CHARACTERIZATION AND APPLICATION OF PHTHALOCYANINE-GOLD NANOPARTICLE CONJUGATES

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DEDICATION

To my late grandmother:

Nayisayi Benhilda Dzvurira-Tombe

My parents:

Kudakwashe Onias Ebrahim and Nyarai Faith Tombe

My siblings:

Nayisayi Laffin, Taaziva Lincy and Yumuna Lara Tombe

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In every victory, my source of strength and hope is Christ.

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ABSTRACT

This work presents the syntheses, photophysical and photochemical characterization of arylthio zinc phthalocyanines and their gold nanoparticle conjugates. Spectroscopic and microscopic studies confirmed the formation of the phthalocyanine-gold nanoparticle conjugates which exhibited enhanced photophysicochemical properties in comparison to the phthalocyanines. The studies showed that the presence of gold nanoparticles significantly lowered fluorescence quantum yields and lifetimes. However, this interaction did not restrict the formation of excited singlet and triplet states and hence the formation of singlet oxygen required for photocatalysis. The conjugates showed significantly higher singlet oxygen quantum yields and therefore enhanced photocatalytic activity compared to the phthalocyanines.

The zinc phthalocyanines and their gold nanoparticle conjugates were successfully incorporated into electrospun polymer fibers. Spectral characteristics of the functionalized electrospun fibers indicated that the phthalocyanines and phthalocyanine-gold nanoparticle conjugates were bound and their integrity was maintained within the polymeric fiber matrices. The photophysical and photochemical properties of the complexes were equally maintained within the electrospun fibers. The functionalized fibers were applied for the photoconversion of 4-chlorophenol and Orange G as model organic pollutants.

CONTENTS

Title Page	i
Dedication	ii
Acknowledgements	iii
Abstract	iv
Contents	v
List of Abbreviations	xii
List of Symbols	xvii
List of Figures	xx
List of Schemes	xxiv
List of Tables	XXV
CHAPTER 1	1
1. INTRODUCTION	1
1.1 Gold nanoparticles	1
1.1.1. History, properties and applications	1
1.1.2 Synthesis and characterization of gold nanoparticles	2

1.2 Phthalocyanine chemistry	5
1.2.1 Background on phthalocyanines	5
1.2.2 Synthesis	6
1.2.2.1 Peripherally and non-peripherally substituted phthalocyanines	7
1.2.2.2 Phthalocyanines synthesized in this work	9
1.2.3 Ground state electronic absorption spectra	15
1.2.3.1 Origins of spectra and general properties	15
1.2.3.2 Phthalocyanine aggregation	17
1.2.4. Photophysical properties	19
1.2.4.1. Jablonski diagram	19
1.2.4.2 Fluorescence quantum yield (Φ_F) and lifetime (τ_F)	20
1.2.4.3 Triplet quantum yield (Φ_T) and lifetime (τ_T)	21
1.2.5. Photochemical properties	23
1.2.5.1 Singlet oxygen	24
1.2.5.2 Photodegradation or photobleaching quantum yields	26
1.2.5.3 Photocatalytic behavior of phthalocyanines	27

1.3 Electrospinning	
1.3.1 Polymer supports used for phthalocyanine applications	31
1.3.2. Factors affecting the morphology of electrospun nanofibers	33
1.3.3. Characterization of electrospun nanofibers	33
1.3.3.1. Fiber diameter and morphology	34
1.3.3.2. Porosity	34
1.3.3.3. Mechanical properties of fiber	34
1.3.3.4. Nanofiber crystallinity	35
1.4 Background on environmental pollutants used in this work	38
1.4.1 Phenols	38
1.4.2 Azo dyes	39
1.5 Summary of aims of thesis	41
CHAPTER 2	42
2. EXPERIMENTAL	42
2.1 Materials	42
2.1.1 Solvents	42
2.1.2 Synthesis reagents	42

2.1.3 Polymers for electrospinning	43
2.1.4 Photocatalysis analytes and products	43
2.1.5 Previously synthesized phthalocyanines and their precursors	43
2.2 Instrumentation	44
2.3 Synthesis of 1(4), 8(11), 15(18), 22(25)-tetrakis (benzylmercapto)	
phthalocyaninato zinc (17)	50
2.4 Synthesis of phthalocyanine-gold nanoparticle conjugates	51
2.5 Preparation of functionalized fibers	52
2.5.1 Preparation of electrospun fibers of polycaprolactone (PCL)	52
2.5.2 Preparation of functionalized poly(methyl methacrylate) polymer fibers	53
2.5.3 Preparation of functionalized polystyrene polymer fibers	54
2.6 Photophysical and photochemical methods	54
2.6.1 Fluorescence quantum yields	54
2.6.2 Triplet quantum lifetimes and yields	55
2.6.3 Singlet oxygen quantum yields	55
2.6.4 Fluorescence micrographs	56
2.7 Photocatalysis and analysis of degradation products	56

2.7.1 Photocatalytic reactions	56
2.7.2 Identification of photocatalytic products	57
RESULTS AND DISCUSSION	58
PUBLICATIONS	59
CHAPTER 3	60
3. SYNTHESIS AND CHARACTERIZATION	60
3.1 Phthalocyanine derivatives	60
3.2 Phthalocyanine-gold nanoparticle conjugates	66
3.2.1 Synthesis and characterization of AuNPs	66
3.2.2 Assembly of phthalocyanine-gold nanoparticle conjugates	71
3.2.2.1 Synthesis and characterization of phthalocyanine-gold	
nanoparticle conjugates	72
3.3 Remarks on chapter	79
CHAPTER 4	80
4. PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES	80

4.1 Fluorescence spectra, quantum yields and lifetimes	80
4.1.1 Phthalocyanine derivatives	80
4.1.2 Phthalocyanine-gold nanoparticle conjugates	82
4.2 Triplet state quantum yields and lifetimes	85
4.2.1 Phthalocyanine derivatives	85
4.2.2 Phthalocyanine-gold nanoparticle conjugates	86
4.3 Singlet oxygen quantum yields	87
4.3.1 Phthalocyanine derivatives	87
4.3.2 Phthalocyanine-gold nanoparticle conjugates	88
4.4 Remarks on chapter	89
CHAPTER 5	90
5. ELECTROSPUN POLYMER FIBERS	90
5.1 Influence of electrospinning conditions on morphology of polymer fiber	90
5.1.1 Effect of polymer viscosity and conductivity on fiber morphology	90
5.1.2 Effect of polymer concentration at various humidity conditions	
on fiber morphology	91

5.1.3 Effect of solvent ratios on polymer solutions viscosity and conductivity	93
5.1.4 Effect of solvent ratios in polymer solutions and humidity conditions	94
5.2 Characterization of functionalized electrospun polymer fibers	95
5.2.1 Microscopic characterization	96
5.2.2 Spectroscopic characterization	98
5.2.2.1 Raman spectral characterization	98
5.2.2.2 X-ray diffraction spectral characterization	99
5.2.2.3 UV-visible spectral characterization	101
5.3 Photophysical and photochemical behavior of functionalized fibers	103
5.3.1 Fluorescence behavior of functionalized fibers	104
5.3.2 Singlet oxygen generation behavior of functionalized fibers	105
5.4 Surface area and porosity studies	108
5.5 Thermal analysis	110
5.6 Remarks on this chapter	111
CHAPTER 6	112
6. PHOTOTRANSFORMATION OF ENVIRONMENTAL POLLUTANTS	112

6.1 Photocatalytic applications of functionalized fibers	112
6.1.1 Photodegradation of 4-chlorophenol	112
6.1.2 Photodegradation of Orange G	119
6.2 Product analysis	123
6.3 Remarks on chapter	126
CHAPTER 7	127
7. GENERAL CONCLUSIONS AND FUTURE PROSPECTS	127
7.1 General Conclusions	127
7.2 Future prospects	128
REFERENCES	129

LIST OF ABBREVIATIONS

Α	absorbance
AA	acetic acid
ADMA	α, α -(anthracene-9,10-diyl)bismethylmalonate
AFM	atomic force microscopy
AOP	advanced oxidation process
BET	Brunauer-Emmett-Teller
ВЈН	Barrett-Joyner-Halenda
BQ	benzoquinone
4-CP	4-chlorophenol
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
DMF	N,N-dimethylformamide
DMLS	direct metal laser sintering
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
ET	energy transfer

F	fluorescence
FA	formic acid
FT-IR	Fourier transform infra-red
номо	highest occupied molecular orbital
HPLC	high performance liquid chromatography
HQ	hydroquinone
IC	internal conversion
IR	infra-red
ISC	intersystem crossing
LUMO	lowest unoccupied molecular orbital
MPc	metallophthalocyanine
Nd: YAG	neodymium-doped yttrium aluminium garnet
NMR	nuclear magnetic resonance
NP	nanoparticle
OG	Orange G
Р	phosphorescence
Pc	phthalocyanine

Pc ^{'+}	radical species of phthalocyanine
³ Pc*	triplet state of phthalocyanine
Pc-AuNP	phthalocyanine-gold nanoparticle conjugate
PCL	polycaprolactone
PDT	photodynamic therapy
РММА	poly(methyl methacrylate)
PS	polystyrene
RH	relative humidity
SEM	scanning electron microscopy
SPR	surface plasmon resonance
TCSPC	time correlated single photon counting
TEM	transmission electron microscopy
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
TLC	thin-layer chromatography
TRES	time-resolved emission spectra
TOABr	tetraoctylammonium bromide

UV-vis	ultraviolet-visible
VR	rotovibrational relaxation
XPS	X-ray photoelectron spectroscopy
XRD	powder X-ray diffraction spectroscopy
aZnTBMPc	zinc tetrakis (α-benzylmercapto) phthalocyanine
βZnTBMPc	zinc tetrakis (β-benzylmercapto) phthalocyanine
ZnTCMPc	zinc tetrakis (7-coumarinoxy-4-methyl)-phthalocyanine

LIST OF SYMBOLS

α	non-peripheral position
β	peripheral position
Δ	change
ΔA_{S}	change in singlet state absorbance
ΔA_{T}	change in triplet state absorbance
3	molar extinction coefficient
ε _s	singlet state molar extinction coefficient
ε _T	triplet state molar extinction coefficient
θ	angle
λ	wavelength
v	frequency
π	double bond
τ	lifetime
τ ₀	fluorescence radiative lifetimes
$ au_{ m F}$	fluorescence lifetime
$ au_{\mathrm{T}}$	triplet state lifetime

t _{1/2}	half-life
Φ	quantum yield
Φ_{F}	fluorescence quantum yield
Φ_{T}	triplet state quantum yield
Φ_{Δ}	singlet oxygen quantum yield
A/abs	absorbance/absorption
K	adsorption coefficient
k _a	apparent reaction rate constant
k _{obs}	observed rate constant
С	concentration
Ε	energy
F	area under fluorescence emission curve
$O_2(^1\Delta_g)$	singlet molecular oxygen
So	singlet ground state
S ₁	singlet excited state
t	time
T ₁	triplet excited state

LIST OF FIGURES

1.1: The molecular structures of metallated and unmetallated phthalocyanines	5
1.2: Structures of peripherally (15,16) and non-peripherally (17) tetrasubstituted	
thio-derivatized phthalocyanines synthesized in this work	11
1.3: Ground state electronic absorption spectra of metallated and	
unmetallated phthalocyanines.	16
1.4: A modified model showing exciton splitting of the Q-band between two MPc	
molecules in (a) cofacial (H-aggregation) and (b) edge-to-edge (J aggregation).	18
1.5: Jablonski diagram displaying transitions of a molecule from its lower ground state	
energy to its higher excited state energy following irradiation with light.	20
1.6: Typical triplet decay curve of a ZnPc standard.	22
1.7: Schematic diagram of an electrospinning set-up.	31
1.8: Structures of polymers used in this work.	37
2.1: Schematic representation of laser flash photolysis set-up.	47
2.2: A schematic diagram of the TCSPC equipment.	48
2.3: Schematic diagram of a photodegradation set-up.	49
3.1: UV-Vis absorption spectra of complexes 15 , 16 and 17 in DMF.	62

