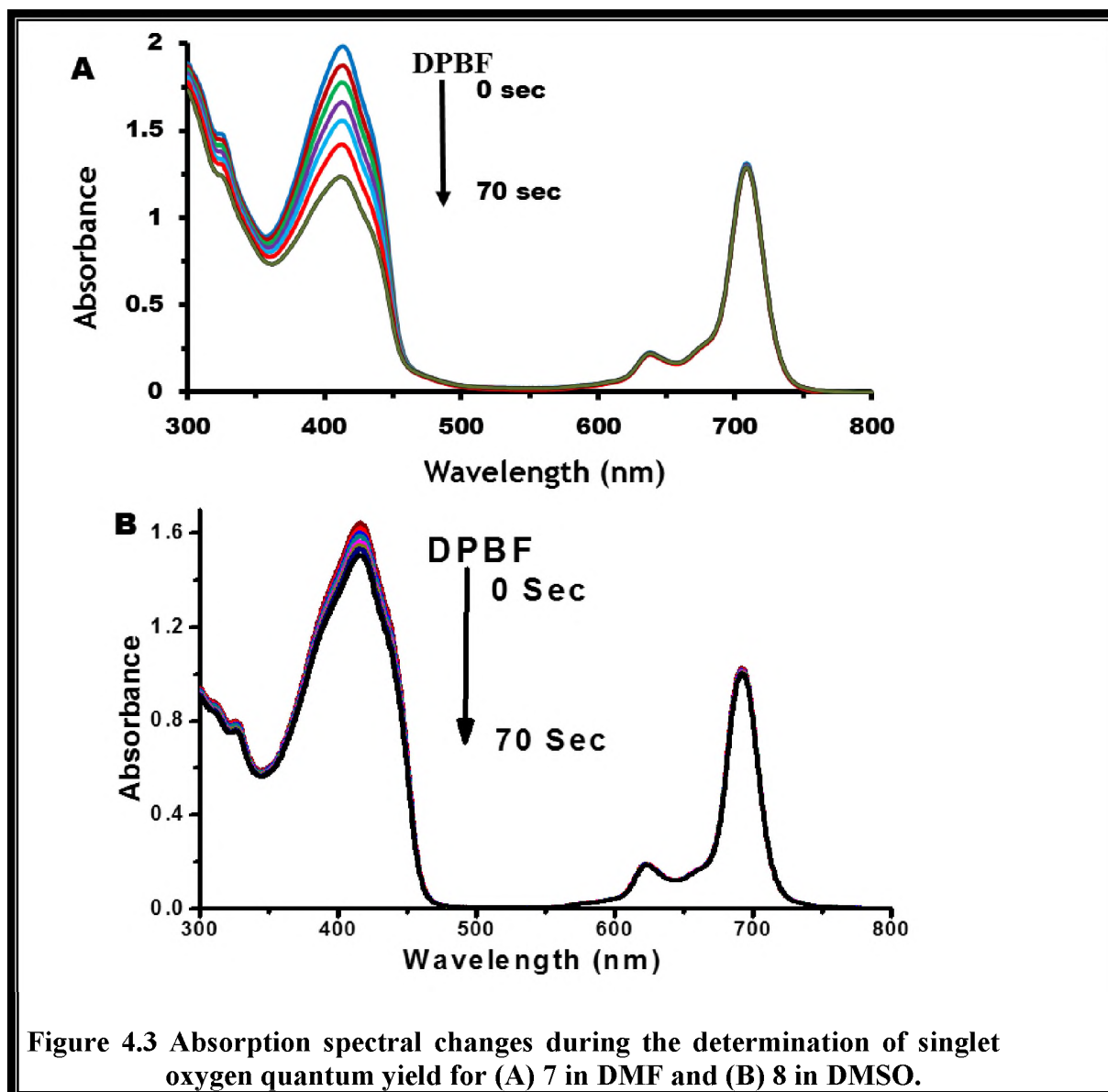
Quantum yields of internal conversion (Φ_{IC}) were obtained from Equation 4.1, which assumes that only three processes (fluorescence, intersystem crossing, and internal conversion), jointly deactivate the excited singlet state of the phthalocyanine complexes.

$$(\Phi_{IC}) = 1 - (\Phi_F + \Phi_T) \quad (4.1)$$

These values are generally low as shown in Table 4.1.

4.1.3 Singlet Oxygen Quantum Yield (Φ_{Δ})

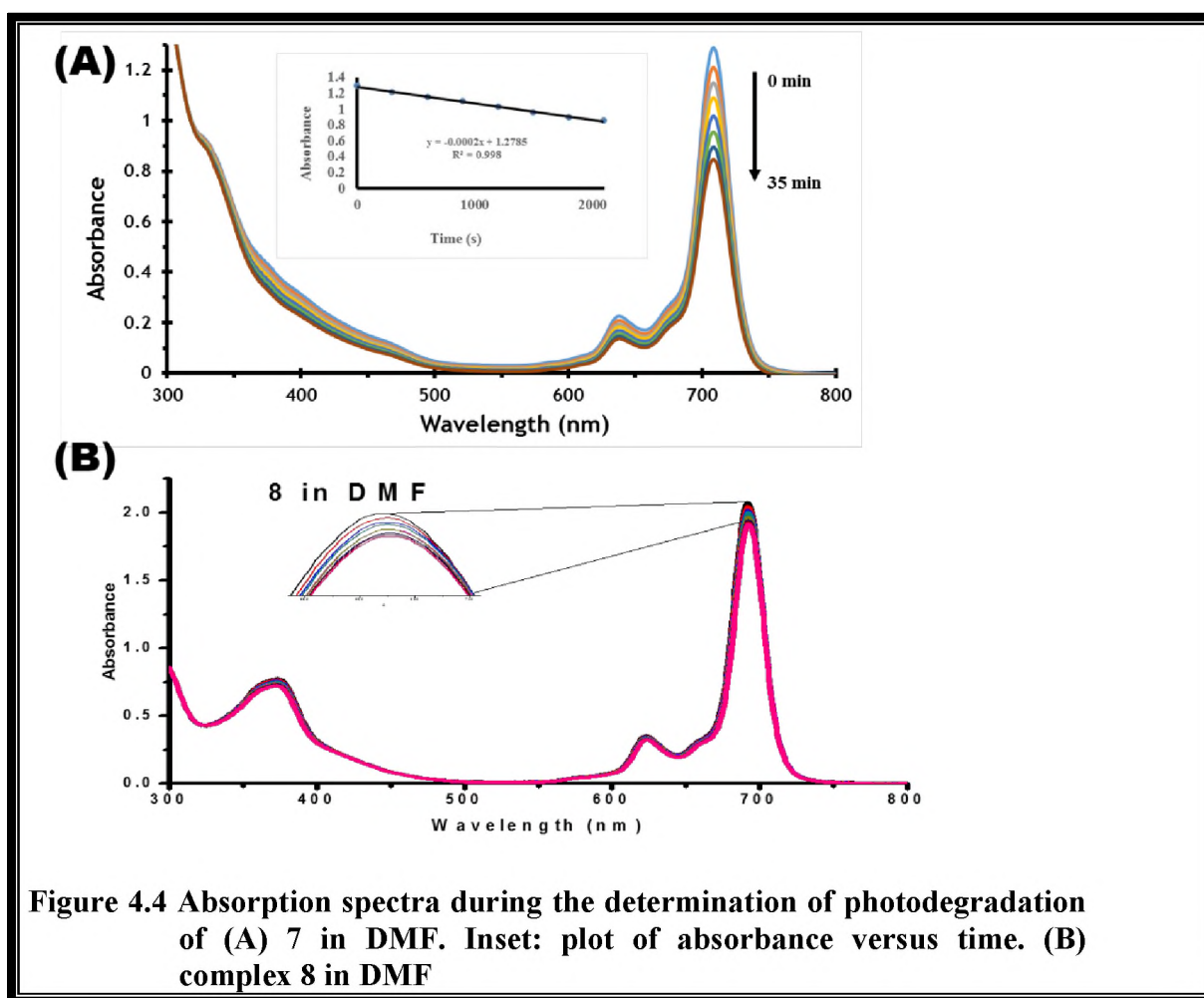
The Φ_{Δ} values were determined using DPBF in DMSO or ADMA in aqueous media (water plus Triton-X 100) as singlet oxygen quenchers. Comparative methods reported before were employed using ZnPc as a standard in DMSO ($\Phi_{\Delta} = 0.67$ in DMSO [99] and AlPcSmix in aqueous media ($\Phi_{\Delta} = 0.44$ [202])). The concentrations of DPBF and ADMA were lowered to $\sim 0.3 \mu\text{mol dm}^{-3}$ for all solutions, to avoid chain reactions. **Figure 4.3** shows absorption spectra changes of DPBF (using complexes **7** and **8** as an example) during photolysis. There was no significant change in the Q-band intensity. The Φ_{Δ} values are 0.68 and 0.60 in DMF for **7** and **7a**, respectively. Φ_{Δ} value less than 0.01 was obtained for **7a** in water, Table 4.1. This value is lower than the value in DMF since water is known to quench singlet oxygen [276] and also **7a** is aggregated in water and aggregates are photoinactive. The differences in values may also be due to the efficiency of energy transfer between the triplet excited state of the phthalocyanines and ground state triplet oxygen to form excited singlet state oxygen. This efficiency of energy transfer (S_{Δ}) is determined using the ratio ($S_{\Delta} = \Phi_{\Delta}/\Phi_T$). For effective transfer of energy S_{Δ} should be close to unity. The values in S_{Δ} are all greater than 0.5 but not all are close to unity (Table 4.1).



4.1.4 Photodegradation Studies

Photodegradation is a process where a phthalocyanine is degraded under light irradiation [99]. It can be used to determinate MPcs' thermal stability, and this is especially important for those molecules intended for use as photocatalysts. The decrease of the intensities of both the Q and B bands was observed (**Figure 4.4**, using **7** and **8** as examples). There was no change in the shape of the spectra with irradiation confirming that only degradation (not phototransformation into other absorbing species) occurred under light irradiation during the photodegradation studies. For the determination of photodegradation quantum yields,

Equation 1.14 was employed [99]. The photodegradation quantum yield (Φ_d) values for **7** and **7a** in DMF were of order of $10^{-7} - 10^{-6}$, showing good stability, Table 4.1. For Pcs with low photostability, the values are of the order of 10^{-3} [99]. Quaternized tetrasubstituted Pcs (**7a** and **8a**) are more stable than unquaternized Pcs, Table 4.1. Singlet oxygen has been implicated in phthalocyanine photodegradation, hence a good correlation is expected between the values of Φ_Δ and Φ_{pd} . This is not always the case in Table 4.1.



For monosubstituted derivatives, the unquaternized **9** was marginally more stable than quaternized **9a**. The values reported in the literature (**17** and **18**) showed that they were less stable than the rest of the complexes, this might be due to the position of the N-group on the pyridyloxy which is in the para position compared with compounds **7a** and **8a** which were in the meta position.

4.2 Asymmetrical MPc (**10** and **10a**) alone or in the Presence of Nanomaterials

4.2.1 Fluorescence Quantum Yields (Φ_F) and Lifetimes (τ_F)

4.2.1.1 Pc-MNP conjugates

The fluorescence quantum yields (Φ_F) and lifetimes (τ_F) of the nanomaterials, MPcs, and their conjugates (**10**-MNPs, **10a**-MNPs) are listed in Table 4.2. As was also the case for **7-9** discussed above Φ_F value is low for **10** alone, due to the heavy atom effect of indium, which encourages intersystem crossing to the triplet-singlet state. For **10**-MNPs, Φ_F value slightly increased compared to **10** alone. However, a decrease would have been expected due to the heavy atom effect of the MNPs. For **10a**-MNPs, the Φ_F value decreased as expected compared to complex **10a** alone in DMSO. This could probably be due to the additional heavy atom effect of iodine in **10a** which is not present in **10**. It has been reported that even though the MNPs core normally quenches the porphyrin fluorescence, covalent bonding of porphyrin to MNPs via an appropriate spacer reduces the quenching [277].