3.2: Normalized absorbance, excitation and emission spectra of (A) complex 15 ,	
(B) complex 16 and (C) complex 17 .	65
3.3: Transmission electron microscopy (TEM) image of (a) TOABr-AuNP	
and (b) 17 -AuNP.	66
3.4: (a) 2D and (b) 3D AFM images (height profile), and (c) size distribution	
histograms of (i) TOABr-AuNPs and (ii) 17-AuNP.	68
3.5: UV-Vis spectra of AuNPs, complexes (15, 16 and 17 and their gold	
nanoparticle conjugates (15-AuNP, 16-AuNP and 17-AuNP).	71
3.6: Absorbance, excitation and emission spectra of 16 -AuNP in DMF.	75
3.7: XPS spectra of (A) wide and (B) expanded wide scan for (i) complex 16 ,	
(ii) 16 -AuNP and (iii) AuNP (the latter only in B).	77
3.8: High resolutions XPS scans for (A) complex 16 (B) AuNPs and (C) 16 -AuNP	78
4.1: Fluorescence decay curves of complex 17 and 17 -AuNP in toluene.	
Insert = TRES analysis of 17 -AuNP in toluene.	82
4.2: Triplet state decay curve of complex 15 in toluene. Excitation wavelength: 695 nm.	87
4.3: Degradation of DPBF in the presence of complex 17 in toluene. Time interval: 5 s.	89
4.4: Spectral changes during the degradation of DPBF in toluene using 17 -AuNP.	
Time interval: 10 s.	90

5.1: SEM images of 13, 15 and 17 wt% PCL electrospun at different	
relative humidities.	92
5.2: Diagrammatic representation of the electrospinning of non-functionalized and	
functionalized polymers.	95
5.3: SEM micrographs of (A) PS alone, (B) PS/15 and (C) PS/15-AuNP fibers.	96
5.4: SEM fiber mats of (A) PMMA, (B) PMMA/17 and (C) PMMA/17-AuNP.	96
5.5: Raman spectra of PS fiber and PS/16-AuNP.	99
5.6: XRD diffraction patterns of electrospun complex 16, PS fibers, PS/16	
and PS/16-AuNP	100
5.7: UV-Vis absorbance spectra of (A) 15 in toluene, (B) 16 in DMF and (C) 17 in	
toluene: (i) Pc alone and polymer/Pc; (ii) Pc-AuNP and polymer/Pc-AuNP	102
5.8: Fluorescence micrographs of (A) PS/16 and (B) PS/16-AuNP functionalized fibers	105
5.9: Spectral changes during degradation of DPBF using PMMA/17-AuNP	
in hexane. Time interval: 30 seconds.	106
5.10: UV-Vis spectra changes observed on photolysis of ADMA in water with	
PS/15-AuNP. Time interval: 1 min.	107
5.11: TGA thermograms of (A) PS, PS/16 and PS/16-AuNP and (B) PMMA,	
PMMA/17 and PMMA/17-AuNP.	111

6.1: Electronic absorption spectra changes of $3.58 \ge 10^{-4} \mod L^{-1}$ 4-chlorophenol in	
the presence of 10 mg PS/15-AuNP. The spectra were recorded at 5 min intervals.	113
6.2: Effects of initial concentration of 4-chlorophenol on its rate of degradation.	
Concentrations were monitored at 243 nm.	114
6.3: Plot of the inverse of initial reaction rate (rate ⁻¹) vs. the reciprocal of the initial	
concentration of 4-chlorophenol for photooxidation using 10 mg PS/15-AuNP.	117
6.4: Electronic absorption spectra changes of $1.66 \ge 10^{-4} \mod L^{-1}$ Orange G during	
visible light photocatalysis in the presence of 10 mg PS/15-AuNP. The spectra were	
recorded at 30 sec intervals.	119
6.5: Effects of initial concentration of Orange G on its rate of degradation.	
Concentrations were monitored at 478 nm.	120
6.6: Plot of the inverse of initial reaction rate (rate ⁻¹) vs. the reciprocal of the initial	
concentration of Orange G for photooxidation using 10 mg PS/15-AuNP.	122
6.7: Chromatograms taken at 350 nm of (A) the standards hydroquinone (HQ),	
benzoquinone (BQ) and of 4-CP, and (B) the 4-CP degradation products.	124

LIST OF SCHEMES

1.1: General synthesis of TOABr-stabilized AuNPs using the Brust method.	3
1.2: Synthetic routes of metallophthalocyanines from different precursors.	7
1.3: Synthesis of tetrasubstituted MPcs from monosubstituted phthalonitriles at	
the non-peripheral (α) (9,10) and peripheral (β) (12,13) positions.	9
1.4: Type I reaction mechanism by free radical production.	28
1.5: Type II reaction mechanism by singlet oxygen generation.	29
2.1: The synthetic route for complex 17 .	51
2.2: Schematic illustration of the synthesis of phthalocyanine	
functionalized gold-nanoparticles.	53
3.1: Synthesis of complex 17 .	61
3.2: Schematic illustration of the synthetic route for Pc-AuNP.	72
6.1: Mechanism of photooxidation of 4-chlorophenol	125

LIST OF TABLES

1.1: Photophysical properties of thio or thiol-derivatized phthalocyanine

complexes conjugated to gold nanoparticles	13
1.2: Polymer supports used for phthalocyanines in photocatalysis	32
3.1: Ground state absorption, fluorescence excitation and emission spectral	
parameters for MPcs and their MPc-AuNP conjugates.	65
4.1: Photophysical and photochemical data of phthalocyanine-gold	
nanoparticle conjugates.	81
5.1: Effect of polymer solution viscosity and electrical conductivity	
of different PCL concentrations.	91
5.2: The average fiber diameter as a function of polymer concentration	
and relative humidity.	92
5.3: Effect of solvent ratios on polymer solutions viscosity and conductivity.	93
5.4: The average fiber diameters (nm) as a function of solvent ratio	
and relative humidity.	94
5.5: Average fiber diameter of electrospun polymer fibers functionalized with	
phthalocyanines and phthalocyanine-gold nanoparticle conjugates.	97
5.6: Fluorescence and singlet oxygen quantum yields of phthalocyanines and	
phthalocyanine-gold nanoparticle conjugates in solution and within solid polymer fibers.	104
5.7: Pore structure parameters of functionalized PS fibers.	109
6.1: The rate, rate constant (k_{obs}) and half-life $(t_{1/2})$ of various initial concentrations	

of 4-chlorophenol.	115
6.2: Langmuir-Hinshelwood parameters for photocatalysis of 4-chlorophenol in water	118
6.3: The rate, rate constant (k_{obs}) and half-life ($t_{1/2}$) of various initial concentrations	
of Orange G	121
6.4: Langmuir-Hinshelwood parameters for photocatalysis of Orange G in water.	123

1. Introduction

Organic-inorganic hybrid nanomaterials such as phthalocyanine-gold nanoparticle conjugates combine the unique physicochemical properties of these functional molecules to create a versatile, robust and multi-functional new class of nanomaterials, providing unique opportunities in photodynamic therapy, drug delivery and photocatalysis. Conjugation of gold nanoparticles to phthalocyanines results in enhanced photophysical and photochemical properties.

1.1 Gold nanoparticles

1.1.1. History, properties and applications

Gold is among the most ancient of all metals and it has been used throughout the history of civilization in a variety of forms. Gold colloids which contain fine particles of gold dispersed in a liquid have been known for centuries for their magnificent colors and used in staining. The scientific approach towards gold colloids dates back to the 1850's and to Michael Faraday, who discovered the relationship between the color and the small size of colloidal particles [1]. Colloidal gold was used to color glass and ceramics for example the Lycurgus Cup. In 1981 Schmid *et al.*, [2] reported the synthesis of gold nanocolloidal clusters which exhibited quantum confinement properties, but it was not until 1993 that the stabilization of nanoparticles was first reported by Mulvaney and Giersig [3].

The unique biological, electronic, physical and chemical properties such as biocompatibility, bioconjugability, non-toxicity, surface plasmon resonance, redox behavior and enhanced tunable optical properties of gold nanoparticles (AuNPs) are dependent on particle size, shape, type of capping agent, interparticle distance and type of surfactant. An important property of AuNPs is surface plasmon resonance [4]. Smaller nanoparticles absorb light intensively whereas scattering

of light becomes an important factor for large nanoparticles. Applications utilizing the SPR of metal nanoparticles include sensing, photonics and medicine [5,6]. One significant feature of AuNPs is their catalytic activity [7-9], a property that is lacking in bulk gold. The non-cytotoxic, non-immunogenic and biocompatible properties of gold nanoparticles are important issues for their potential application in nanoimmunology, nanomedicine, and nanobiotechnology. Biocompatibility of gold nanoparticles has garnered great interest in biological applications and they have found applications in a number of biological fields such as drug and gene delivery [10], tissue engineering [11], fluorescent biological labels [12] and tumor destruction by heating (photothermal therapy, hyperthermia) [13].

1.1.2 Synthesis and characterization of gold nanoparticles

Widely used methods for the synthesis of spherical gold nanoparticles are citrate reduction introduced by Enüstün and Turkevich [14] in 1951 and a two-phase method using thiols by Brust *et al.* [15] in 1994. In both of these reactions, the particles are formed by reduction of gold precursors and stabilized against aggregation with organic molecules as ligands or capping agents. Brust *et al.* [15] achieved a breakthrough in 1994 by creating organic soluble alkanethiolstabilized gold nanoparticles through a biphasic reduction protocol, Scheme 1, using tetraoctylammonium bromide (TOABr) as the ligand and sodium borohydride (NaBH₄) as the reducing agent. The Brust methodology produces gold nanoparticles from 1.5 to 5 nm by varying the reaction conditions such as gold-to-thiol ratio, reduction rate and reaction temperature [16]. The Brust method has since inspired a plethora of gold nanoparticle syntheses using alkane thiols [17], alkylamines [18] and dialkylsulphides [19,20]. The alkanethiol-protected AuNPs are highly stable due to the synergistic effect of the strong thiol-gold interactions and van der Waals attractions between the neighboring ligands [21].



Scheme 1.1: General synthesis of TOABr-stabilized AuNPs using the Brust method [15].

The ligand or capping agent plays a major role in the stabilization of the nanoparticles and prevents agglomeration. The multiple surface functionalities and the ease of functionalization of AuNPs provide a platform for assemblies with antibodies [22-24], oligonucleotides [25-27], proteins [28-30] and phthalocyanines [31-34]. There are limited reports available in literature on the use of phthalocyanines as capping agents for gold nanoparticles. Phthalocyanines are excellent candidates for the functionalization of metal nanoparticles because they can act as structurally and chemically well-defined templates for providing good stabilization. Phthalocyanines with different substituents and with different metal atoms at the centre can stabilize and functionalize metal nanoparticles. Phthalocyanine-functionalized gold nanoparticles (Pc-AuNPs) may have improved photophysical, photochemical, catalytic and optical properties. Thiol, aryl or alkylthio-functionalized phthalocyanines have been used as capping agents to prepare phthalocyanine-gold nanoparticle conjugates [31-34].

There are various characterization techniques for assessing AuNP size, shape, chemical content, and reactions on nanoparticle surfaces or their interaction with other chemical species. Gold nanoparticle characterization parameters include particle size, composition and shape, size distribution, surface area and porosity. Microscopic and spectroscopic characterization techniques include atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunneling microscopy (STM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-Vis and fluorescence spectroscopy. Surface topological information and imaging of the surface structure can be provided by AFM and STM. XPS is used for surface analysis and depth profiling. SEM and TEM are used for imaging of the sample surface and morphological structural details respectively. UV-Vis spectroscopy is employed for the analysis of the AuNP optical properties.

This work is based on the synthesis of gold nanoparticles by the Brust method using TOABr as both the ligand and phase transfer agent, their conjugation to phthalocyanines and their subsequent morphological and chemical characterization by AFM, TEM, UV-Vis spectroscopy and XPS.

1.2 Phthalocyanine chemistry

1.2.1 Background on phthalocyanines

Phthalocyanines (Pcs) are two-dimensional 18- π electron aromatic porphyrin synthetic analogues consisting of four isoindole subunits linked together through nitrogen atoms [**35-37**]. Pcs were accidentally discovered in the early 1900's and subsequent studies confirmed their structure, **Figure 1.1**, [**38-47**]. A variety of substituents can be incorporated to the outer hydrocarbon moiety of the molecule at positions designated α (non-peripheral) and β (peripheral), **Figure 1.1** and these play a critical role in the design, solubility and properties of phthalocyanines.