Table 4.2 Photophysical properties of Indium (III) phthalocyanines in DMSO, excitation at 670 nm unless otherwise stated

Complex	Φ_F	τ_F (ns)	Φ_T	τ_T	Φ_Δ	Φ_{IC}	Φ_{pd}	S_Δ
				(μ S)			10^{-5}	
QDs	0.24 ^a	12.80 ^a	NA	NA	NA	NA	NA	NA
10	<0.01	0.26	0.74	55	0.44	0.25	1.22	0.60
10a	0.013	0.33	0.48	66	0.26	0.51	1.88	0.51
	0.018 ^b	0.33 ^b	-	-	0.31 ^b	-	13.20 ^b	-
10 -MNPs	0.013	0.24	0.53	56	0.35	0.46	1.34	0.66
10a -MNPs	<0.01	0.24	0.69	67	0.31	0.30	4.22	0.44
10 -QDs	0.013	0.35	0.81	62	0.52	0.18	0.05	0.64
	(<0.001) ^c	(1.33) ^c						

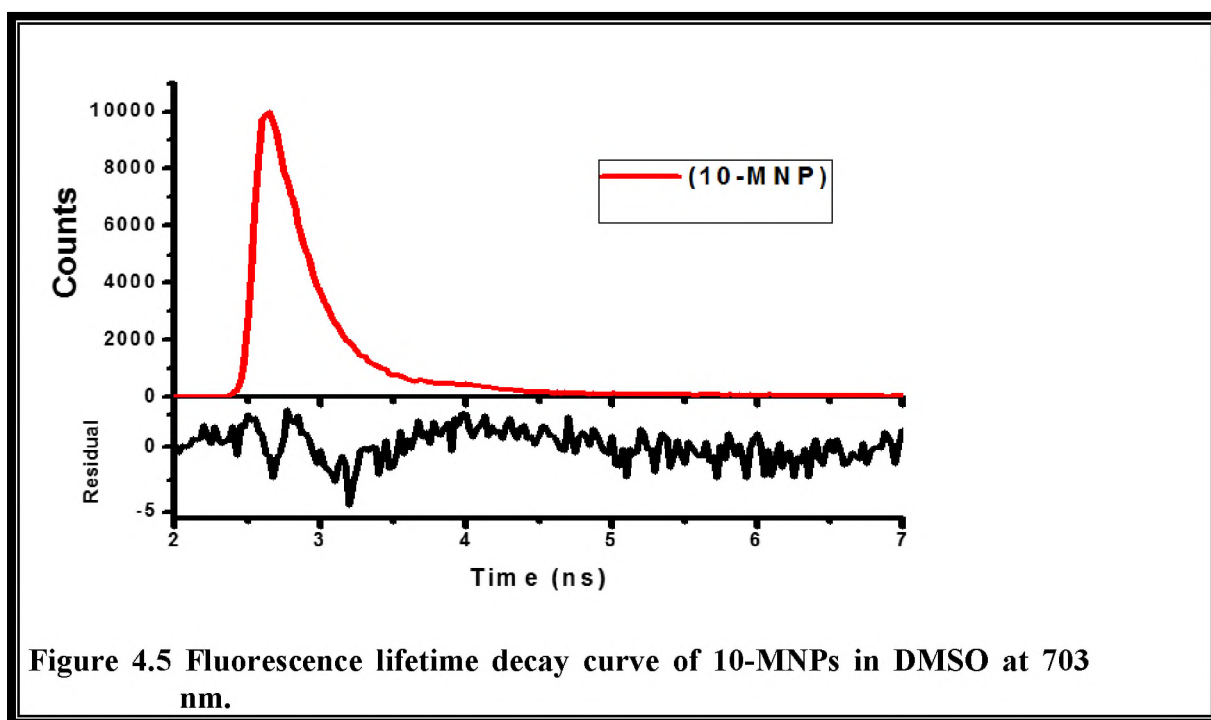
^aExcitation at 400 nm, values in water.

^b in the water/Triton-X 100

^cExcitation at 400 nm, value represented as $\Phi_{F(QD)}^{conjugate}$ Equation 1.2

NA = Not applicable

Hence the lack of decrease in the Φ_F value for **10**-MNPs compared to **10** may be as a result of the long spacer between the magnetic nanoparticle core and the Pc in **Scheme 3.6**, which could also be the case for **10a** and **10a**-MNPs. However, for **10a**-MNPs, the presence of iodide following quaternization, results in the quenching of fluorescence through the heavy atom effect of the iodine. The fluorescence lifetimes (τ_F) were determined using the TCSPC method; (**Figure 4.5**, for **10**-MNPs as an example) mono-exponential decay processes were observed for **10** alone, and two lifetimes were observed in the presence of MNPs. The presence of two lifetimes for **10** in the presence of MNPs could be a result of different orientations. Average fluorescence lifetimes ranged from 0.24-0.33, **Table 4.2** were obtained for **10**, **10a** and their conjugates. The fluorescence lifetimes become slightly shorter for both complexes in the presence of MNPs.



4.2.1.2 Pcs-QDs

Excitation at the wavelength where **10** absorbs, and QDs do not, the Φ_F value increases for **10** in the presence of QDs. When exciting at the wavelength where QDs absorb and **10** has minimal absorption, the Φ_F value for QDs decreases from 0.24 to <0.01 (Table 4.2). The

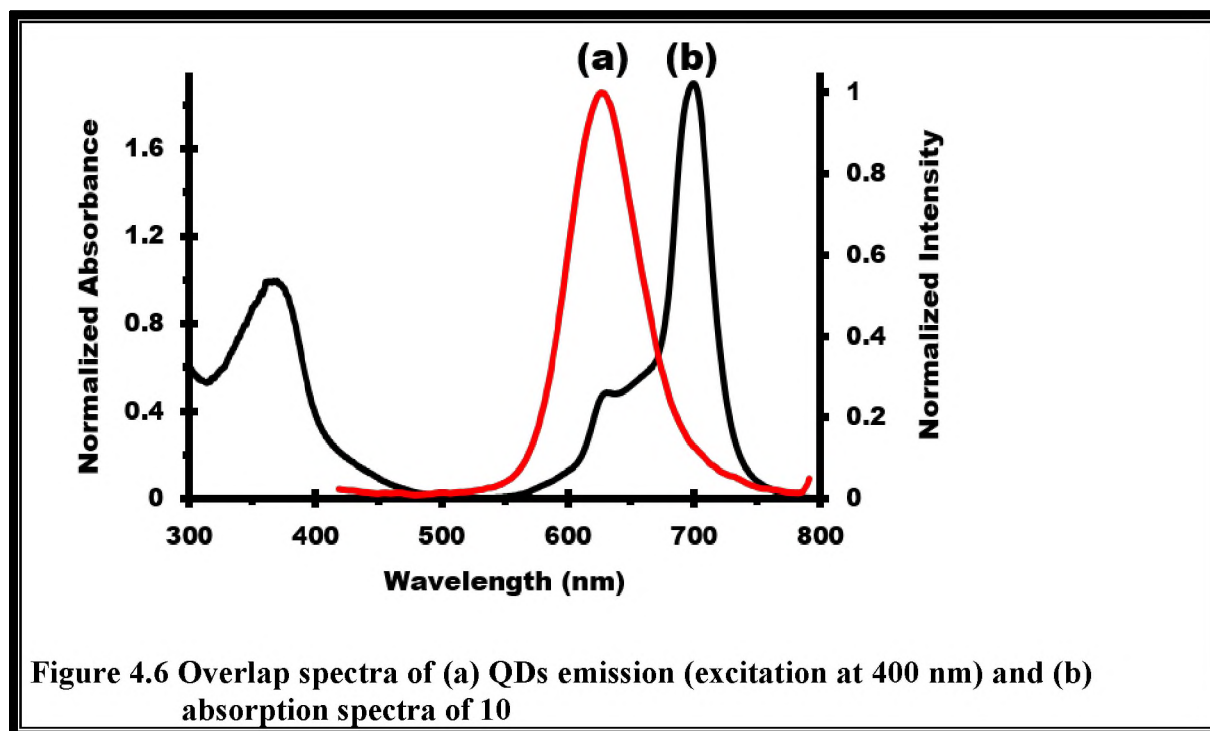
decrease is due to FRET and other processes which deactivate QDs emission [278,279]. Also, Pcs exert strains on QDs capping ligand and eventually create new trap states on the QDs surface, leading to decrease in the fluorescence emission [278]. Two fluorescence lifetimes were observed for **10**-QDs and average lifetimes are shown in Table 4.2. There is a small reduction in a lifetime for **10**-QDs compared to **10** alone. Three fluorescence lifetimes were obtained for QDs alone; this is typical of QDs [280]. The average lifetimes decrease in the presence of **10** due to FRET and other processes [278,279].

For FRET to occur, there has to be a good overlap between the emission spectra of the donor (QDs) and the absorbance spectrum of the acceptor as observed in **Figure 4.6**. A large decrease in QDs emission was observed in the presence of Pcs, but with a weakly stimulated emission (figures not shown). A weak stimulated emission compared to the large decrease in QDs emission could be due to other processes in addition to FRET, which deactivates the QDs emission. Many other factors influence photoluminescence decrease in QDs other than FRET [281,282]. The FRET efficiency was calculated to be 85%, Table 4.3 which is high due to the good spectral overlap between absorption spectrum of **10** and the emission spectrum of QDs in **Figure 4.6**. The Förster distance (R_o) and overlap integral (J) are 55.40 Å and $9.42 \times 10^{-13} \text{ cm}^6$, respectively. J value expresses the proximity of the donor to the acceptor. The J value is within the range reported for other Pc-QDs conjugates [145], Table 4.3.

Table 4.3 Förster resonance energy transfer (FRET) parameters

Complexes	Eff	$J (\times 10^{-13} \text{ cm}^6)$	$R_o (\times 10^{-10} \text{ m})$	$r (\times 10^{-10} \text{ m})$
10-QD	0.85	9.42	55.40	41.49
11-QD	0.80	0.15	60.11	47.71
12-QD	0.96	0.21	63.08	37.14

Förster resonance energy transfer (FRET)



4.2.2 Triplet Quantum Yield (Φ_T) and Lifetimes (τ_T).

The transient absorption spectrum of the complex **10** is similar to **Figure 4.2** in DMSO. The complexes (alone or in the presence of NPs) shows a broad absorption band from 400 nm to 600 nm with absorption maxima around 550 nm which correspond to triplet-triplet absorption spectra. The Φ_T values for **10** and **10a** are 0.74 and 0.48 respectively, Table 4.2 and the conjugated complexes (**10**-MNPs, **10a**-MNPs, and **10**-QDs) gave 0.53, 0.69 and 0.81, respectively. There is a reduction in the triplet quantum yield upon quaternization of **10** to form **10a**. This contradicts the observation for **8**, **8a** and **9**, **9a** whose Φ_T increased upon quaternization. The decrease in Φ_T values on quaternization has been reported before [283]. Linking of MNPs also results in the decrease in Φ_T values when comparing **10** with **10**-MNPs. This corresponds to the observed increase in Φ_F since the two are competing processes. For **10a**-MNPs, there is an increase in Φ_T values compared to complex **10a** alone, corresponding to the decrease in Φ_F value. These observations are a result of the heavy atom effect of iodine for **10a**. A large increase in Φ_T value was observed for **10** in the presence of QDs, showing the heavy atom effect of QDs (Table 4.2). The triplet lifetimes (τ_T) values ranged

from 55 μ s to 67 μ s, and the values for **10**-MNPs and **10a**-MNPs remains the same as for **10** and **10a**, respectively. The triplet life lengthened slightly for **10**-QDs. The triplet state lifetime values are low for **10** and its conjugates due to the heavy atom effect of Indium(III) ion.

4.2.3 Singlet oxygen quantum yield (Φ_{Δ})

The DPBF and ADMA degradation was monitored at ~417 nm and ~378 nm respectively. There was no change in the Q-band intensity during Φ_{Δ} determinations, confirming that **10** and **10a** are not degraded during singlet oxygen studies for DPBF spectral changes are similar to those shown in Figure 4.3. Φ_{Δ} values are higher for **10** compared to **10a**, corresponding to Φ_T values which are larger for the former. Φ_{Δ} values are higher for **10** compared to **10**-MNPs, but lower to **10a** compared to **10a**-MNPs, Table 4.2. These changes correspond to the changes in Φ_T values. The Φ_{Δ} values are related to Φ_T values since singlet oxygen is generated from the triplet state. Carvalho et al [237] observed insignificant changes in the singlet oxygen generating abilities of conjugates of porphyrins with MNPs when compared to porphyrins alone. The singlet oxygen quantum yield of **10**-QDs is higher than the value for both unconjugated phthalocyanines and MNPs conjugated phthalocyanines, corresponding to the trend with triplet quantum yields, where **10**-QDs had the largest value (Table 4.2). These S_{Δ} values were greater than 0.5 except for **10a**-MNPs, Table 4.2. The value of quantum yields of internal conversion (Φ_{IC}), increased for **10**-MNPs compared to **10** alone and decreased for **10a**-MNPs compared to **10a**, Table 4.2. The lowest value of Φ_{IC} was obtained for **10** which also had the largest Φ_T value.

4.2.4 Photodegradation Studies (Φ_{Pd})

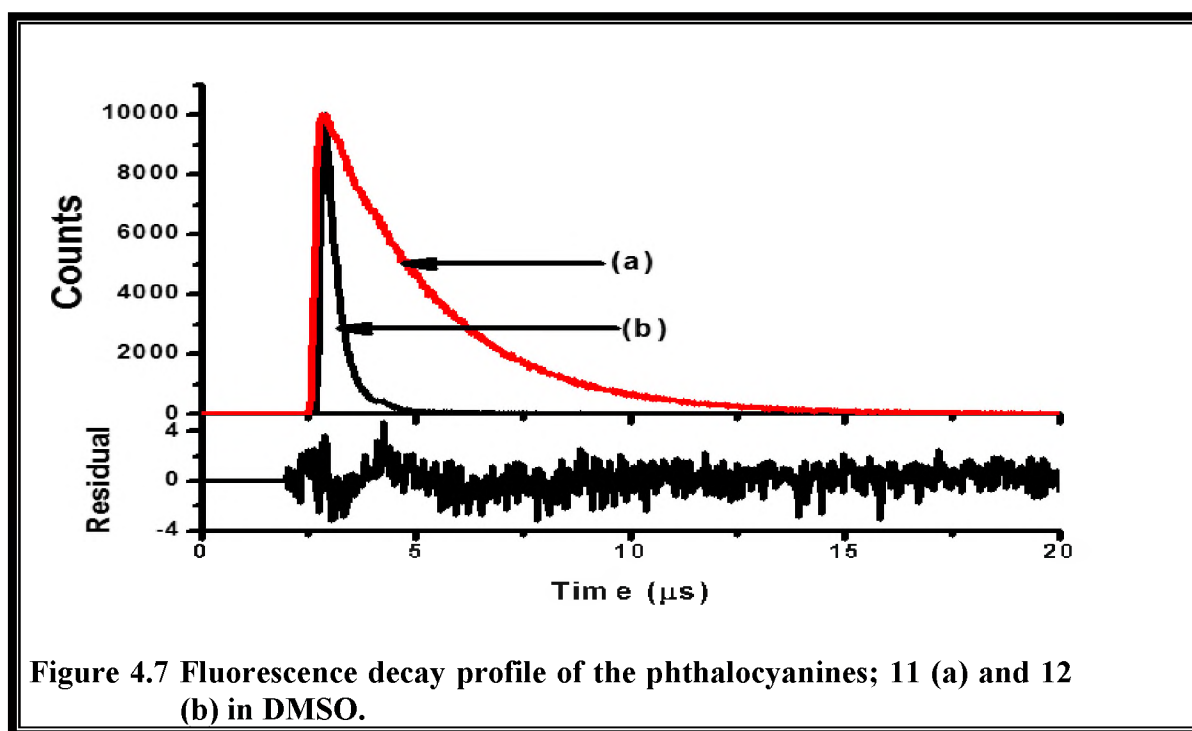
Both complexes **10** and **10a** (and their conjugates) are relatively stable in DMSO, Table 4.2. The stability is lower for complex **10a** in water plus Triton-X 100. **10**-QDs is the most stable of all the complexes indicating that the conjugation with QDs enhances its stability during

irradiation. **10**-MNPs and **10** are however still relatively stable. For unstable complexes, the photodegradation quantum yields are of the order of 10^{-3} [99].

4.3 Photophysical and Photochemical Parameters of Symmetrical MPc (**11** and **12**) alone or in the Presence of Nanomaterials

4.3.1 Fluorescence Quantum Yield (Φ_F) and Lifetimes (τ_F).

The fluorescence quantum yields of complexes **11**, **12** and their conjugates, and for QDs alone are listed in Table 4.4 (Table 4.1). Complex **11** gave a larger Φ_F value compared to **12** and all the other complexes in Table 4.1, due to the presence of Zn in **11** which is smaller than In. The heavy atom effect of indium metal encourages intersystem crossing to the triplet state reducing fluorescence.



Following conjugation to all the NPs, there is a further decrease in Φ_F values of the Pc. When exciting where QDs absorb there is a decrease in the Φ_F value of QDs alone at 0.24 to values less than 0.01 Table 4.4, most likely due to FRET. Typical fluorescence decay curves are shown in **Figure 4.7** for complexes **11** and **12**. Complex **12** and its conjugates give

biexponential fit (hence two lifetimes) while complex **11** and its conjugates gave single exponential fit.

Table 4.4 Photophysical properties of complexes/conjugates in DMSO unless otherwise stated. Excitation for emission at 640 nm, unless otherwise stated

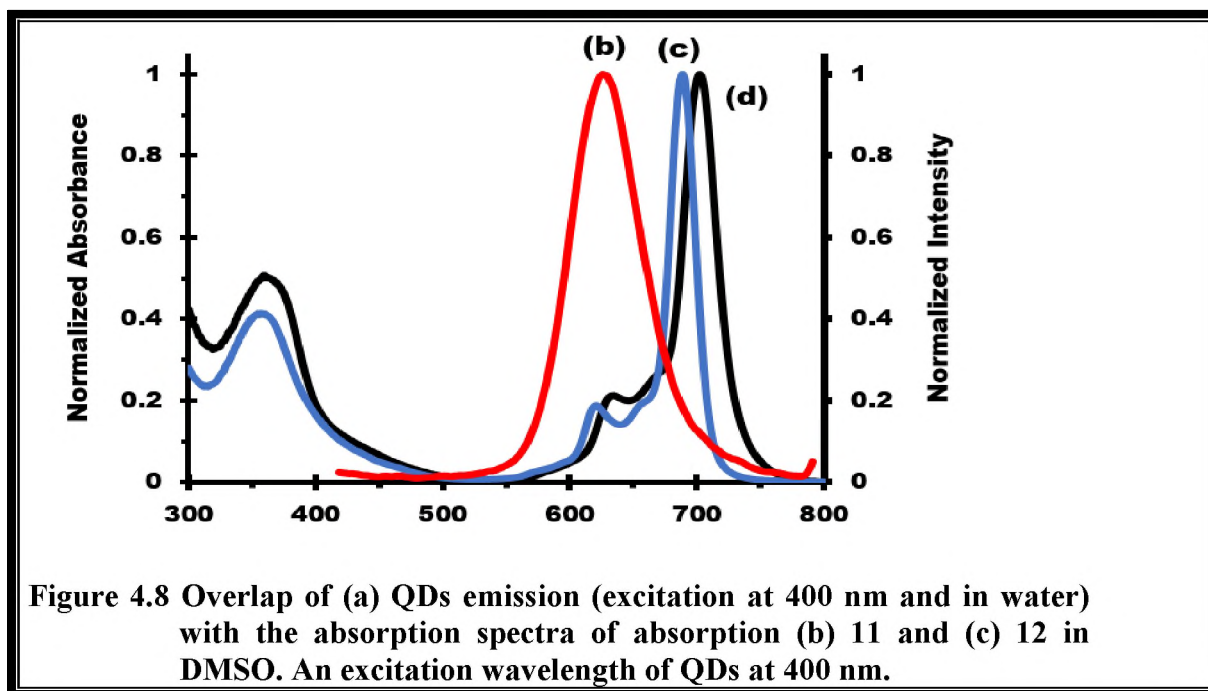
Pc/nanomaterial	Size (nm) (from TEM)	Pc Loading ($\mu\text{g}/\text{mg}$)	$^b\lambda_{\text{abs}}$ (nm)	Φ_{F}	τ_{F} (ns)	Φ_{T}	τ_{T} (μS)	Φ_{Δ}	Φ_{pd} 10^{-6}
QDs	8.53	-	582 ^c	0.24 ^c	12.80 ^c	-	-	-	-
11	-	-	689	0.11	2.53	0.83	351	0.30	2.59
12	-	-	704	0.01	0.30	0.88	57	0.33	4.56
11-AuNPs	7.48 (5.35) ^a	60	689	0.03	2.52	0.84	244	0.47	0.08
12-AuNPs	7.64 (5.35) ^a	27	700	<0.01	0.34	0.92	107	0.52	0.34
11-MNPs	18.39 (17.80) ^a	105	689	0.062	2.52	0.63	323	0.41	3.96
12-MNPs	18.46 (17.80) ^a	72	703	<0.01	0.28	0.85	56	0.46	6.52
11-QDs	10.22	72	688	0.068 (<0.01) ^d	2.56 (0.83) ^d	0.90	330	0.32	0.42
12-QDs	10.45	70	700	<0.01 (<0.01) ^d	0.54 (2.32) ^d	0.92	69	0.34	3.35

^a values in brackets are for NPs alone; ^b λ_{abs} = absorption wavelength, ^c values for QDs alone in water excitation 400 nm where QDs absorb, ^dExcitation at 400 nm, value represented as $\Phi_{\text{F(QD)}}^{\text{Conjugate}}$ Equation 1.2 Values in water

Average lifetimes are shown in Table 4.4 for **12** and its conjugates. The presence of two lifetimes for Pcs alone may be attributed to quenched (shorter) and unquenched (longer) lifetimes, due to the formation of aggregates which are non-fluorescent, but which can quench the monomer [270] as explained above. There were no significant changes in fluorescence lifetimes of the Pcs following conjugation, but there is a shortening of the QDs lifetimes after conjugation due to FRET.

4.3.2 FRET

Figure 4.8 shows that the spectral overlap area is not too different for complexes **11** and **12** even though the former has a blue shifted Q-band. No emission peak was observed for complexes **11** and **12** when they were excited at 400 nm (the wavelength used for exciting QDs for FRET).