Figure 1.1: The molecular structures of metallated (MPc) and unmetallated (H₂Pc) phthalocyanines

The two hydrogen atoms of the central cavity of complex **1**, **Figure 1.1**, can be replaced by more than 70 central metals including actinides, lanthanides and some non-metals to form metallophthalocyanines (MPcs, complex **2**) by a coordinate-covalent bond between the nitrogen atoms and metal ions. MPcs, **Figure 1.1**, are of D_{4h} geometry while their unmetallated counterparts, H_2Pcs , exhibit D_{2h} symmetry.

Phthalocyanines have been used in a range of fields not only due to their unique properties such as their thermal and chemical stability, high degree of aromaticity, photophysical, photochemical, redox and coordination properties but also because of their tunable properties and designable structures [**36**,**48**,**49**]. The application of phthalocyanines in industry as dyes began as a consequence of their inherent dark blue-green color [**50**]. Pcs are versatile functional molecules and they have found applications as photosensitizers in photodynamic therapy (PDT) [**51**], sensors [**52**], nonlinear optics [**53**], photovoltaic cells [**54**], and photocatalysis [**55**].

1.2.2 Synthesis

Synthesis of phthalocyanines can be achieved via different routes depending on the type of phthalocyanine to be synthesized; metal-free, symmetrical or asymmetrical phthalocyanines. Success of the synthetic approach is dependent on several factors namely choice of: precursor, metal salt (metals, metal salts, oxides, sulphates and halides), solvent (high boiling point solvents), temperature (to facilitate melting of the precursor and rapid cyclotetramerization), base and catalyst. The synthesis of Pcs in general can be achieved by cyclotetramerization of phthalonitrile precursors, phthalimides, phthalic acids, phthalic anhydrides (complexes **3-8**) in

the absence of a metal salt for unmetallated Pcs and in the presence of a metal salt (for MPcs), **Scheme 1.2 [56,57]**.



Scheme 1.2: Synthetic routes of metallophthalocyanines from different precursors.

1.2.2.1 Peripherally and non-peripherally substituted phthalocyanines

Introducing substituents at either the α (non-peripheral) or β (peripheral) positions of the phthalocyanine ring results in tetra-substituted phthalocyanines with improved solubility.

1(4),8(11),15(18),22(25)-Tetra-substituted (α position) phthalocyanines are synthesized from 3substituted phthalonitriles, while 2(3),9(10),16(17),23(24)-tetra-substituted (β position) phthalocyanines are synthesized from 4-substituted analogues, various reaction conditions have been described. The cyclotetramerization of a mono-substituted phthalonitrile at either the α (complexes **9,10**) or β position (complexes **12,13**) (**Scheme 1.3**) affords a mixture of products made up of four structural isomers. The four probable isomers are designated by their molecular symmetry as C_{4h}, C_{2v}, C_s and D_{2h}. Theoretically it is possible to separate these isomers, however separation of the mixture to obtain individual isomers is cumbersome and time-consuming [**58**] and can only be achieved by specifically designed high performance liquid chromatographic (HPLC) column [**59,60**]. For the non-peripherally tetra-substituted phthalocyanine, the composition depends on the central metal ion and the structure of the peripheral substituent. However for the peripherally tetra-substituted phthalocyanines, the isomers always occur in an expected statistical ratio of 12.5% C_{4h}, 25% C_{2v}, 50% C_s and 12.5% D_{2h}[**59,61**].



Scheme 1.3: Synthesis of tetrasubstituted MPcs from monosubstituted phthalonitriles at the non-peripheral (α) (9,10) and peripheral (β) (12,13) positions, rf=reflux

1.2.2.2 Phthalocyanines synthesized in this work

Cook and co-workers [62-64] and Lieberman and co-workers [65,66] have been actively involved in the synthesis of thio- and thiol-derivatized Pcs for the fabrication of self-assembled monolayers (SAMs).

The photophysical and photochemical properties of Pcs are strongly influenced by the presence and nature of the central metal ion. Closed shell and diamagnetic ions such as Zn^{2+} , Ga^{3+} and Si^{4+}

give Pc complexes excellent photophysical and photochemical properties [67-69]. Zinc phthalocyanines have intensive red-visible region absorption, high triplet and singlet quantum yields making them photoactive and valuable as photosensitizers or photocatalysts [67-69]. For the above mentioned reasons, zinc was chosen as the central metal for this work. The choice of substituents employed in this work is influenced by the possibility of forming self-assembled monolayers of the phthalocyanine complexes on gold nanoparticle surfaces, thus promoting their use as photocatalysts. The syntheses of 2,9,16,23-tetrakis(benzylmercapto) phthalocyaninato zinc $(\beta ZnTBMPc)$ **[70]** 2.9.16.23-tetrakis(7-coumarinoxy-4-methyl)-(complex 15) and phthalocyaninato zinc (β ZnTCMPc) (complex 16) [71], Figure 1.2, have been reported but this work reports on the photophysical and photochemical properties of these complexes for the first time. Generally non-peripherally substituted thio Pcs have been less explored than their peripherally substituted counterparts hence a novel non-peripherally substituted phthalocyanine, 1,8,15,22-tetrakis(benzylmercapto) phthalocyaninato zinc (α ZnTBMPc) (complex 17), Figure **1.2.** was studied in this work. The benzylmercapto substituent was chosen because of enhanced solubility and reduction of aggregation [72,73] due to their ability to impose steric repulsion. The coumarin substituent was of interest due to its excellent photostability, high fluorescence emission yields and strong absorption in the visible region [74-76]. Coumarins absorb and emit at energies less than 500 nm, where MPc complexes have low absorption and their presence in the Pc structure allows for excitation at a wide range of wavelengths.



Figure 1.2: Structures of peripherally (15,16) and non-peripherally (17) tetrasubstituted arylthio-derivatized phthalocyanines synthesized in this work.

Thio-derivatized MPc complexes show rich spectroscopic, redox and photochemical properties. However, the preparation of thio-derivatized MPc complexes with thio groups at the end of substituents is relatively more difficult than other MPc derivatives, which explains why MPc complexes containing thio groups rank among the least reported MPc complexes in literature especially the non-peripheral thio MPcs. The thio moiety serves as a point of attachment for functionalization of gold nanoparticles. There are few studies on Pc-AuNP conjugates and **Table 1.1** shows the photophysical properties of some MPc complexes containing SH or RS groups
which have been conjugated to AuNPs [**31,33,34,77-79**]. **Table 1.1** shows that studies on phthalocyanine-gold nanoparticle conjugates are limited and the complexes of interest in this work (**15-17**) have not been conjugated to gold nanoparticles. In this work, we report for the first time on the conjugation of β ZnTBMPc (complex **15**), and β ZnTCMPc (complex **16**) and α ZnTBMPc (complex **17**), to gold nanoparticles for the fabrication of multi-functional nanomaterials.

Table 1.1: Pl	notophysical	properties o	of thio or	thiol-derivatized	phthalocyanine	complexes
conjugated to) gold nanopa	rticles				

SR/SH Pc complex	Φ_{T}^{a}	$\Phi_F{}^a$	$ au_{\mathrm{T}} \left(\mu s \right)^{\mathrm{a}}$	$\tau_{\mathrm{F}} \left(\mathrm{ns} \right)^{\mathrm{a,b}}$	Ref
$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$	-	-	-	1.80 ± 0.1 (98 %) 3.60 ± 0.1 (2 %)	33
	-	0.09	-	4.23 ± 0.07 (73 %) 1.74 ± 0.11 (27 %)	77
F = F $N = N$ $K = F$	0.71	0.02	92	2.60 (70 %) 1.10 (30 %)	78



^a Φ_{T} - triplet quantum yield, Φ_{F} - fluorescence quantum yield, τ_{T} - triplet lifetime, τ_{F} fluorescence lifetime; ^b abundances in brackets.

1.2.3 Ground state electronic absorption spectra

1.2.3.1 Origins of spectra and general properties

The absorption spectra of phthalocyanines are highly influenced by a number of factors which include presence or absence of central metal ion, nature of substituents, substituent number and position, solvents and aggregation tendencies. Metallophthalocyanines are characterized by two major absorption bands in the visible region of the spectrum (600-750 nm), namely the Q band (Q_{00}) in the near-IR region and a weaker absorption band towards the ultra-violet region of the spectrum called the Soret or B band, Figure 1.3. The Q band is accompanied by one or two weak vibronic bands (Q_{vib}) and the B band consists of B_1 and B_2 bands. The degeneracy of the LUMOs (e_g) is maintained in MPcs because of their high symmetry, D_{4h} . In the case of unmetallated Pcs, $D_{2h}\!\!$, the low symmetry results in a breakdown of the degeneracy of the e_g orbitals resulting in additional spectral features of the phthalocyanine such as a split Q band, Figure 1.3. Thus if the symmetry of a Pc is altered from the D_{4h} geometry, changes in the optical spectral features will be expected. The basic model that is widely used to explain the origin of the characteristic bands of phthalocyanines is the Gouterman's four orbital model based on linear combination of atomic orbitals (LCAO) [80]. According to this model, the Q band arises from π - π * (x/y polarized) transitions best explained in terms of the transitions from a_{1u} , the highest occupied molecular orbitals (HOMO) of the phthalocyanine ring to the lowest unoccupied molecular orbitals (LUMO), eg*. Additional bands referred to as N, L and C in terms of ascending energy, are accessible below 300 nm in UV-transparent solvents such as dichloromethane [81,82].



Figure 1.3: Ground state electronic absorption spectra of metallated (red) and unmetallated (black) phthalocyanines.

The electronic properties of Pcs can be modified by extension of the conjugation through fusion of additional benzene rings at the periphery of the macrocycle [**83**] or construction of conjugated oligomers [**84**]. Changes or shifts in the electronic absorption spectra can be induced by changing the central coordinating atom; exciton interaction in non-conjugated dimers [**84**], by introducing electron donating or withdrawing substituents on the ring or by phthalocyanine aggregates [**85,86**].

1.2.3.2 Phthalocyanine aggregation

Phthalocyanine aggregation is referred to as a coplanar association of Pc rings progressing from monomer to dimer and higher-order complexes often driven by non-covalent interactions i.e. π - π interactions between the conjugated Pc rings or hydrophobic interactions in polar solvents that arise as a function of their lipophilicity [87-89]. The tendency of Pcs to aggregate is dependent on the central metal and axial ligands, nature and position of substituents on the Pc ring as well as solvent polarity [89-91] and coordinating power [92]. MPc aggregation is recognized by broadening and/or splitting of the O band and a hypsochromic (blue) or bathochromic (red) shift [93] indicating the presence of additional electronic levels of the aggregates due to non-covalent, π - π interactions between the conjugated Pc rings. According to the exciton coupling theory [94] when two adjacent MPc complexes interact there is an appearance of four degenerate states leading to broadening of spectra showing the formation of aggregates. The four degenerate states arise from splitting of ¹E_u excited states, Figure 1.4, resulting in a pair of symmetry allowed transitions and a pair of symmetry forbidden transitions. The transitions that are symmetry forbidden will still occur to a small extent resulting in the spectral behaviors which are observed as either broadening of the spectra or complete split in the Q band and shifts in the Q-band to higher energies. The exciton coupling theory is usually used to explain the incidences of H and Jaggregates. The type of interactions of the Pc macrocycles and their arrangement in solution influences to a great degree the spectroscopic behavior of any resulting aggregates. A co-facial arrangement of Pc macrocycles results in a hypsochromic (blue) shift (with parallel dipole moments) of the Q-band absorption and these aggregates are referred to as H-aggregates. An edge to edge arrangement of Pc macrocycles forms aggregates that cause a bathochromic (red)

shift and are known as J-aggregates (with head to tail dipole moments). Unlike H-aggregates, J-aggregates are photoactive [95].



Figure 1.4: A modified model showing exciton splitting of the Q-band between two MPc molecules in (a) cofacial (H-aggregation) and (b) edge-to-edge (J aggregation). The solid vertical arrows represent allowed transitions, the dashed vertical arrows represent forbidden transitions, the dashed vertical arrows represent the phase transitions. The monomer and dimer ground states are placed at the same energy level for simplicity [36].