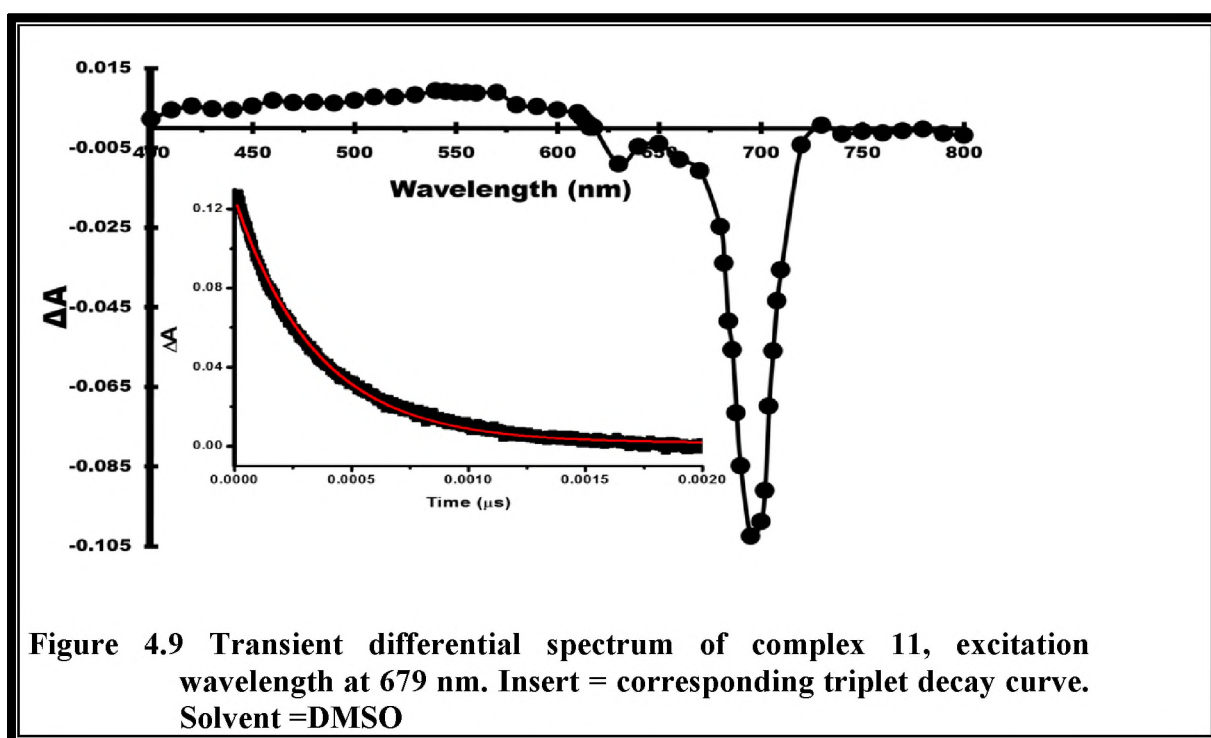


The spectral overlap area is about the same, hence, the J values are not too different in Table 4.3. J values are larger than for 10-QDs, due to better spectral overlap in **Figure 4.6** compared to **Figure 4.8**. The Förster distances (R) for 11-QD and 12-QD are 60.11 nm and 63.08 nm respectively, which are larger than r (the donor-acceptor distance) hence resulting in the efficiencies of energy transfer which are large at 0.80 and 0.96 for 11-QD and 12-QD, respectively, Table 4.3.

4.3.3 Triplet quantum yield (Φ_T) and lifetimes (τ_T).

The transient differential spectrum for complex **11** in DMSO shown in Figure 4.9 (as an example) and it shows a maximum at 550 nm. The insert shows the triplet decay curve. The

triplet decay curves obeyed second order kinetic which is typical of MPc complexes at high concentration ($>1 \times 10^{-4}$ M) due to the triplet-triplet recombination as stated above. Complex **12** has a larger Φ_T value (0.88) than complex **11** (0.83) due to the presence of the heavy In central metal in the former. For conjugates with QDs, there is a large increase in Φ_T values of complexes **11** and **12** to 0.90 and 0.92, respectively, due to the additional heavy atom effect of the QDs Table 4.4.



An increase in Φ_T value is also observed for **12** in the presence of AuNPs for **12**-AuNPs, though there is no significant increase for complex **11**. For the MNPs conjugate, there is surprisingly a decrease in Φ_T value regardless of the heavy atom effect of MNPs for the reason given above for **10**, Table 4.4. Triplet state lifetimes are longer for complex **11** and its conjugates compared to complex **12** and its conjugates which correspond to the higher Φ_T values for the latter [273]. The triplet lifetimes increase or remain the same for **12** following conjugation. The triplet lifetimes for **11** became shorter following conjugation. The changes

in a lifetime could be a result of the different orientation of closely packed Pc molecules on the NP surface.

4.3.4 Singlet Oxygen Quantum Yield (Φ_{Δ}) and Photodegradation

Quantum Yield (Φ_{Pd})

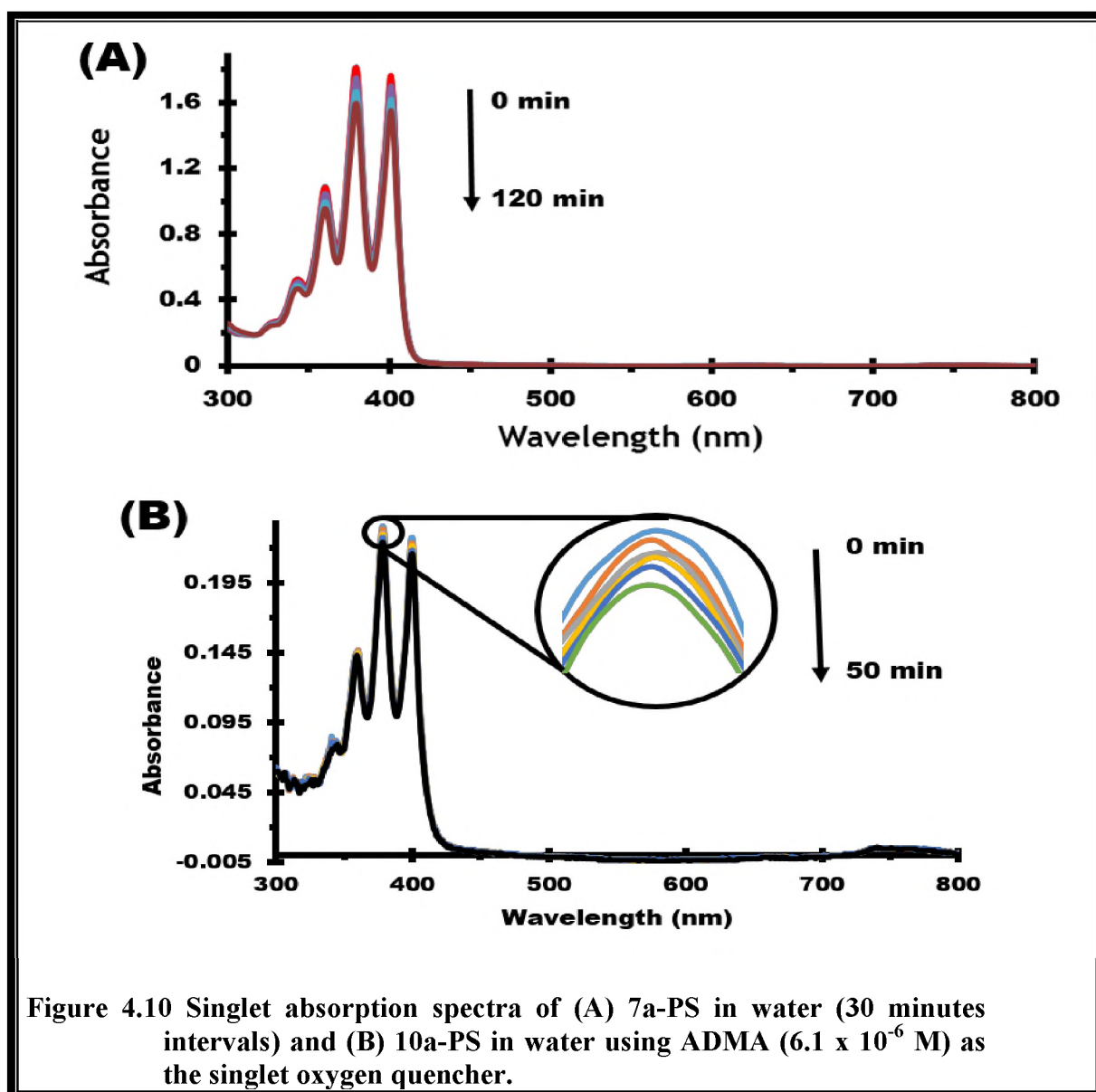
There is an increase in Φ_{Δ} values of the Pcs in the presence of AuNPs and MNPs, Table 4.4. The increase in the presence for QDs is marginal or insignificant. Photodegradation studies are the measure of the stability of molecules under irradiation [284]; the higher the Φ_{Pd} value, the lower the photostability. Complex **11** and its conjugates are more stable than complex **12** and its corresponding conjugates. In general, MNPs conjugates are less stable than the rest of the corresponding conjugates, Table 4.4.

4.4 Singlet Oxygen Quantum Yields of Phthalocyanines When Embedded in Electrospun Fiber

As stated already, singlet oxygen is involved in photocatalytic reactions. Hence, it is important to determine the singlet oxygen generating ability of the modified fiber in the aqueous medium which is to be used for PACT and photocatalysis.

The Φ_{Δ} values for the fibers (**7-PS**, **7a-PS**, **8a-PS**, **9a-PS** and **10a-PS**) were determined in unbuffered aqueous media using ADMA as a quencher and its degradation was monitored at 380 nm. **Figure 4.10A** shows the spectral changes of ADMA during the photolysis of **7a-PS** as an example. There is evidence of photoconversion of the ADMA due to singlet oxygen production by the phthalocyanines within the fiber matrix, through an extended period (120 min at 60 W) of irradiation was required compared to seconds in **Figure 4.3A** (in solution for DPBF). It is of note that during the photochemical studies, the embedded photosensitizers did not leach out into solution since there is no absorption around the Q-band corresponding to the phthalocyanines. The observed spectral changes as shown in **Figure 4.10** (A and B) do not show absorption corresponding to cationic water phthalocyanines (complexes **7a**, **8a**, and

10a are water soluble). The absence of peaks where Pcs absorb indicates that there was no leaching of the photosensitizer from the fiber during photolysis. Hence, the toxicity of Pb or In is not expected to play a role and this affirming the suitability of the complexes for the intended applications. The Φ_{Δ} values Table 4.1 in water for modified fibers, are lower than for DMF solutions since water quenches singlet oxygen as discussed above and also the values are estimates as explained in the experimental section.



4.5 Conclusion

The photophysical and photochemical properties of the metallophthalocyanines alone and when conjugated to nanomaterial were studied. The effects of different nanoparticles on the photophysical properties of metallophthalocyanines are evaluated. The asymmetrical phthalocyanine **9**, **9a**, **10** and **10a** were compared with the symmetrical MPcs **7**, **7a**, **8**, **8a**, **11** and **12**; the general pattern expected of the effect of a heavy atom (Pb and In) influence the values obtained for Φ_F , τ_F , Φ_T and Φ_Δ . There are improvements in the physicochemical properties of the complexes upon conjugations with the nanomaterial (except for MNPs), and their photodegradation studies indicate that all the complexes and their conjugates are thermally stable and do not undergo phototransformation.

CHAPTER 5

5 Application studies with synthesized phthalocyanines

The applications of the synthesized metallophthalocyanines were studied in this chapter. The quarternized MPcs (**7a**, **8a**, **9a** and **10a**) as well as unquarternized MPc (**7**) and magnetic nanoparticles conjugates of **10** and **10a** were employed in photodynamic antimicrobial chemotherapy of *Escherichia coli* in water. The non-charged MPc (**7**) was used in other to confirm what has been reported elsewhere that only cationic photosensitizers can inactivate Gram (-) bacteria. The magnetic nanoparticles were incorporated because of its magnetic properties (electrostatic effect) and reusability of the photosensitizer. Furthermore, cationic MPc (**8a**, **9a** and **10a**) were immobilized onto polymer support via electrospinning techniques for photooxidation of bisphenol A (an endocrine disruptor) and 4-chlorophenol in water.