1.2.4. Photophysical properties

Photophysical processes are processes that involve, on absorption of light, changes in the quantum states of a molecule with no effect on its chemical nature [96]. In these processes, energy transfer may result in a variety of physical changes but the chemical integrity of the molecule is retained at the end of the process. A Jablonski diagram, **Figure 1.5**, is usually used to explain the possible photoprocesses that occur when photoactive molecules such as phthalocyanines absorb light of appropriate wavelength. The determination of photophysical properties of phthalocyanine and phthalocyanine-gold nanoparticle conjugates is of utmost importance in phthalocyanine applications. **Table 1.1** shows SH or SR-substituted Pcs that have been conjugated to AuNPs are limited and photophysical properties have only been reported for a few.

1.2.4.1. Jablonski diagram

The origin of photophysical processes is illustrated by the Jablonski diagram, **Figure 1.5** [97-99]. Physical and chemical processes in phthalocyanines on interaction with light have been widely researched because of the Pc complexes' high molar absorptivity in the visible region [100,101]. Phthalocyanines containing non-transitional diamagnetic metal ions such as Zn^{2+} are known to enhance intersystem crossing of the singlet excited state to the triplet excited state, resulting in the photogeneration of singlet oxygen. Singlet oxygen is a highly reactive oxygen species useful for applications in photodynamic therapy (PDT) [102], and photochemical transformation of various analytes [103,104]. Phthalocyanines are useful for the preparation of photocatalysts

based on singlet oxygen because many reactants do not absorb light in the visible red to near-IR regions.



Figure 1.5: Jablonski diagram displaying transitions of a molecule from its lower ground state energy to its higher excited state energy following irradiation with light; A =absorption, VR = rotovibrational relaxation, ISC = intersystem crossing, F = fluorescence, IC = internal conversion, P = phosphorescence, S₀ = singlet ground state, S₁ = singlet excited state, T₁ = first excited state and T₂ = second excited triplet state.

1.2.4.2 Fluorescence quantum yield (Φ_F) and lifetime (τ_F)

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 the fluorescence quantum yield (Φ_F); i.e. the longer the lifetime, the higher the quantum yield of fluorescence. Any factor that shortens the fluorescence lifetime of a fluorophore indirectly reduces the value of $\Phi_{\rm F}$, such as internal conversion, intersystem crossing, the nature and environment of the fluorophore.

Fluorescence quantum yields (Φ_F) may be determined by the comparative method [105], Equation. 1.1,

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

where F and F_{std} are the areas under the fluorescence emission curves of the samples and the standard, respectively. A and A_{std} are the respective absorbances of the sample and the standard at the excitation wavelength and n and n_{std} are the refractive indices of solvents used for the sample and the standard respectively. Unsubstituted zinc phthalocyanine is usually employed as a standard.

Fluorescence lifetimes are usually of the order of nanoseconds (10^{-9} s) . Several techniques are available for the determination of fluorescence lifetimes [**106-108**]. In this work, time-correlated single photon counting (TCSPC) technique is used [**109,110**].

1.2.4.3 Triplet quantum yield (Φ_T) and lifetime (τ_T)

The triplet quantum yield (Φ_T) is used to quantify the fraction of molecules that undergo rapid intersystem crossing from the lowest excited state to populate the lowest excited triplet state (T₁). The triplet lifetime is the amount of time it takes the triplet state to be completely depopulated and it indicates the time window available for the triplet state molecules to transfer photons to the ground state molecular oxygen and/or the substrates. Experimentally, the triplet state parameters (Φ_T , τ_T) of phthalocyanines are determined using laser flash photolysis. Laser flash photolysis involves rapid introduction of a pulse of laser light into a sample solution of the phthalocyanine. A time-resolved absorption signal is obtained if the triplet state of the phthalocyanine is populated. The signal originates from a transition from T₁ to T₂ or higher states, **Figure 1.6**, and information on Φ_T and τ_T may be obtained.



Figure 1.6: Typical triplet decay curve of a ZnPc standard.

Triplet state quantum yields of phthalocyanines may be determined using a comparative method based on triplet decay, using a standard, **Equation. 1.2**. Unsubstituted zinc phthalocyanine is most often used as a standard for phthalocyanines.

$$\Phi_T^{Sample} = \Phi_T^{Std} \frac{\Delta A_T^{Sample} \varepsilon_T^{Std}}{\Delta A_T^{Std} \varepsilon_T^{Sample}}$$
(1.2)

where ΔA_T^{Sample} and ΔA_T^{Std} are the changes in the triplet state absorbance of the sample and the standard, respectively. ε_T^{Sample} and ε_T^{Std} are the triplet state extinction coefficients of the sample and the standard respectively. Φ_T^{Std} is the triplet quantum yield for the standard in a particular solvent.

The molar extinction coefficient of the triplet state, ε_T is determined from Equation 1.3 [111]:

$$\varepsilon_T = \varepsilon_T \frac{\Delta A_T}{\Delta A_S} \tag{1.3}$$

where ΔA_T and ΔA_S are the changes in the triplet state and singlet state absorptions respectively. ε_S is the singlet state molar extinction coefficient.

1.2.5. Photochemical properties

Photochemical processes focus on the chemistry involved when a material is impacted by photons, while photophysics deals with physical changes that result from the impact of photons but the chemical integrity of the molecule is retained at the end of the process. The determination of photochemical properties of phthalocyanines and phthalocyanine-gold nanoparticles is of utmost importance in elucidating the competence of these complexes as photosensitizers. Phthalocyanines as photoactive molecules absorb visible light of appropriate wavelength resulting in photochemical processes with the ability to effect chemical transformation of organic compounds [**103**].

1.2.5.1 Singlet oxygen

Singlet oxygen (${}^{1}O_{2}$), a metastable excited state of ground state molecular oxygen (${}^{3}O_{2}$), is produced by energy transfer from an electronically excited triplet state of a photosensitizer to the latter. This species is the principal target of our studies. Singlet oxygen is a highly reactive oxidation agent used in photodynamic therapy (PDT) and in the photocatalytic oxidation of many unsaturated organic compounds including phenols [**112**], sulfides [**113**] and thiols [**114**]. In order for phthalocyanines to generate singlet oxygen efficiently, the energy of the phthalocyanine in the triplet state (T₁) must be higher than 94 kJ mol⁻¹ so as to foster efficient energy transfer to ground state oxygen to produce ${}^{1}O_{2}$ (${}^{1}\Delta_{g}$) [**55,115**].

Experimentally, singlet oxygen quantum yields of phthalocyanines can be determined using optical or chemical methods.

The optical method involves the time-resolved phosphorescence decay of singlet oxygen at 1270 nm [**116**].

The chemical method is the most commonly used method for quantifying singlet oxygen and it requires the use of singlet oxygen quenchers that react rapidly with singlet oxygen in a 1:1 ratio without side reactions. It is anticipated that the decomposition product of the quencher should neither react with the singlet oxygen nor interfere with the detection of singlet oxygen [117]. In this work, 1,3-diphenylisobenzofuran (DPBF) or anthracene-9,10-diyl-bismethylmalonate (ADMA), known quenchers in organic and aqueous solvents respectively, were employed. The experiment is conducted by irradiating a sample solution containing the phthalocyanine, oxygen and the quencher. The disappearance of the quencher is monitored spectroscopically [118,119].

Singlet oxygen quantum yields can be determined using the comparative method based on **Equation 1.4**.

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \frac{R \cdot I_{abs}^{Std}}{R^{Std} \cdot I_{abs}}$$
(1.4)

where Φ_{Δ}^{Std} is the singlet oxygen quantum yield for the standard, *R* and *R*^{Std} are the quencher photobleaching rates in the presence of sample and standard respectively; I_{abs} and I_{abs}^{Std} are the rates of light absorption by the sample and standard respectively.

Alternatively, absolute methods based on **Equation 1.5** can be used:

$$\Phi_{quencher} = \frac{(C_0 - C_t)V_R}{I_{abs} \cdot t}$$
(1.5)

where C_0 and C_t are the concentrations based on the chemical quencher prior to and after irradiation, respectively; V_R is the solution volume; t is the irradiation time per cycle and I_{abs} is defined by **Equation 1.6**:

$$I_{abs} = \frac{\alpha \cdot A \cdot I}{N_A} \tag{1.6}$$

where $\alpha = 1 - 10^{-A(\lambda)}$, $A(\lambda)$ is the absorbance of the sensitizer at the irradiation wavelength, *A* is the irradiated area, *I* is the intensity of light expressed as photons (cm⁻² s⁻¹) and *N_A* is Avogadro's constant. The singlet oxygen quantum yields Φ_{Δ} can then be calculated using **Equation 1.7** [120]

$$\frac{1}{\Phi_{quencher}} = \frac{1}{\Phi_{\Delta}} + \frac{1}{\Phi_{\Delta}} \cdot \frac{k_d}{k_a} \cdot \frac{1}{quencher}$$
(1.7)

where k_d is the decay constant of singlet in respective solvent and k_a is the rate constant of the reaction of the quencher with $O_2({}^1\Delta_g)$. The intercept obtained from the plot of $1/\Phi_{quencher}$ versus 1/[quencher] gives $1/\Phi_{\Delta}$.

1.2.5.2 Photodegradation or photobleaching quantum yields

The stability of a phthalocyanine is of paramount importance for any applications involving singlet oxygen. Photobleaching is the process of photochemically induced oxidative fragmentation of photosensitizers into low molecular weight compounds such as phthalimides by singlet oxygen. Photobleaching quantum yield (Φ_p) refers to the fraction of phthalocyanines molecules decomposed per quanta of light absorbed. This singlet oxygen mediated process is experimentally identified by a collapse in the intensity of the Q-band by measuring the intensity of the Q-band upon irradiation. **Equation 1.5** may be employed for the determination of photodegradation quantum yields where $\Phi_{quencher} = \Phi_{Pd}$.

1.2.5.3 Photocatalytic behavior of phthalocyanines

Photocatalysis is the initiation of degradation or transformation reactions of molecules using a combination of light and photoactive materials as catalysts (photosensitizers). Pcs are efficient photo-oxidative catalysts due to their excellent absorption of visible light, high chemical stability, remarkable photoactivity and most importantly their ability to produce reactive singlet oxygen. Photocatalytic applications of phthalocyanines arise from their ability to produce highly active oxidizing species upon illumination. MPc complexes containing non-transition metals such as Zn^{2+} , Al^{3+} and Si^{4+} possess outstanding photosensitizing properties towards environmentally photo-assisted reactions.

Photoinduced events occur due to the ability of Pcs to produce singlet oxygen ($^{1}O_{2}$). Intersystem crossing generates triplet state of the photosensitizer, T₁, which has a longer lifetime (μ s) than that of the S₁ state (ns), **Figure 1.5**, allowing it to react in one of two ways, known as Type I and Type II mechanisms.

In Type I mechanism, **Scheme 1.4**, the triplet state of the phthalocyanine (${}^{3}Pc^{*}$) transfers an electron to ground state molecular oxygen resulting in the formation of radicals (Pc^{+} and ${}^{3}O_{2}^{-}$). In a series of subsequent intermediate reactions, **Scheme 1.4**, the oxygen radical is transformed into hydroxyl radicals, hydroxide ions and other reactive species. All these reactive species are then able to effect the phototransformation of the substrate.



Scheme 1.4: Type I reaction mechanism by free radical production.

In Type II mechanism, **Scheme 1.5**, singlet oxygen is generated from the ground state molecular oxygen by energy transfer from the triplet excited state of the phthalocyanine. It is the singlet oxygen that is responsible for the transformation of the analyte.



Scheme 1.5: Type II reaction mechanism by singlet oxygen generation.

1.3 Electrospinning

In order to facilitate recovery of the phthalocyanine from the sample matrix during photocatalysis, various support systems such as mesoporous molecular sieves [121], amberlite [104], nano and microcrystalline TiO₂ [122], polydivinylbenzene [123], silica/zeolite [124] and TiO₂-SiO₂ composites [125] have been used to anchor phthalocyanines. These support systems have been applied in the photoconversion of various analytes such as phenols [104,121,122,124] and azo dyes [125] using Pcs, but there are limited reports on electrospun fibers [126-128].

Anchoring phthalocyanine-gold nanoparticle conjugates (Pc-AuNPs) onto electrospun nanofibers has not been explored and we report for the first time on the functionalization of electrospun fibers with Pc-AuNPs. Phthalocyanine-gold nanoparticle functionalized nanofibers have large surface area that would enhance the catalytic activity of these functional molecules immobilized on them.