5.1 Photodynamic Antimicrobial Chemotherapy (PACT) in Solution

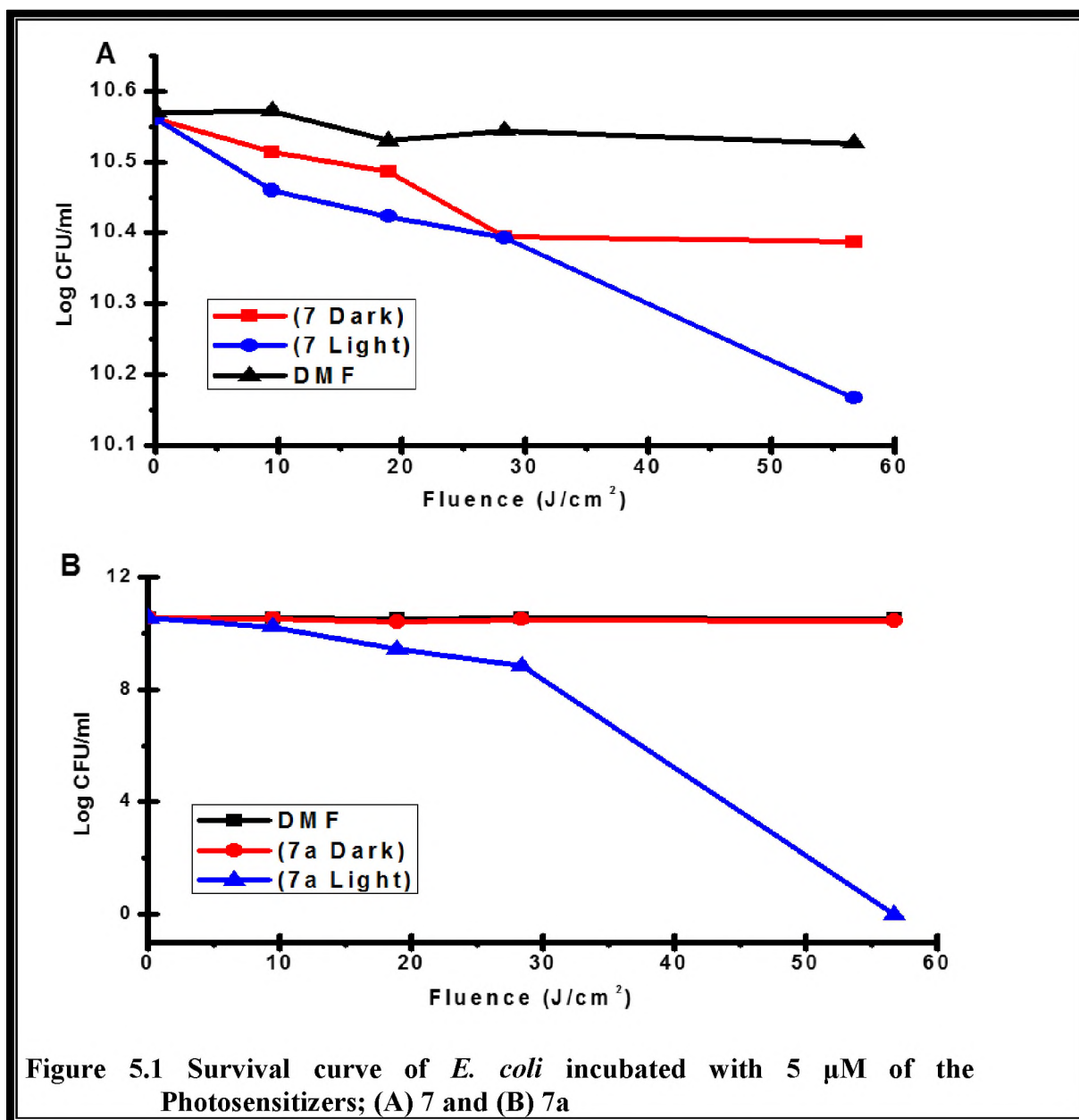
The photosensitizers were dissolved in either DMF (**7** and **7a**) or DMSO (**8a**, **9a**, **10a**, **10a**-MNP, **17** and **18**) as a 1 mM stock solution and further diluted with PBS to a final concentration (DMF/DMSO $\leq$ 0.5%). Even though **7a**, **8a** and **10a** are water soluble, DMF/DMSO were employed for comparison with **7** and **9a** which are not water soluble. A control sample solution with an equal volume of DMF or DMSO as that used in the final concentration without photosensitizer (**Figure 5.1**) indicates that the effect of DMF or DMSO on the culture is negligible. All experiments were done in triplicate, statistical significance (p value) was determined using ANOVA (analysis of variance) and a Student's t-test (analysis between two components) using error limits from at least three determinations. The analysis of variance for photoinactivation effect of the photosensitizers was determined at the highest fluence at which comparisons could be made [285], and p-value < 0.05 was considered significant.

5.1.1 Pyridyloxy MPcs

5.1.1.1 PbPc (**7** and **7a**)

Photodynamic inactivation of *Escherichia coli* (10^6 CFU mL⁻¹ bacteria suspension) was investigated with 5 mM concentrations of **7** and **7a** in PBS-DMF. The photo-inhibition potential of the photosensitizers were evaluated by plotting logarithmic reduction in log CFU/mL of viable bacteria of the tested and control samples versus the time of exposure to irradiation (**Figure 5.1**). On exposure to light, a remarkable log decrease (>10), Table 5.1 was observed for viable cells for **7a** with no colony on the agar plates after irradiation for 30 min. A 0.4 log decrease was observed for **7** under the same conditions, Table 5.1. The cationic **7a** is more active than the non-ionic **7** due to its hydrophilic/lipophilic nature which enhances the dye binding to the cells hence the cytotoxic efficiency as stated above. Minimum dark toxicity is observed for both **7** and **7a** (both <0.2 log). Similar observations have been

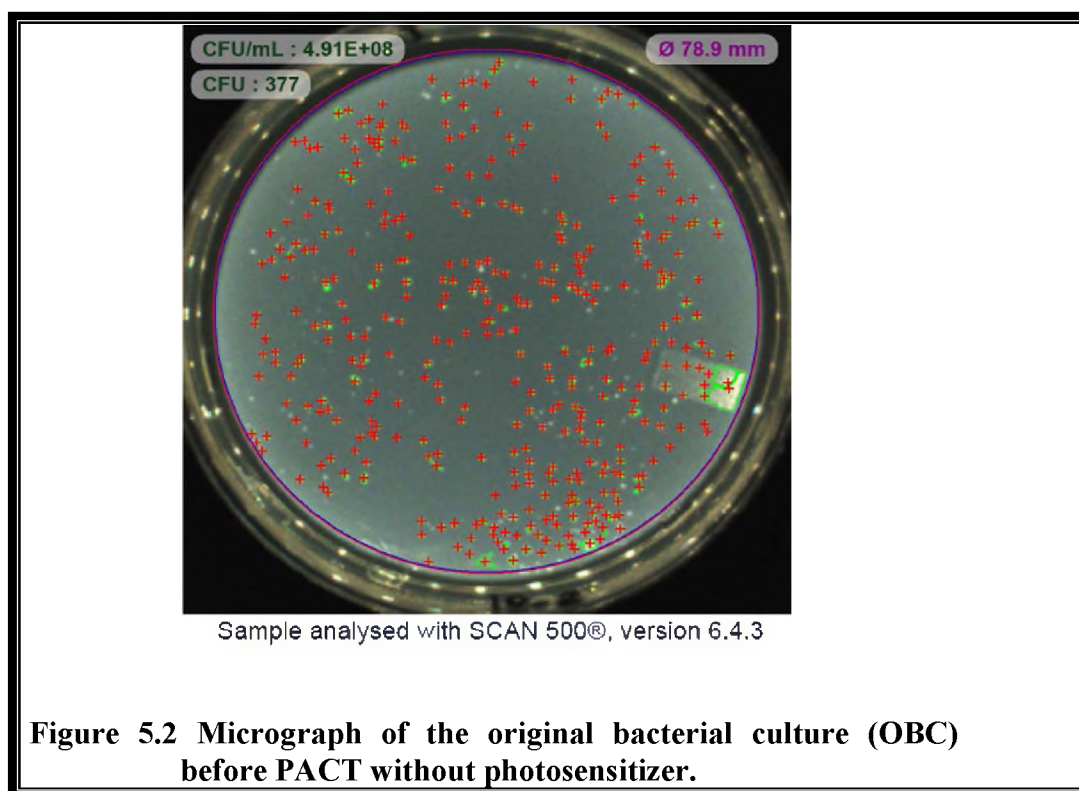
reported by various researchers as well. Kussovski et al. reported some decreases of viable cells for photosensitizers in the dark [242]. Ryskova et al. also reported on some antibacterial effects without irradiation using pyridyloxy substituted zinc or aluminum phthalocyanines [286].



5.1.1.2 InPc (8a, 9a, 17 and 18)

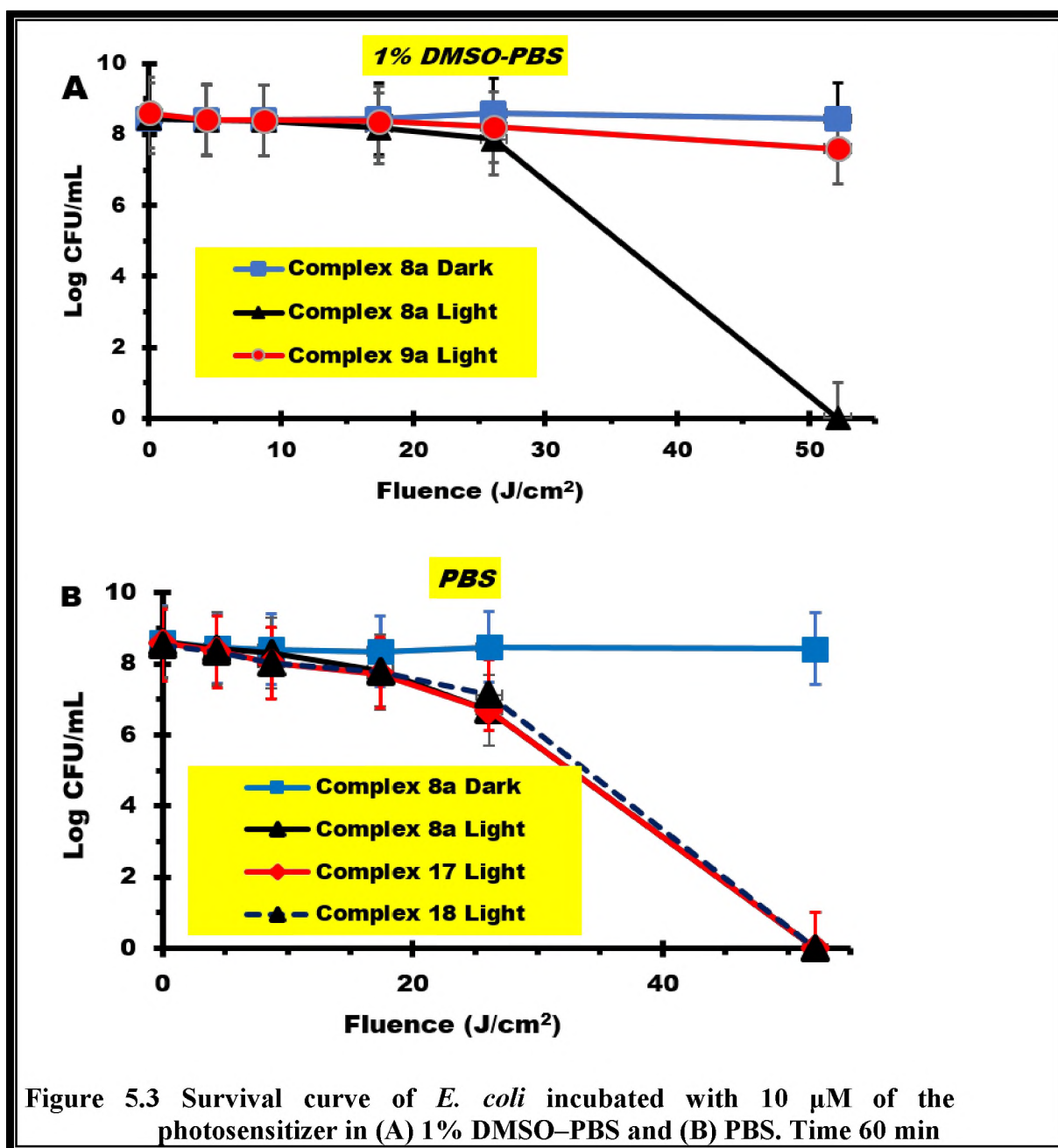
Figure 5.2 the photographs of the starting bacteria colonies used in this work and **Figure 5.3** shows the log plots. Following PACT, there were no colonies left hence the photograph is not

shown. The photodynamic killing properties of the phthalocyanines, **Figure 5.3**, indicate that the tetrasubstituted quaternized indium phthalocyanine (**8a**, **17**, **18**) were able to reduce the viable bacteria efficiently compared to the monosubstituted quaternized photosensitizers **9a**, this could be attributed to the number of charges that enhance binding ability to the Gram (-) bacteria [90]. A viable bacteria inactivation with log reduction ranging from 8.49 to 8.61 (Table 5.1) was observed for the tetrasubstituted cationic indium phthalocyanines (**8a**, **17**, **18**).



Only 1 log reduction of the bacteria after exposure to 28.99 mW of light for 1 h was achieved, Table 5.1, for **9a**. The effectiveness of the photosensitizers to kill the *E. coli* was compared to the control (without photosensitizers and irradiation). A significant reduction ($p < 0.05$) in the cell viability for all the tetrasubstituted phthalocyanines using 60 min exposure was observed except complex **18** ($p < 0.09$). The difference between log reduction for **8a** (containing 4-pyridyloxy) and **17** (containing 3-pyridyloxy) is insignificant. The differences in the log reduction between **17** and **18** were also not significant. Thus, the point of

substitution does not affect the PACT activity of phthalocyanines. The log reduction values observed in this work are much higher than reported for the same Pc ring containing Zn as a central metal, with a log reduction value of 4.5 [80]. The results presented in this work show the importance of using a heavier metal like In instead of Zn for PACT studies. However, **7a** containing Pb and quaternized showed the best PACT activity. The better behavior for Pb could be due to shuttle shock (low symmetry). **7a** does not have the largest Φ_{Δ} but has the best PACT activity, Table 5.1. showing that the effect of Φ_{Δ} are not important as symmetry.



The absorption spectra of the mixed cell suspension before incubation, immediately after the incubation time of 30 min, finally at the end of the PACT activity are shown in **Figure 5.4** for **8a** as an example. The spectra show that the photosensitizer is aggregated in this cell medium before PACT and the spectra also show that aggregation continues during PACT without undergoing phototransformation. The decrease in absorbance might suggest some small degradation of the complex after PACT experiments. However, aggregation does not affect PACT as judged by the large log value for **8a**. Quaternization and symmetry for **7a**, play a major role for PACT.

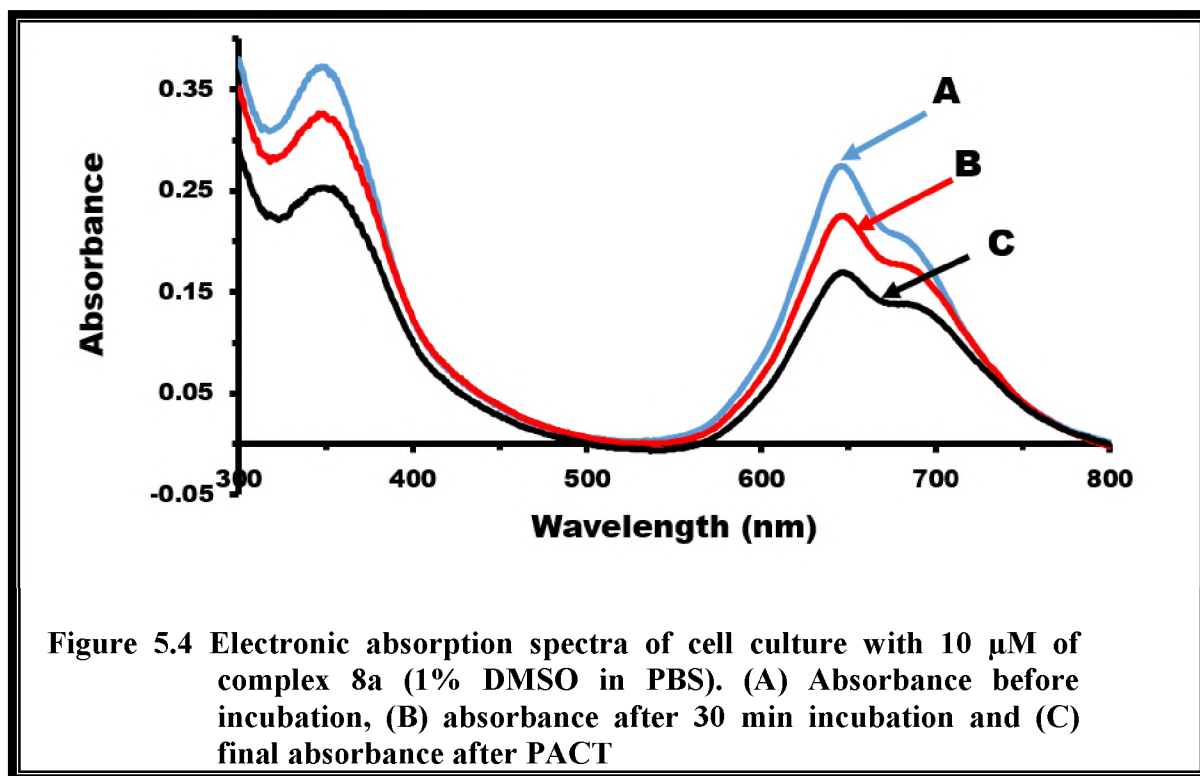


Table 5.1 Log reduction values (after 60 min irradiation) for *Escherichia coli* using different photosensitizers when cells are grown in PBS or DMSO (1%)/PBS.

Complex	solvent	Log reduction	Φ_{Δ} in DMSO
7	PBS	0.4	0.68 (0.21) ^a
7a	PBS	>10	0.60 (0.41) ^a
8a	PBS	8.61 ± 0.03	0.69 (0.39) ^a
	DMSO(1%)/PBS	8.49 ± 0.07	
9a	DMSO(1%)/PBS	1.04 ± 0.09	0.56 (0.31) ^a
10a	PBS	6.45 ± 2.01	0.26 (0.51) ^a
	DMSO(1%)/PBS	4.90 ± 1.79	
17	DMSO(1%)/PBS	8.59 ± 0.04	0.68 (0.56) ^a
18	PBS	8.52 ± 0.05	0.44 (0.57) ^a

^a Value in brackets are modified fiber in water

5.1.2 Asymmetric 10a, 10-MNPs, 10a-MNPs.

As stated above, cationic photosensitizers are more effective hence, **10** was not studied for PACT. **10a**, **10-MNPs**, and **10a-MNPs** were studied for PACT even though **10-MNPs** is not cationic. The later was studied for comparative purposes. The inactivation of the bacteria with complex **10a** in PBS was carried out at a constant concentration of 10 mM (14 mg L⁻¹) at varying irradiance time (**Figure 5.5A**). A log reduction value for *Escherichia coli* of 6.45 (Table 5.1) was obtained after 60 min. This is lower than for **7a**, **8a**, **17**, and **18** which have more positive charges. The PACT experiments using **10-MNPs** and **10a-MNPs** were not as effective at a lower concentration. **10a-MNPs** was able to achieve a reasonable log CFU per mL with 200 mg L⁻¹, Table 5.2; the same concentration was used for **10-MNPs**. Carvalho et al. [237] also observed similar trend as recorded in this work, i.e. larger amounts of the nanocomposites were required to achieve a similar anti-bacterial activity as for the porphyrin

alone. The major advantage of using the MNPs (as opposed to non-magnetic nanoparticles or Pc alone) together with the photosensitizer is the possibility of removal following use. **10a**-MNP_s gave an acceptable log reduction which was similar to that of **10a** alone in PBS/DMSO within error limits. The non-cationic conjugate (**10**-MNP_s) was not effective even at a higher concentration (log CFU = 0.8), Table 5.2. Singlet oxygen is cytotoxic to the targeted bacteria. Singlet oxygen quantum yield values for **10a**-MNP_s and **10**-MNP_s are not too different, Table 5.2, hence their differences in activity is related to the differences in charge. **Figure 5.5B** shows that the nanoconjugates did not show dark toxicity.