Electrospinning is a technique that generates fibers with diameters in micro- and nanometer scale through an electrically charged jet of the polymer solution and the general electrospinning set-up is shown in **Figure 1.7**. The discharged polymer solution jet undergoes a whipping process wherein the solvent evaporates and the highly stretched polymer fiber deposits on a collector. Electrospinning is a technique that is applicable to virtually every soluble or fusible polymer and a variety of materials, such as polymers, inorganic compounds **[129,130]** and polymeric/inorganic composites **[131]** have been used to prepare electrospun fibers.

There are three basic electrospinning components [132]:

• a high voltage source

- electrically conductive collector (grounded or rotating collector) where the fiber mat is deposited
- a spinneret

After the solvents are evaporated during the course of jet spraying, the electrospun polymer materials are collected on a rotating or a grounded collector.



Figure 1.7: Schematic diagram of an electrospinning set-up [132]

1.3.1 Polymer supports used for phthalocyanine applications

The combination of phthalocyanines and phthalocyanine-gold nanoparticle conjugates with macromolecules is a powerful tool for designing new materials with outstanding properties. Phthalocyanines have been incorporated into polymers as a side group, in the main chain and in a polymeric network [133-135] and Table 1.2 shows examples of Pcs that have been anchored on polymer supports for photocatalysis [124,128,136-140].

 Table 1.2: Polymer supports used for phthalocyanines in photocatalysis

Phthalocyanine	Support system	Analyte	Ref
Zinc phthalocyanine	Polydivinylbenzene	2,4-dichlorophenol	123
Lutetium tetraphenoxy-phthalocyanine	Polystyrene	4-chlorophenol	127
ZnTmPyPc	Polysulfone	Methyl orange	136
Zinc phthalocyanine	Polyurethane	Iodide	137
Cobalt tetraamino-phthalocyanine	Cellulose	Reactive Red X-3B	138
Iron tetranitro-phthalocyanine	TiO ₂ /polyurethane	Methyl orange	139
Lutetium acetate tetra-2-pyridiloxy phthalocyanine	Polystyrene	4-nitrophenol	140

Table 1.2 shows that no Pc-AuNP complexes have been reported when confined to electrospun polymer fibers. This work reports for the first time on the use phthalocyanine-gold nanoparticle conjugates in a fiber polymeric matrix as photocatalysts for the photodegradation of 4-chlorophenol and the azo dye Orange G. The advantage of this approach is that AuNPs increase conductivity which increases the extent of fiber stretching during electrospinning leading to smaller fiber diameters and large surface areas which are beneficial to photocatalytic applications.

1.3.2. Factors affecting the morphology of electrospun nanofibers

Many parameters can influence the transformation of polymer solutions into polymer fibers in the electrospinning process.

These parameters include:

- Solution properties such as polymer molecular weight, polymer concentration, viscosity, conductivity, surface tension and volatility of solvents.
- Processing parameters such as applied voltage, flow rate, tip-to-collector distance and collector composition and geometry.
- Ambient parameters such as temperature, humidity and atmospheric pressure.

The properties of the polymer solution have the most significant influence in the electrospinning process and the resultant fiber morphology. One of the conditions necessary for electrospinning to occur where fibers are formed is that the solution must consist of polymer of sufficient molecular weight and the solution must be of sufficient viscosity. In this work, the effect of polymer solution parameters (solvent ratio, conductivity and viscosity) and ambient parameters (humidity) on polymer fiber diameter and morphology was investigated to study the effects of solution parameters on the electrospinning process.

1.3.3. Characterization of electrospun nanofibers

Various characterization techniques have been introduced to comprehend the basic properties of electrospun fibers: morphology (fiber diameter, porosity), molecular structure and mechanical properties.

1.3.3.1. Fiber diameter and morphology

Microscopic imaging is routinely used in the initial characterization of fiber geometric properties such as fiber diameter, diameter distribution, orientation and morphology. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are valuable techniques in understanding fiber morphology and both techniques yield two-dimensional representations of electrospun fibers and pores. Atomic force microscopy (AFM) has been used to investigate morphological features on the fiber surface as well as fiber defects such as beads [141,142].

1.3.3.2. Porosity (pore size, pore size distribution, pore geometry and density)

Pores play an important role in determining the chemical and physical properties of porous materials and have a deterministic effect on the performance of adsorbents, catalysts and membranes. The interstitial porosity of an electrospun fiber membrane is referred to as the fractional void space contained within it. There are two types of pores in fibrous membranes; pores on/within the fiber and pores between the fibers. Pore size discriminates between the type (size or molecular weight) of species that can permeate through whereas porosity determines the flux or flow across the fibrous membrane. AFM, TEM and SEM are useful tools to investigate pore size. Porosity can be measured using various techniques such as Brunauer-Emmett-Teller (BET) surface area, Capillary Flow Porosimetry, Mercury Intrusion Porosimetry, Liquid Extrusion Porosimetry.

1.3.3.3. Mechanical properties of fiber (modulus, tensile strength and elongation)

Conventional techniques available to measure the mechanical properties of films and textile materials can be applied with some modification to electrospun polymer fiber mats. The tensile and bending properties of single nanofibers can be determined using an AFM-based nanoindentation system [143] or nano tensile tester [144]. One of the most commonly used techniques is tensile property measurement using the same general experimental technique used for film or woven textile samples. Because of the random alignment of single fibers in electrospun polymer fiber mats various researchers have described cutting the mats into regular shapes and using a universal testing machine to obtain the tensile properties [145,146]. Successful measurement of the mechanical properties of 100 mm thick poly(vinyl alcohol) (PVA) electrospun fibers has been reported by Wang *et al.* [147]. Electrospinning affects the molecular and chemical structure of polymeric fibers and the arrangement of polymer chains influences their mechanical properties. Electrospun fibers of the same polymer obtained from different solvents often exhibit different mechanical properties. These differences are due to the morphology of the electrospun fibers being affected by different rates of solvent evaporation and consequently different kinetics of development of the relevant phase morphologies, giving rise to different fiber defects, branching and fusion of individual fibers.

1.3.3.4. Nanofiber crystallinity

The crystallinity of fibers is a result of processing parameters (voltage, fiber collecting speed) and solution properties (polymer concentration, molecular weight and additive influence). The crystalline structure of electrospun polymer fibers has been investigated using Differential Scanning Calorimetry (DSC), XRD and TEM. DSC is a comparative thermoanalytical technique in which differences in the thermal capacity or heat flow between a sample and a reference material is measured as a function of time or temperature when they are subjected to the same heating rate in a controlled atmosphere. Heat flow from the reference to the sample is indicative

of the sample melting, a process which requires a large intake of energy with very little change in temperature. Heat flow from the sample to the reference is indicative of crystallization which produces a large amount of energy, resulting in more rapid heating of the sample pan. The amount of heat or energy to be supplied or withdrawn to maintain a zero temperature differential between sample and reference is recorded and generated as a DSC curve.

Various thermal transitions of polymeric materials such as crystallization, melting, decomposition, first- and second-order transitions, chemical reactions and solvent evaporation can generally be observed as distinctive patterns in the DSC curve. These thermal data are particularly useful for polymer fibers containing functional molecules such as phthalocyanines [148] and gold nanoparticles [149-151].

Another technique that is commonly used for the determination of the crystalline structure of polymeric fibers is X-ray diffraction spectroscopy though phase transitions and loss of residual solvent cannot be obtained as with the DSC technique.

For fiber applications to be successful, electrospun polymer fibers must be functionalized because they are chemically inert and do not have specific functions. Incorporation of gold nanoparticles [152-154] and phthalocyanines [137,155,156] into electrospun polymer fibers has been reported with the properties of both molecules still maintained within the fiber matrix. Such functionalized electrospun fibers are promising fabric materials for various applications such as photocatalysis [127,157], biosensors [158] and nano-contaminant removal from aqueous environments [159]. However incorporation of phthalocyanine-gold nanoparticle conjugates into polymeric fiber matrices is still in its infancy. Phthalocyanine-gold nanoparticle electrospun

fibers form stable polymeric materials and are ideal candidates for catalytic supports as they can provide a large surface area and a high porosity for catalytic interaction.

The polymers used in this work are shown in **Figure 1.8**. Polycaprolactone (PCL) was chosen because it is one of the most commonly applied synthetic polymers for medical use due to its biocompatibility and biodegradability. By combining the favorable intrinsic properties of PCL with the unique properties of a phthalocyanine-gold nanoparticle nanofibrous structure, promising nanomaterials can be obtained for drug delivery and tissue engineering. In this work PCL was used to investigate the influence of electrospinning parameters on fiber morphology and diameter and was not functionalized with phthalocyanine complexes. Poly(methyl methacrylate) (PMMA) is a widespread thermoplastic polymer commonly employed as a matrix for non-linear optical composite materials and microelectronics owing to its excellent optical properties, excellent weather resistance, porosity, chemical inertness, good mechanical properties, formability and moldability. Polystyrene (PS) was chosen because of its extensive aromatic system which allows for π - π electronic interactions between the aromatic systems of the phthalocyanine and the polymers, hence preventing the leaching of the Pc from the polymer.



Figure 1.8: Structures of polymers used in this work.

1.4 Background on environmental pollutants used in this work

Phthalocyanine-gold nanoparticle conjugates have unique properties; hence their incorporation into electrospun polymer fibers is attractive for developing functional polymer composites having promising physical, chemical, optical and catalytic properties. The unique properties and the multi-functionality of these polymeric fibers are therefore applicable in fields such as sensors, optoelectronics, drug delivery and photocatalysis. In this work, the photocatalytic degradation of common water pollutants, 4-chlorophenol (4-CP) and Orange G (OG), is used as an example of the application of phthalocyanine-gold nanoparticle conjugates incorporated in electrospun fibers.

1.4.1 Phenols

Phenol and phenol-derivatives are widespread pollutants of the aquatic environment because of their importance in the production of fungicides and herbicides. As a result of the immense economic importance associated with the removal of chlorophenols during water purification, various attempts to oxidize these pollutants including biodegradable processes [160-162], electrochemical oxidation [163,164], adsorption [165,166] and photocatalytic oxidation [167,168] have been described. Photocatalytic oxidation of phenolic compounds using semiconductors such as TiO_2 [169,170] or photo-assisted Fenton reaction [171] have been reported and are receiving attention because of the potential use of sunlight. The use of phthalocyanines in activating the oxygen for such photocatalytic processes is gaining ground because Pcs absorb much more abundantly in the visible region of the electromagnetic spectrum. Zinc and aluminum Pcs have been reported to catalyze such photocatalytic conversions [172-

174]. However, no cases have been reported involving the use of phthalocyanine-gold nanoparticle conjugates. Thus this work also reports on the use zinc phthalocyanine derivatives and their gold nanoparticle conjugates anchored on electrospun polymer fibers in the photocatalytic oxidation of 4-chlorophenol. The use of phthalocyanine-gold nanoparticle conjugates on electrospun polymer fibers is reported for the first time for phenolic transformation.

1.4.2 Azo dyes

Azo dyes constitute the most important and widespread chemical class of commercial organic pollutants and account for around 60 - 70% of the dyes associated with textile, cosmetic, food colorants, printing and pharmaceutical industries [**175**]. Azo dyes contain one or more azo bonds (-N=N-) usually associated with one or more aromatic systems which may also contain sulfonic groups. The azo bond determines the color of the dye and is the most reactive usually undergoing oxidation leading to a fading of the color of the solution [**176**]. Because of their non-degradability, toxicity, potential mutagenicity and carcinogenicity, wastewaters originating from azo dye production or application industries pose a major threat to the surrounding ecosystems and human beings' health [**177-180**].

Complete degradation of azo dyes is difficult due to their complex structure [**180**]. Various physico-chemical techniques have been applied in the removal of azo dyes. These techniques included filtration, coagulation, precipitation, adsorption and ion exchange [**181**]. However these methods are not destructive, but only transfer the dye from one phase to another requiring yet a different kind of treatment [**182,183**].

Among the recent treatment processes, advanced oxidation processes (AOPs), such as the Fenton processes, H_2O_2 or UV/ H_2O_2 oxidation and ozonation are widely used. Photocatalytic oxidation is one of AOPs and can decompose organic pollutants in a short reaction time. Photocatalytic degradation of azo dyes has been reported in several studies [**184,185**] and many investigations focused on the UV-illuminated TiO₂ processes [**186-188**].