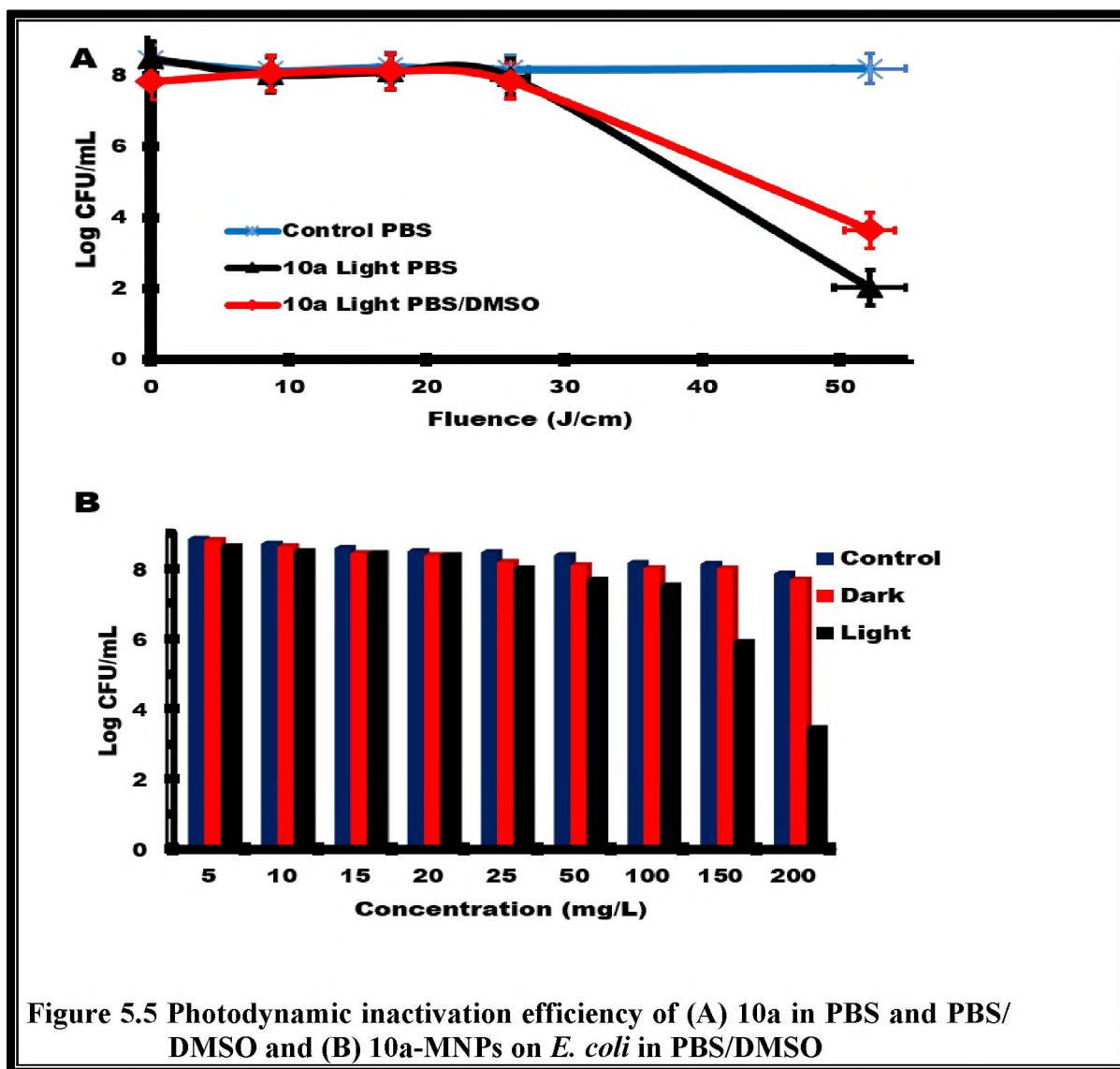


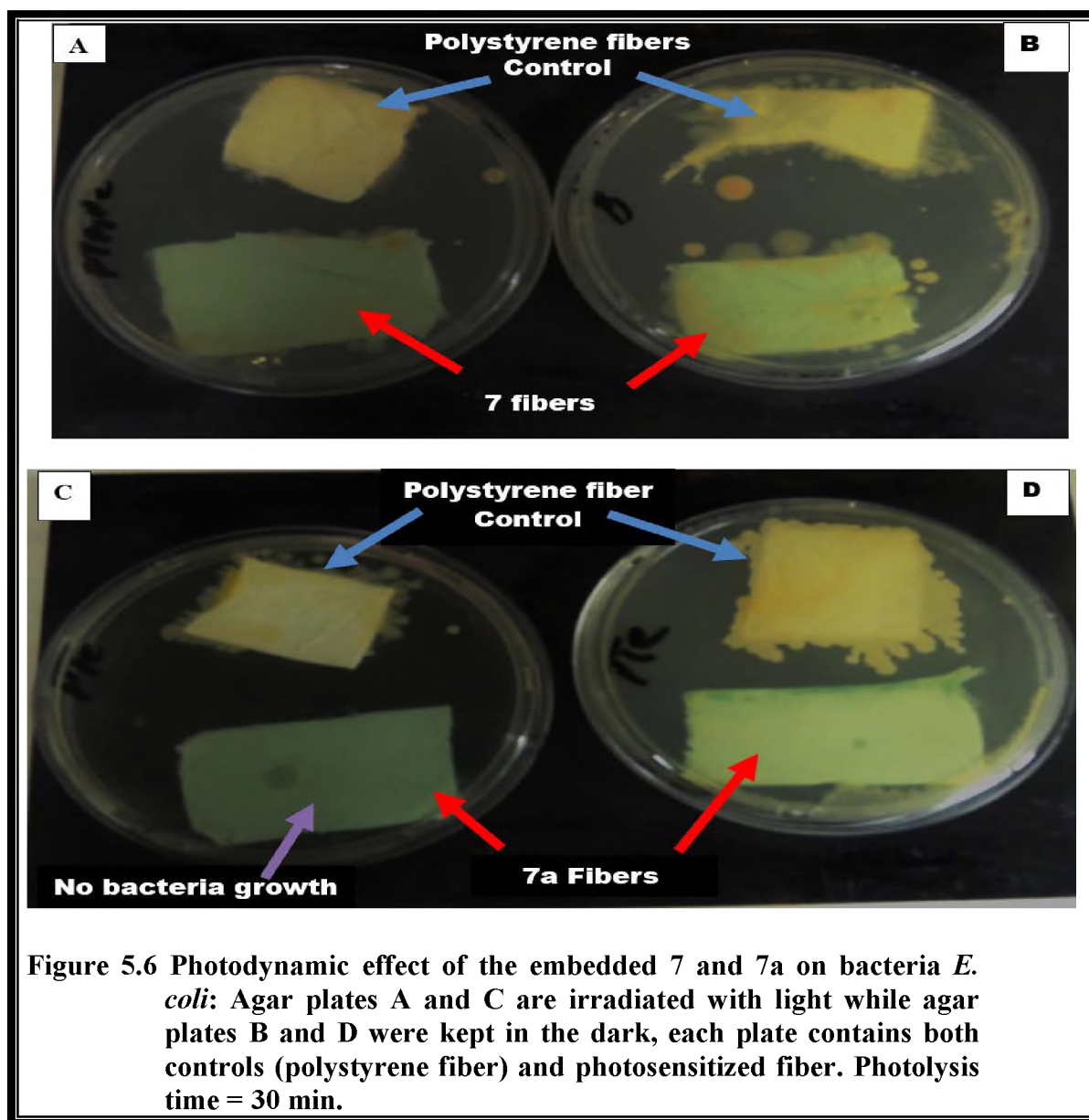
Table 5.2 Log reduction values for the photoinactivation effect on *E. coli* inactivation

Complexes	solvents	Concentration (mg/L)	Φ^a_{Δ}	Log Reduction
10a	PBS	14 (10 mM)	0.26	6.45 ± 2.01
	DMSO(1%)/PBS	14 (10 mM)		4.90 ± 1.79
10-MNPs	DMSO(1%)/PBS	200	0.35	0.80 ± 0.03
10a-MNPs	DMSO(1%)/PBS	200	0.31	4.39 ± 1.65

^a value in DMSO

5.2 PACT Studies Using 7 and 7a Electrospun Fiber

The toxicity of lead (a central metal for the phthalocyanine) has to be considered for practical applications. It has been reported before [101] that phthalocyanines do not leach from the fibers when employed for photocatalysis. Hence, the phthalocyanines were embedded in electrospun fibers. **7a** is water soluble, and if it leached during biological studies, its spectrum would have been observed, but this was not the case as stated above hence the toxicity of Pb is not expected to play a role when the phthalocyanines are embedded in electrospun fibers.



The illuminated agar plate that contain **7a-PS** (**Figure 5.6C**) is blue and show no bacteria on top. For **7-PS** fiber, there is some limited bacterial growth following irradiation, **Figure 5.6A**. **7a-PS** shows no bacterial growth on illumination due its larger singlet oxygen quantum yield of 0.41 compared to 0.21 for **7-PS**, Table 5.1. The **7-PS** and **7a-PS** kept in the dark (**Figure 5.6B** and **D**), show extensive bacterial growth. This is judged by *E.coli* colony growing over and around the fiber. This is also observed for the control (PS fiber alone) without **7** or **7a** in the dark or irradiated.

5.3 Photocatalytic Degradation of Pollutants

5.3.1 UV-Vis Spectral Changes

The modified fibers (10 mg) were cut into smaller pieces (increasing the surface area) and suspended in 10 ml of the pollutants in a glass vial containing a magnetic stirrer; the suspension was stirred in the dark for 1 h. This was done to allow for adsorption of the adsorbate (BPA and 4-chlorophenol) onto the adsorbent (modified fibers) since it has been established elsewhere that the degradation of organic compounds depends on the adsorption (sorption-desorption equilibrium) of the substrate on the adsorbent surface [287,288]. The photocatalytic studies were carried out on the equilibrated samples by irradiating at 30 min intervals, and the corresponding absorption spectra recorded **Figure 5.7**. The fibers maintained their integrity following use. The changes in the spectra during photolysis for 4-chlorophenol in the presence of **8a-PS** fiber, are similar to those reported before [105]. The catalytic products for photocatalytic oxidation of 4-chlorophenol have been identified as benzoquinone, hydroquinone and 4,4'-oxydiphenol using gas chromatography [105]. The benzoquinone photo-product originates from the reaction of singlet oxygen with 4-chlorophenol (Type II mechanism) while hydroquinone originates from electron transfer reactions (Type I mechanism) **Scheme 5.1**.

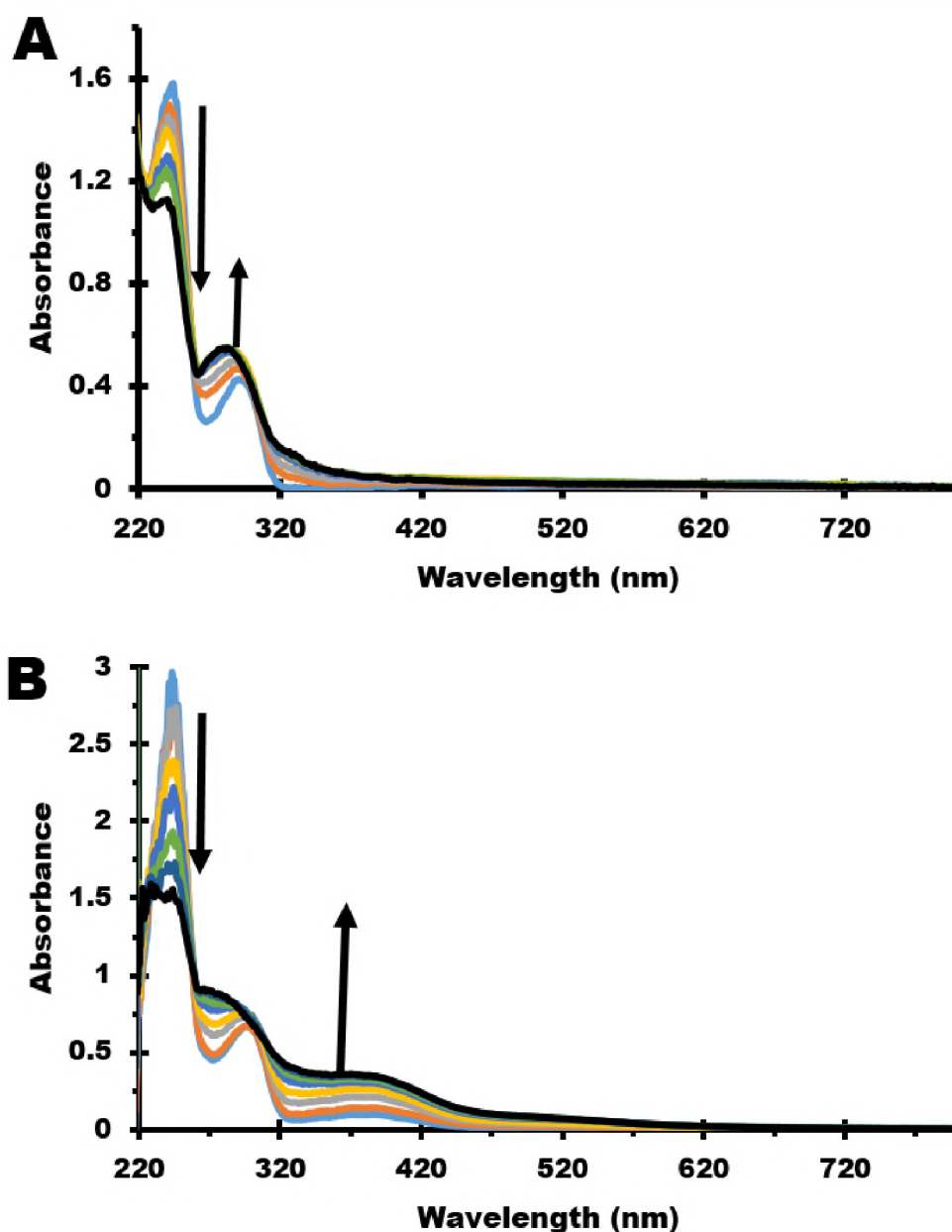
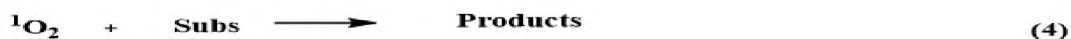
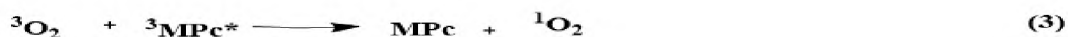
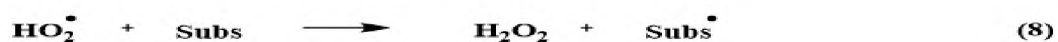
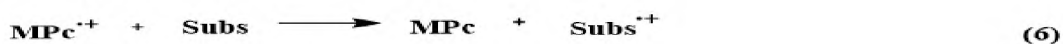


Figure 5.7 Electronic absorption spectral changes of (A) 4-chlorophenol (5 μ M) and (B) bisphenol A (0.02 mM) during the photo-oxidation at 30 min intervals. Irradiation intervals using 8a-PS fiber.