The use of electrospun fibers functionalized with phthalocyanine- and phthalocyanine-gold nanoparticle conjugates offers promising heterogeneous catalytic mimetric systems for the photoconversion of azo dyes. However very few cases are reported for phthalocyanines [126-128,140,156] and to the best of our knowledge, there are no reports on the use of phthalocyanine-gold nanoparticle functionalized polymeric fibers for photocatalysis. Immobilization of Pcs and Pc-AuNP complexes onto solid supports such as electrospun fibers exhibits advantages over the corresponding homogeneous systems because of their facile recovery, reusability and recyclability, leading to potentially minimal material use hence a reduction in the cost of the treatment. In this work we explore the use of electrospun fibers functionalized with phthalocyanines and phthalocyanine-gold nanoparticle conjugates for the conversion of Orange G (OG), a typical azo dye.

1.5 Summary of aims of thesis

The aim of this work is the fabrication of multi-functional nanocomposites based on phthalocyanines, gold nanoparticles and polymer fibers. The combination of different types of functional nanostructured materials enables the development of multi-functional nanomaterials to be used as photocatalysts in the photodegradation of organic pollutants.

The sub-aims of the thesis are:

1. Syntheses and characterization of zinc phthalocyanines with arylthio substituents at peripheral and non-peripheral positions.

2. Synthesis and characterization of phthalocyanine-functionalized gold nanoparticle conjugates.

3. Electrospin polymer fibers and investigate the effect of polymer solution parameters on the electrospinning process.

4. Fabrication of electrospun polymer fibers functionalized with phthalocyanine and phthalocyanine-gold nanoparticle conjugates.

5. Characterization of multi-functional polymer fibers using spectroscopic (Raman, XRD) and microscopic (AFM, SEM) techniques.

6. Investigation of the fluorescence and photoactivity of phthalocyanine and phthalocyanine-gold nanoparticle complexes within the functionalized fibers.

7. Investigation of the photocatalytic activity of phthalocyanine and phthalocyanine-gold nanoparticle functionalized fibers for the photodegradation of 4-chlorophenol and Orange G in aqueous media.

41

2. Experimental

This chapter reports on all the experiments procedures used during the course of the study. This includes all synthetic procedures and methods of characterization for all complexes used in this work.

2.1 Materials

2.1.1 Solvents

Acetonitrile (ACN) and N,N-dimethylformamide (DMF) were purchased from MERCK Chemical Ltd. Acetic acid (AA) (99.8%), and formic acid (FA) (99.8%) were purchased from Sigma-Aldrich. Chloroform, dimethylsulfoxide (DMSO), methanol (MeOH), n-hexane, 1pentanol, quinoline, tetrahydrofuran (THF) and toluene were purchased from SAARChem. Phosphate buffer solutions were prepared using reagent grade potassium dihydrogen orthophosphate (ACE) and dipotassium phosphate (PAL Chemicals).

2.1.2 Synthesis reagents

Ammonia, gold (III) chloride (HAuCl₄·3H₂O), anthracene-9,10-diyl-bismethylmalonate (ADMA), benzyl mercaptan, 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), potassium carbonate, 7-mercapto-4-methylcoumarin, sodium borohydride, tetraoctylammonium bromide (TOABr), thionyl chloride unsubstituted zinc phthalocyanine, zinc acetate and 1,3-diphenylisobenzofuran (DPBF) were purchased from Aldrich. Silica gel 60 P_{F254} and 3-nitrophthalic acid were purchased from Merck. Bio-beads S-X1 beads were from Bio-Rad.

2.1.3 Polymers for electrospinning

Polystyrene (PS) ($M_w = 192\ 000\ g/mol$) was purchased from MERCK Chemical Ltd. Poly (methyl methacrylate) (PMMA) ($M_w \sim 120\ 000\ g/mol$) and polycaprolactone (PCL) ($M_w \sim 70\ 000\ -90\ 000\ g/mol$) were purchased from Sigma-Aldrich.

2.1.4 Photocatalysis analytes and products

4-chlorophenol (4-CP) (99%) was purchased from Fluka. Hydroquinone (HQ) was from May and Baker LTD. Benzoquinone (BQ) and Orange G (OG) were purchased from Sigma Aldrich.

2.1.5 Previously synthesized phthalocyanines and their precursors

Zinc phthalocyanine (ZnPc) was purchased from Sigma Aldrich. 3-(Benzylmercapto) phthalonitrile, **Scheme 3.1** [**189**], 4-(benzylmercapto) phthalonitrile [**70**], zinc tetrakis (β -benzylmercapto) phthalocyanine (β ZnTBMPc) (complex **15**) [**70**], zinc tetrakis (β -7-coumarinthio-4-methyl) phthalocyanine (β ZnTCMPc, complex **16**) [**71**] were synthesized according to literature procedures.

2.2 Instrumentation

(a) Elemental analyses for CHNS were done using a Vario-Elementar Microcube ELIII Series.

(b) Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in positive ion mode using a m/z range of 400 – 3000 amu. The voltage of the ion sources was set at 19 and 16.7 kV for ion sources 1 and 2 respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV respectively. The spectra were acquired using α -cyano-4-hydroxycinnamic acid as the MALDI matrix and a 354 nm nitrogen laser as the ionizing source.

(c) ¹H-NMR spectra were recorded on a Bruker AMX600 MHz in deuterated DMSO.

(d) UV-Vis absorption spectra were measured at room temperature on a Shimadzu UV-2550 spectrophotometer using a 1 cm pathlength cuvette for solution studies. The UV-Vis spectra of the functionalized fibers were measured by placing them on a glass slide.

(e) Infrared (IR) spectra were recorded using the Perkin-Elmer Universal Attenuated Total Reflectance (ATR) Sampling accessory spectrum 100 FT-IR Spectrometer.

(f) Fluorescence excitation and emission spectra were recorded on a Varian Cary Eclipse spectrofluorometer.

(g) The fluorescence images were taken with a Direct Metal Laser Sintering (DMLS) fluorescence microscope. The excitation source was a high voltage mercury lamp and light in the wavelength range of 550 - 730 nm.

(h) AFM images were obtained in intermittent tapping mode using a Nanoscope IIIa controller with Multi Mode AFM head and with an E-type scanner (maximum xyz range of

44

 $12 \times 12 \times 3.6 \,\mu\text{m}^3$; Veeco Digital Instruments) under ambient environmental conditions (<40% relative humidity). Silicon cantilevers (Veeco, model RTESP) with a force constant of 20–80 N/m and a resonance frequency of 250–325 kHz were used. Scan parameters were optimized for each experiment. Scan frequencies were typically 1–2 Hz (lines per second), and the data collection resolution was 512×512 pixels. All images shown are height images and are presented essentially unfiltered. Samples for AFM were prepared by spin coating toluene solutions of TOABr-AuNPs or Pc-AuNP samples.

(i) X-ray spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra X-ray Photoelectron Spectrometer equipped with a monochromatic Al source K α source (1486.6 eV) to generate the X-rays. The base pressure of the system was below 3×10^{-9} torr. XPS survey scans were recorded using a 75 W, a hybrid lens acquisition in slot mode at 160 eV pass energy and 500 ms dwell time. XPS data analysis was performed with Kratos Version 2 program.

(j) A Bruker Vertex 70-Ram II Raman spectrometer (equipped with a 1064 nm Nd:YAG laser and a liquid nitrogen cooled germanium detector) were used to collect Raman data. Raman spectral data was obtained from powdered mixtures of KBr pellets and electrospun fibers.

(**k**) Nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Prior to each measurement, the functionalized and non-functionalized fibers were degassed at 70 °C for five days. The surface BET area, total pore volume and pore size distribution were calculated from the isotherms.

(1) Thermal degradation properties of the PS and functionalized PS fibers were studied using a thermogravimetric analyzer, Simultaneous DTA-TG (Shimadzu) and a thermal analyzer, (TA-

60WS, Shimadzu) at a heating rate of 10 °C/min under a nitrogen atmosphere with a gas flow rate of 120 ml/min.

(m) X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8, Discover equipped with a Lynx Eye Detector, using Cu K_a radiation ($\lambda = 1.5405$ Å, nickel filter). Data were collected in the range from $2\theta = 5^{\circ}$ to 100°, scanning at 1° min⁻¹ with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. Samples were placed on a zero background silicon wafer slide. The X-ray diffraction data were treated using Eva (evaluation curve fitting) software. Baseline correction was performed on each diffraction pattern by subtracting a spline fitted to the curve background and the full width at half maximum values used in this study was obtained from the fitted curves.

(n) A laser flash photolysis system, Figure 2.1, was used for the determination of triplet the decay kinetics. Samples were prepared in deoxygenated DMSO by bubbling with argon for 15 min. The excitation pulses (3-5 ns) were produced by a EKSPLA NT342N-20-AW tunable wavelength laser. A Thermo Oriel 66902 xenon arc lamp provided the analyzing beam source, and a Kratos Lis Projekte MLIS-X3 photomultiplier tube was used as the detector. Signals were recorded with a two-channel, 300 MHz digital real time oscilloscope (Tektronix TDS 3032C); the kinetic curves were averaged over 128 laser pulses. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 8 software.



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

(**o**) Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup, **Figure 2.2**, (Fluo Time 200, Picoquant GmbH) with a diode laser as an excitation source (LDH-P-670 driven by PDL 800-B, 670 nm, 20MHz repetition rate, Picoquant 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 4 nm was used to select the required emission wavelength. The response function of the system, which was measured 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. The luminescence decay curve was measured at the maximum of the emission peak. The data were
analyzed with the FluoFit Software program (Picoquant GmbH, Germany). The support plane approach was used to estimate the errors of the decay times.



Figure 2.2: A schematic diagram of the TCSPC equipment

(**p**) Time-resolved emission spectra (TRES) were plotted from TCSPC traces obtained at different wavelengths of the steady state emission spectra.

(**q**) Transmission electron microscopy (TEM) was used to investigate the morphological and structural properties of the non-functionalized and Pc-functionalized gold nanoparticles. TEM investigations were carried out using a JEOL JEM 1210 microscope. Samples were prepared by evaporation of a very dilute solution of the nanoparticles (or the Pc-AuNP conjugates) on a standard carbon-coated copper TEM grid.

(**r**) Scanning electron microscope (SEM) images were obtained using a JEOL JSM 840 scanning electron microscope. Prior to SEM measurements, the electrospun fiber samples were coated

with gold using a sputter coater (Balzers Union SCD 030). Average fiber diameters were obtained using Cell^D software by taking fifty diameter measurements on each sample.

(s) Determination of singlet oxygen and photodegradation quantum yields as well as photocatalytic conversion of 4-chlorophenol (4-CP) and Orange G (OG) were done using the General Electric Quartz lamp (300 W) as irradiation source, **Figure 2.3**, a 600 nm glass (Schott) and water filters were used to filter off ultra-violet and far infrared radiations respectively. An interference filter 670 nm with band of 40 nm was placed in the light path just before the cell containing the sample. The intensity of the light reaching the reaction vessel was measured with a power meter (POWER MAX 5100, Molelectron Detector Inc).



Figure 2.3: Schematic diagram of a photodegradation set-up

(t) The of 4-CP and OG degradation products were profiled out on high performance liquid chromatography (HPLC), by comparison with the retention time of the standard compounds. The chemical structures of the CP and OG degradation products were elucidated by an Agilent HPLC 1200 series (Agilent Technologies Inc., Germany), equipped with a quaternary pump (G1311A),

an autosampler (G1329A), a diode array detector (DAD SL G1315C) and a degasser unit (G1322A). An Eclipse XBD-C₁₈ (i.d. 4.6 x 150 mm; 5 μ m) column was used for the separation of product intermediates. Gradient elution was used starting with a mobile phase of a mixture of ACN-water (0.2 % acetic acid) (20/80 v/v) for 10 min which was then vamped to 100 % ACN at 20 min, the flow rate was 0.8 ml/min and the injection volume was 25 μ l. The solvent was then kept at 100 % ACN for a further 10 min. The total run time was 30 min.