Thus, both singlet oxygen and radicals are involved, Scheme 5.1. For photocatalytic oxidation of BPA, hydroxyacetophenone and hydroquinone have been identified as products [289]. It is possible that both Type I and Type II mechanisms are involved as is the case for 4-chlorophenol.

Type II Mechanism**Type I Mechanism****Scheme 5.1 Type I and II mechanisms**

MPc- metallophthalocyanine, ${}^1\text{MPc}^*$ - MPc excited state, ${}^3\text{MPc}^*$ - MPc triplet excited state

ISC- intersystem crossing, ${}^3\text{O}_2$ - molecular oxygen, ${}^1\text{O}_2$ - singlet oxygen, Subs- substituents

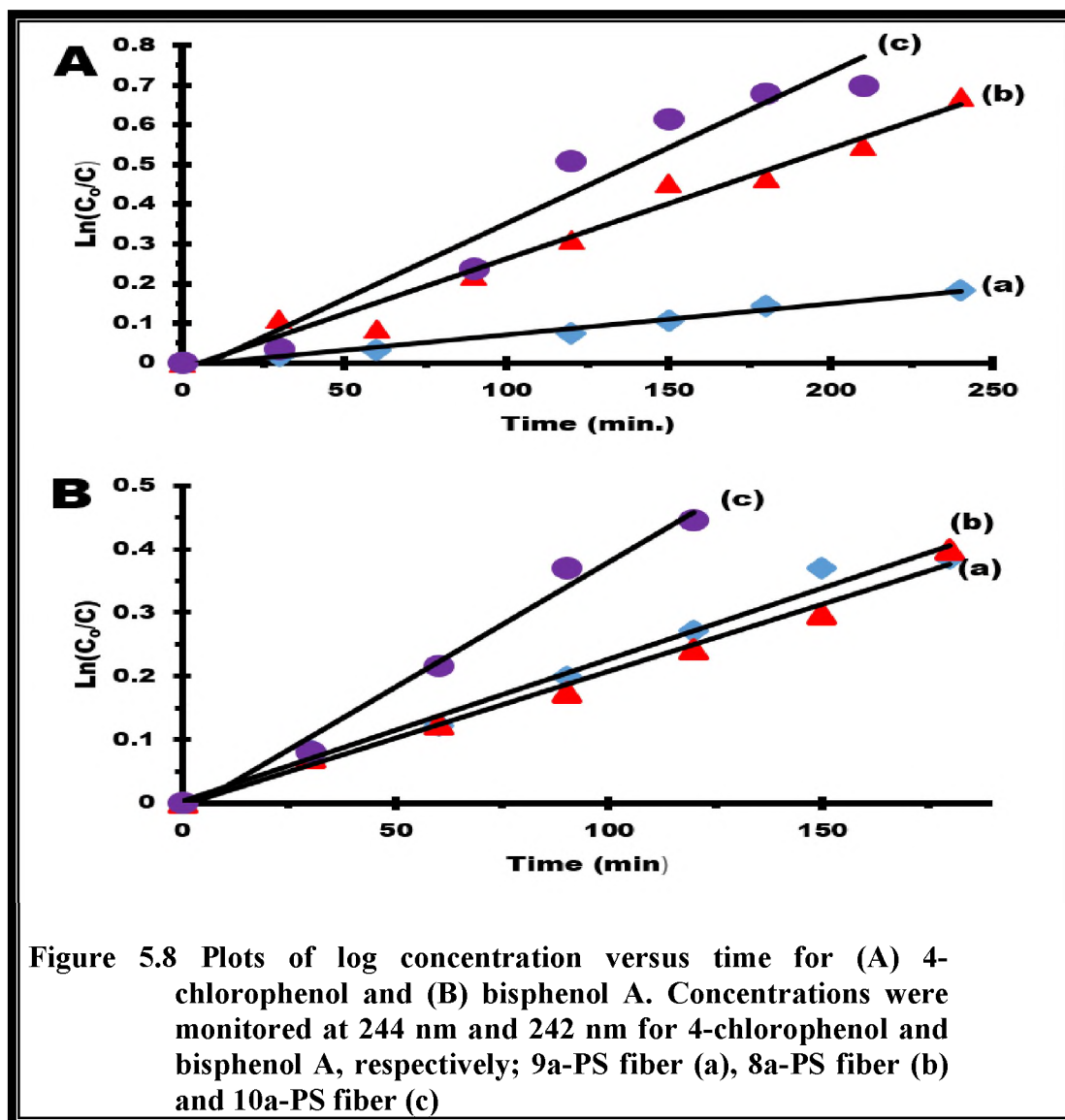
5.3.2 Kinetic Studies

Plots of $\ln(C_0/C)$ vs. time (t) (C_0 is initial concentration and C is the concentration at time t) are shown in **Figure 5.8**, and the corresponding data are given in Table 5.3. For both BPA and 4-chlorophenol **10a**-PS fiber gave the largest observed rate constant (k_{obs}) and **9a**-PS has the smallest. This corresponds perfectly with the singlet oxygen values for the complexes when embedded in fiber Table 5.3. Except for **9a**-PS fiber, k_{obs} values are higher for 4-chlorophenol compared to BPA, showing that the former is more easily degraded than the

later. The half-life for the degradation of **10a**-PS fiber are the lowest in Table 5.3. A half-life indicates the time it takes for half of BPA or 4-chlorophenol to be degraded. Half-lives should be shorter when the reaction rates (k_{obs}) were larger. This is observed in Table 5.3 for BPA and 4-chlorophenol.

Table 5.3 Kinetic data of the photodegradation of the pollutants

Fiber	Φ_{Δ}	Pollutant	K_{obs} (10^{-3} min^{-1})	Half-Life
9a-PS Fiber	0.31	4-chlorophenol	0.8	866
		BPA	1.8	385
8a-PS Fiber	0.39	4-chlorophenol	3.2	217
		BPA	2.0	267
10a-PS Fiber	0.50	4-chlorophenol	3.8	182
		BPA	2.8	178



5.4 Conclusion

The application of the metallophthalocyanines for bacterial inactivation and photo-oxidation of pollutants in water were studied in this chapter. The phthalocyanines where quaternized with alkyl halide based on the understanding that *Escherichia coli* is susceptible mainly to cationic photosensitizers. The photosensitizer's efficiency were quantified by log reductions of cell viability. All the cationic metallophthalocyanines in solutions were able to achieve over 3 log cell reduction at a low concentration, except complex **9a** which has only one quaternizable pyridyl substituents. PACT studies were also employed in modified fiber; complex **7a** pictorially confirmed that there is evidence of bacteria inactivation on the surface

of the electrospun modified fiber. **10a**-MNPs inactivation of gram-negative bacteria required 200 mg/L of the photosensitizer before a log reduction of above 3 logs could be obtained. Re-usability of the conjugates and non-toxicity of the MNPs is a great advantage. Phototransformation of pollutants using modified fibers was successfully carried out on bisphenol A and 4-chlorophenol. **10a**-PS show a superior activity in degrading the pollutants in water when compared to **8a**-PS and **9a**-PS.

Chapter 6

6 Conclusions and Future Perspective

The summary of the work done in this thesis are presented in this chapter and future prospect.

6.1 Conclusion

This work report for the first time synthesis of a series of In and Pb novel phthalocyanines and their photophysical properties. Lead and indium pyridyloxy substituted phthalocyanines and asymmetric pyridylsulfanyl-aminophenoxy (3:1) substituted phthalocyanines were quaternized. The pyridyl group enables easy quaternization of the MPcs, allowing solubility in an aqueous medium which is essential for PACT studies. Amino group substituents on the novel phthalocyanines reported in this work were fabricated for easy covalent linkages to the carboxylic acid functionalized nanomaterials. The morphology, sizes, and crystallinity of the

nanomaterials and their conjugates were determined using EDX, TEM and XRD. The nanoparticles studied are: semiconductors quantum dots (QDs), gold (AuNPs) and Fe₃O₄ magnetic (MNPs) nanoparticles. The QDs and MNPs were linked to the Pcs via an amide bond and by chemisorption onto AuNP surface. XPS characterization confirmed the covalent amide linkage of the phthalocyanine with MNPs and QDs. The effects of different nanoparticles on the photophysical properties of metallophthalocyanines are evaluated. All the photosensitizers show a monomeric behavior in DMF and DMSO and the quaternized forms of the photosensitizers exhibit aggregation in water. There is a general decrease in fluorescence quantum yields of the Pcs in the presence of all the nanoparticles. There is an increase triplet quantum yields for Pcs in the presence of AuNPs and QDs than the parent phthalocyanines, but not in the presence of MNPs. This work evaluates the photodynamic antimicrobial chemotherapy (using *E. coli*) of tetra pyridyloxy substituted (lead or indium) phthalocyanines and the monosubstituted indium phthalocyanines. There was no clear-cut difference in the potency of the tetrasubstituted phthalocyanines against *E. coli*, but there was a greater efficiency of the tetrasubstituted compared to the monosubstituted photosensitizer against *E. coli*. Hence, this work shows that the number of positive charges plays a more important role than symmetry for PACT. **10a**-MNPs gave log reduction which was similar (within experimental error) to that for **10a** alone in the same solvent medium, but the former at a higher concentration. The log reduction values for quaternized MPc and its MNPs conjugates are greater than the accepted 3 log reductions of cell viability, and the latter has the advantage of ease of separation (with a magnet) following use and the low dark toxicity. The results in this work show that the magnitude of singlet oxygen quantum yield is less important than charge in PACT.

Cationic phthalocyanines were embedded in electrospun polystyrene polymer and employed for photodegradation of 4-chlorophenol and bisphenol A. The embedded cationic MPcs

possess good singlet oxygen quantum yields which is essential for the photo-oxidation of 4-chlorophenol and bisphenol A. Asymmetrical **10a**-PS fiber indicates that it is a better photocatalyst than the other two modified fibers considered in this work **8a** and **9a**.

6.2 Future Prospects

All the quaternized MPcs in this thesis showed potentials for antimicrobial photodynamic inactivation of gram-positive bacteria at low concentration in solution, and when embedded in polymer hence they can be engineered for use in water purification. The study on photodegradation of environmental pollutants using the modified cationic photosensitizers should be extended to other pollutants such as effluents from textiles industries, and the degraded products should be qualitatively characterized using high precision instruments such as high-pressure liquid chromatography (HPLC) and gas chromatography techniques.

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