(**u**) Electrospun fibers were obtained from a set-up consisting of a syringe pump, a KD Scientific Syringe Pump Series 100, used to feed the polymer solution through a 20 ml plastic syringe fitted with a 15.24 cm needle with an inner diameter of 1.024 mm at varying flow rates depending on the polymer solution. The voltage was adjusted using a Glassman High Voltage Series EL source. Polymer solution viscosity and conductivity were measured with a Brookfield Viscometer LVDV-II and a CDM210 conductivity meter (Radiometer Analytical) respectively. The morphology of the electrospun nanofibers was examined using a scanning electron microscope at an accelerating voltage of 20 kV. Before SEM analysis, the sample was coated with gold using a sputter coater (Balzers Union SKD 030). The diameter of a nanofiber sample was calculated by taking an average of 50 measurements.

2.3 Synthesis of 1(4), 8(11), 15(18), 22(25)-tetrakis(benzylmercapto) phthalocyaninato zinc (Scheme 3.1)

Synthesis of zinc tetrakis (benzylmercapto) phthalocyanine (α ZnTBMPc, complex 17), Scheme 3.1, was achieved by heating a mixture of 3-(benzylmercapto) phthalonitrile (1 g, 4 mmol), zinc acetate (0.19 g, 1.05 mmol) and DBU (1 ml) at 180 °C in quinoline (2 ml) for 6 h under a nitrogen atmosphere. After cooling, the mixture was precipitated with methanol and the formed

precipitate was isolated by centrifugation and washed several times with the same solvent. The crude product was subjected to column chromatography and eluted with chloroform/methanol (4:1) mixture to obtain the pure phthalocyanine. Yield: (52 %). IR (KBr cm⁻¹): 725, 752, 889, 1058, 1087, 1166, 1286 and 1330 (Pc skeleton), 691 (C-S), 2956 (C-H aromatic). ¹H NMR (DMSO-*d6*): δ ppm 4.1 (s, 8H, -*CH*₂), 7.3-7.6 (m, 20H, -*phenyl*), 7.98 (m, 4H, -*Pc*), 7.7-7.9 (m, 8H, -*Pc*). UV/Vis (toluene) λ_{max} (nm) (log ε): 710 (5.24), 670 (3.33). Calc. for C₆₀H₄₀N₈S₄Zn: C 67.05, H 4.50, N 10.43, S 11.93; Found: C 67.77, H 4.91, N 10.80, S 11.15. MALDI-TOF MS *m/z*: Calc: 1074 amu. Found [M]⁺ 1074 amu.

2.4 Synthesis of phthalocyanine-gold nanoparticle conjugates (Scheme 3.2)

The syntheses of TOABr-capped AuNPs (TOABr-AuNP), and phthalocyanine-gold nanoparticle conjugates, have been reported before [**31**]. Briefly, a gold(III) chloride trihydrate solution (25 mM, 2 mL toluene) was vigorously stirred with a toluene solution of TOABr (85 mM, 3 mL) until all of the gold chloride was transferred to the organic phase. The reducing agent, NaBH₄, in an aqueous solution (36 mM, 2 mL) was added dropwise for 10 min. The Au solution changes color from brownish yellow, to milky, to scarlet and finally purple. After the addition of NaBH₄, the mixture was stirred vigorously for 30 min. The gold nanoparticles were washed repeatedly with deionized H₂O to remove the reducing agent and were stored in a minimum amount of toluene (1 ml).

The as-synthesized TOABr-AuNPs were mixed with 2 mg of Pc in 1 ml toluene (complexes **15** and **17**) or DMF (complex **16**) and the mixture was stirred vigorously for 32 h to facilitate ligand exchange forming β ZnTBMPc-AuNP (**15**-AuNP), ZnTCMPc-AuNP (**16**-AuNP) and

αZnTBMPc-AuNP (**17**-AuNP). The reaction mixture was diluted with 2 ml solvent and the unreacted Pc was separated in a size-exclusion column (Bio-Beads S-X1 from Bio-Rad) using the same solvent as an eluent. Toluene was employed for complexes **15** and **17** since the gold nanoparticles were synthesized in solution. However complex **16** was not soluble in toluene, so the AuNP sample had to be used in the solid state by evaporating off the toluene solution and synthesizing **16**-AuNP in DMF. Any toluene left in the sample was eliminated during the purification step by size-exclusion using DMF as the eluent. For all the following comparative studies, toluene was used as the solvent for complexes **15** and **17** whereas DMF was used for complex **16** and unsubstituted ZnPc.

2.5 Preparation of functionalized fibers

2.5.1 Preparation of electrospun fibers of polycaprolactone (PCL)

To obtain polycaprolactone fibers, PCL pellets were dissolved in a mixed solvent of acetic acid (AA) and formic acid (FA) to produce various spinning solutions with PCL concentrations ranging from 13 to 17 wt%. The solutions were magnetically stirred at room temperature for 3 h, which was needed for complete dissolution. After high voltage ranging from 10 to 26 kV was applied to the needle, a positive charged jet of PCL solution formed from a Taylor cone and sprayed to a grounded aluminium collector, with a tip-to-collector distance of 12.5 cm from the needle tip. With the evaporation of solvent, PCL fibers were deposited on the collector to form fibrous membrane. Electrospinning experiments were carried out at room temperature in different solvent ratios and relative humidity (RH) of 20, 50 and 70% RH. To obtain 50 % RH, the electrospinning set-up was under open laboratory conditions. For 20 and 70 % RH, a closed

electrospinning chamber was used in which air was dried using silica or wetted using a saturated solution of potassium nitrate. A humidity sensor, Vaila HMI 41 indicator was used to continuously monitor the humidity in the closed electrospinning chamber. SEM images of the fiber mats were taken and the fiber diameters were measured using Cell^D software from Olympus.

2.5.2 Preparation of functionalized poly(methyl methacrylate) (PMMA) polymer fibers

Complex **17** was used as an example for the functionalization of electrospun PMMA fibers. Homogeneous PMMA solutions of 22 wt % in DMF were produced by stirring a polymer solution of PMMA in DMF for 24 h at room temperature until the polymer was completely dissolved. Electrospun PMMA fibers were produced under the following conditions; 0.2 ml/h flow rate, + 25 kV potential at a distance of 18 cm between the needle tip and the collector, and a grounded 12 cm x 6 cm substrate covered with aluminum foil. With the evaporation of solvent, PMMA fibers were deposited on the collector to form a fibrous mat. Similar conditions were used for the functionalized fibers; PMMA/αZnTBMPc (PMMA/17) and PMMA/αZnTBMPc-AuNP (PMMA/17-AuNP). To obtain these functionalized fibers, 6 mg of complex **17** or 4 mg of **17**-AuNP were added to a dissolved PMMA solution and stirred for another 24 h. Due to its poor mechanical properties and its tendency to form a polymer gel in water, PMMA was not suitable for photocatalytic applications in aqueous media. As a result of partial solubility in water, the phthalocyanine and phthalocyanine gold nanoparticle conjugates eventually diffuse out of the PMMA fiber, hence further studies were done on a more suitable polymer, polystyrene (PS).

2.5.3 Preparation of functionalized polystyrene (PS) polymer fibers

Complexes **15** and **16** were used as examples for functionalization of electrospun PS fibers. Homogeneous PS solutions were prepared by dissolving 2.5 g of PS beads in DMF:THF (4:1) and stirring for 24 h at room temperature. For the functionalized fibers; PS/βZnTBMPc (PS/**15**), PS/ZnTCMPc (PS/**16**), PS/βZnTBMPc-AuNP (PS/**15**-AuNP), and PS/ZnTCMPc-AuNP (PS/**16**-AuNP), Pc (3 mg) or Pc-AuNP (6 mg) were added separately to PS polymer solution and the solutions were allowed to stir for a further 24 h. Electrospinning parameters were set at; applied voltage of 20 kV, tip-to-collector distance of 15 cm and solution flow rates of 0.1 and 0.2 ml/h for the pure PS and functionalized PS fibers respectively. The phthalocyanines were employed for this polymer to enable electrostatic interaction between their aromatic systems that will prevent leaching of the Pc complexes from the polymer fibers during photocatalytic applications.

2.6 Photophysical and photochemical methods

2.6.1 Fluorescence quantum yields

The fluorescence quantum yields of the phthalocyanines and phthalocyanine-gold nanoparticle conjugates were determined in either DMF or toluene using a comparative method, **Equation 1.1**. Unsubstituted ZnPc in DMF $\Phi_F^{Std} = 0.30$ [167] or DMSO $\Phi_F^{Std} = 0.20$ [190] was employed as the standard. Both sample and standard were excited at the same wavelength. The absorbances of the solutions at the excitation source were about 0.05 to avoid any filter effects.

2.6.2 Triplet quantum lifetimes and yields

The decay kinetics of the triplet absorption of the phthalocyanines and phthalocyanine-gold nanoparticle conjugates were recorded using the laser flash photolysis set-up, **Figure 2.1**. The absorbances of the phthalocyanines and phthalocyanine-gold nanoparticle conjugates were adjusted to be approximately 1.5 and 1, respectively at their Q-band maximum. After introducing the solution into a 1 cm quartz cell, argon was bubbled through the solution to remove dissolved oxygen. The triplet quantum yields were determined using **Equation 1.2**. Unsubstituted ZnPc in DMF $\Phi_T^{Std} = 0.58$ [**191**] or toluene $\Phi_T^{Std} = 0.65$ [**192**] was employed as the standard. Triplet lifetimes were determined from the kinetic data obtained using Origin Pro 8 software.

2.6.3 Singlet oxygen quantum yields

A chemical method was used for the determination of Φ_{Δ} of the phthalocyanines and phthalocyanine-gold nanoparticle conjugates in solution (DMF or toluene). The experiments were conducted in air with 1.5 ml of each Pc or Pc-AuNP solution with approximate absorbance of 1 at the Q band mixed with an equal volume of a DPBF solution with approximate absorbance of 2 at 416 nm. The resulting solution was irradiated using the set-up shown in **Figure 2.3** and the degradation of the DPBF was monitored by recording the UV-Vis spectra of the sample solution at 5 s time intervals. The Φ_{Δ} values were determined using **Equation 1.4** and employing ZnPc in DMF, $\Phi_{\Delta}^{std} = 0.56$ [**193**] or toluene $\Phi_{\Delta}^{std} = 0.58$ [**174**].

For the singlet oxygen quantum yield of the phthalocyanine complexes and AuNP conjugates within the fiber polymeric matrices, ADMA was used as the singlet oxygen quencher since the

fabric materials were intended for use in aqueous media. For each experiment, 10 mg of functionalized fibers were suspended as small pieces in an aqueous solution of ADMA and irradiated using the photolysis set-up, **Figure 2.3**. The quantum yields (Φ_{ADMA}) were estimated using **Equation 1.5**, using the extinction coefficient of ADMA in water, log (ε) = 4.1 [**194**] and using the absorbance of the phthalocyanine complexes in the polymer fiber matrix. **Equation 1.7** (the absolute method) was employed for Φ_{Δ} values. The Φ_{Δ} values are estimates due to light scattering and the intensity of light was the one reaching the spectrophotometer cell but not the fibers.

2.6.4 Fluorescence micrographs

Fluorescence micrographs of phthalocyanine and phthalocyanine-gold nanoparticle functionalized fibers were taken by placing the fiber on a glass slide. The fluorescence images were taken with a Direct Metal Laser Sintering (DMLS) fluorescence microscope. The excitation source was a high voltage mercury lamp and light in the wavelength range of 550 – 730 nm. Pictures of the micrographs were taken using a digital camera.

2.7 Photocatalysis and analysis of degradation products

2.7.1 Photocatalytic reactions

Photocatalytic reactions were carried out in a magnetically stirred batch reactor (glass vial). The irradiation experiments were carried out using the photolysis set-up described above for singlet oxygen detection, **Figure 2.3**. The intensity of the light reaching the reaction vessel was

measured with a power meter (POWER MAX 5100 Molelectron Detector Inc) and found to be 3.2×10^{20} photons cm⁻² s⁻¹. The transformation was monitored by observing the absorption bands of 4-chlorophenol at 243 and 297 nm and Orange G at 478 nm after 15 min and 1 min photolysis cycles respectively using a Shimadzu UV-2550 spectrophotometer. The experiments were carried out using a range of concentrations of 4-chlorophenol in pH 11 phosphate buffer and pH 6.5 phosphate buffer for Orange G. Each sample (6 ml) contained 10 mg of functionalized fiber, suspended in small pieces.

2.7.2 Identification of photocatalytic products

The 4-chlorophenol and Orange G degradation products were profiled out on high performance liquid chromatography (HPLC), by comparison with the retention time of the standard compounds. The chemical structures of the CP and OG degradation products were elucidated by an Agilent HPLC 1200 series (Agilent Technologies Inc., Germany), equipped with a quaternary pump (G1311A), an autosampler (G1329A), a diode array detector (DAD SL G1315C) and a degasser unit (G1322A). An Eclipse XBD-C₁₈ (i.d. 4.6 x 150 mm; 5 μ m) column was used for the separation of product intermediates. Gradient elution was used starting with a mobile phase of a mixture of ACN-water (0.2 % acetic acid) (20/80 v/v) for 10 min which was then ramped to 100 % ACN at 20 min, the flow rate was 0.8 ml/min and the injection volume was 25 μ l. The solvent was then kept at 100 % ACN for a further 10 min. The total run time was 30 min.

RESULTS AND DISCUSSION

- **3.** Synthesis and characterization
- 4. Photophysical and photochemical parameters
- 5. Electrospun polymer fibers
- 6. Phototransformation of organic pollutants

Publications

The results discussed in the following chapters have been presented in the articles below that have been published or submitted for publication to peer-reviewed journals. These articles have not been referenced in this thesis:

1. Sekai Tombe, Wadzanayi Chidawanyika, Edith Antunes, Georgios Priniotakis, Philippe Westbroek, Tebello Nyokong, **Physicochemical behavior of zinc tetrakis (benzylmercapto) phthalocyanine when used to functionalize gold nanoparticles and in electrospun fibers**, Journal of Photochemistry and Photobiology A: Chemistry, 2012, 240, 50-58.

2. Sekai Tombe, Edith Antunes, Tebello Nyokong, **The photophysical and photochemical behavior of coumarin-derivatized zinc phthalocyanine when conjugated with gold nanoparticles and electrospun into polymer fibers**, New Journal of Chemistry, DOI: 10.1039/C2NJ40984D, **in press**

3. Sekai Tombe, Edith Antunes, Tebello Nyokong. Electrospun fibers functionalized with phthalocyanine-gold nanoparticle conjugates for photocatalytic applications, Journal of Molecular Catalysis A: Chemical, DOI: 10.1016/j.molcata. 2013.01.033, in press

3. Synthesis and characterization

This chapter reports on the syntheses and characterization of phthalocyanines and phthalocyanine-gold nanoparticle conjugates employed in this work.

3.1 Phthalocyanines

Substituted phthalocyanines are normally prepared by cyclotetramerization of substituted phthalonitriles. Tetra-substituted Pcs can be synthesized from their 4-substituted phthalonitrile precursors. The syntheses of phthalocvanines β ZnTBMPc (15) and ZnTCMPc (16), Scheme 3.1, have been reported [70,71] but this work reports on their photophysical and photochemical characterization for the first time. Scheme 3.1 shows the synthetic pathway for α ZnTBMPc (17). The synthesis and characterization of α ZnTBMPc (17) is reported for the first time in this work. The synthesized Pc, complex 17, was characterized spectroscopically by UV/Vis, IR, ¹H NMR and elemental analysis and satisfactory spectroscopy results were obtained. The C=N peak of the benzylmercapto phthalonitrile at 2228 cm⁻¹ disappeared upon the formation of complex **17** as expected. The ¹H NMR spectra showed aromatic ring protons between 8 and 10 ppm and peak integration correctly gave the anticipated total number of protons, confirming the relative purity of complex 17. In addition mass spectra as well as elemental analysis confirmed the phthalocyanine structure of 17. For complex 17, a molecular ion peak corresponding to [M+] at 1074 amu was obtained for 17. Complexes 15 and 17 were soluble in organic solvents such as DMF, DMSO, THF and in non-polar solvents like chloroform and toluene, whereas complex 16 was only soluble in DMF and DMSO.



Scheme 3.1: Synthesis of the arylthio-derivatized phthalocyanine, α ZnTBMPc (17) and the structures of β ZnTBMPc (15) and ZnTCMPc (16).

The UV-vis spectra of unsubstituted ZnPc and the arylthio zinc phthalocyanines used in this work are shown in **Figure 3.1**. The ground state electronic absorption spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical of metallated phthalocyanines for all Pc complexes. The spectra are red shifted compared to unsubstituted ZnPc (with a Q band at 671 nm in DMF, **Figure 3.1**), due to the electron donating properties of

the arylthio substituents. The Q bands are at 696 nm, 684 nm, and 712 nm for complexes **15**, **16** and **17** respectively. The non-peripherally tetra-substituted zinc phthalocyanine (complex **17**) was red shifted 16 nm compared to the peripherally substituted counterpart (complex **15**). The observed red spectral shift is typical of phthalocyanines with substituents at the non-peripheral position [**195**]. This shift has been explained to be a result of linear combination of the atomic orbitals coefficients at the non-peripheral positions of the highest molecular orbital (HOMO) being greater than those at the peripheral positions [**81**].



Figure 3.1: UV-Vis absorption spectra of 1×10^{-5} M ZnPc (blue), β ZnTBMPc (15) (green) ZnTCMPc (16) (black) and α ZnTBMPc (17) (red) DMF.

Figure 3.2 shows the absorbance, fluorescence excitation and emission spectra of complexes 15, 16 and 17. Figure 3.2 shows that the absorbance and excitation spectra are similar and are mirror images of the fluorescence emission spectra. The ground state absorption, fluorescence excitation and emission spectral parameters for the MPcs are shown in Table 3.1. The proximity of the wavelength of the Q-band absorption to the Q-band maxima of the excitation spectra, Table 3.1, for the Pcs suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in either toluene or DMF. The slight differences between absorbance and excitation wavelengths are due to the differences in equipment used.



Wavelength (nm)



Figure 3.2: Normalized absorbance (black), excitation (red) and emission spectra of (A) complex 15 in toluene, (B) complex 16 in DMF and (C) complex 17 in toluene.

Table 3.1: Ground state absorption, fluorescence excitation and emission spectralparameters for MPcs and their MPc-AuNP conjugates.

Complex	Solvent	$\lambda_{abs} (nm)$	λ_{exc} (nm)	$\lambda_{em} (nm)$
15	Toluene	694	694	703
15-AuNP		691	691	700
16	DMF	684	685	696
16-AuNP		682	683	693
17	Toluene	710	713	725
17-AuNP		699	700	708

abs = absorbance, exc = excitation, em = emission

3.2 Phthalocyanine-gold nanoparticle conjugates

3.2.1 Synthesis and characterization of AuNPs

TOABr-AuNPs were synthesized following a literature procedure [**31**], using TOABr as both the phase transfer agent and the protecting ligand. The nanoparticles were characterized using TEM, AFM, UV-vis spectroscopy and XPS.

The TEM image of TOABr-AuNPs is shown in **Figure 3.3A**. Analysis of the nanoparticle size by means of TEM evidenced the formation of spherical, non-aggregated nanoparticles with a particle size distribution in the range measuring 2-5 nm.



Figure 3.3: Transmission electron microscopy (TEM) image of (A) TOABr-AuNPs and (B) Pc-AuNP conjugate.

AFM results from **Figure 3.4 (ai, bi)**) show the surface topography of TOABr-AuNPs. An average roughness (Ra) value of 0.276 nm was obtained for AuNPs alone from **Figure 3.4 (bi)**. The histogram in **Figure 3.4 (ci)**, shows populations of AuNPs with size distribution from 4.5 nm and below in the section analyzed, to occur more frequently. These results are in agreement with the TEM results.



Figure 3.4: (a) 2D and (b) 3D AFM images (height profile), and (c) size distribution histograms of (i) TOABr-AuNPs and (ii) 17-AuNP.

The surface plasmon resonance (SPR) absorption band of TOABr-AuNP was determined from UV-Vis spectroscopy to be 525 nm in both DMF and toluene, **Figure 3.5**. The absorbance peak observed in **Figure 3.5** is in the range of 500–550 nm and typical for the surface plasmon resonance of gold nanoparticles with sizes less than 50 nm [**31,33,196**], thus confirming the AFM and TEM results.





Figure 3.5: UV-Vis spectra of (A) AuNPs (blue), complex 15 (black) and 15-AuNP (red) in toluene (B) AuNPs (blue), complex 16 (black) and 16-AuNP (red) in DMF and (C) AuNPs (blue), complex 17 (black) and 17-AuNP (red) in toluene.

3.2.2 Assembly of phthalocyanine-gold nanoparticle conjugates

Ligand exchange was used as a method for Pc attachment to the nanoparticles, where loosely bound TOABr ligands were partially exchanged by Pcs. To attach the Pc molecule to the gold nanoparticle surface, the Pc complexes were derivatized with arylthio moieties, **Scheme 3.2**, which provided direct linkage to the nanoparticle surface via self-assembly. The partial presence of TOABr is important since the presence of the bromine atom adds to the enhancement of spin-orbit coupling via the heavy atom effect [**33**]; hence increasing the population of the triplet state and increasing generation of singlet oxygen.



Scheme 3.2: Schematic illustration of the synthetic route for phthalocyanine-functionalized gold nanoparticles (Pc-AuNPs).

3.2.2.1 Synthesis and characterization of phthalocyanine-gold nanoparticle conjugates

Figure 3.3B shows the TEM image of Pc-AuNPs. A clear indication of agglomeration was observed from the TEM images of the conjugate with a size distribution in the range 6-9 nm, suggesting successful conjugation. The aggregation could be a result of the method used in preparing the samples for TEM since phthalocyanines readily form aggregates. The wide planar organic surface of the Pc molecule causes aggregation of the complexes in solution and in a solid state due to the π – π * stacking interactions [**197**]. Phthalocyanines form face-to-face-oriented H-aggregates and side-by-side-oriented J-aggregates. The former are characterized by blue-shifted absorption bands and are considered non-fluorescent, whereas the latter are characterized by red-shifted bands and are fluorescent [**198**]. The Pc molecules in the conjugate are most likely to

form irregular aggregates as a result of their flexible linkers, edge and terrace of the gold cores and the AuNP ligand and phase transfer agent, TOABr [**31**].

AFM results from **Figure 3.4** revealed pronounced differences of the surface topographies of the gold nanoparticles (**Figure 3.4** (**ai, bi**)) and the phthalocyanine-functionalized gold nanoparticles (**Figure 3.4.** (**aii, bii**)). The average roughness (Ra) value of 0.276 nm obtained for AuNPs alone increased to 1.290 nm for the Pc-AuNP conjugate. The increase may be due to aggregation in the presence of ZnPc derivative. The histogram in Figure **3.4** (**cii**) for AuNPs in the presence of Pc shows that there is domination by the larger sizes, with size distribution of up to 11 nm, showing increased aggregation and confirming successful conjugation.

The absorption spectra of Pc-AuNP conjugates, **Figure 3.5**, are the sum of the phthalocyanine and gold nanoparticles absorption spectra. For complexes **15** and **16**, **Figures 3.5A** and **3.5B**, small blue shifts of the Q band were observed after conjugation to gold nanoparticles, **Table 3.1**. The blue shifts were due to the engagement of S groups involved in conjugation to AuNPs.

Such small shifts have been reported for conjugation of a Co tetraamino (CoTAPc) with Ag or Au NPs [199]. Hence, the spectra in Figures 3.5A and 3.5B does confirm conjugation. A blue shift in the Q band of MPc complexes has been observed for complexes substituted with long chain thiol, arylthio or alkyl thio groups [32,34,78,200]. Figure 3.5C shows that there is significant broadening and blue shifting of the Q band for complex 17. In phthalocyanine chemistry, blue shifting and broadening of the Q-band in most cases is explained as a result of coplanar association of phthalocyanine rings progressing from monomers leading to aggregates. The most likely aggregates in phthalocyanines are the so called H aggregates (face to face) which result in blue shifting or broadening of the spectra. In the case of complex 17–AuNP, there is blue shifting but the shape of the Q band is not typical of aggregation. The blue shifting is also usually attributed to the presence of electron withdrawing ligands [201,202] and in this case, it is due to the engagement of S groups to gold nanoparticles as stated above. The differences between complex 17 and complexes 15 and 16 in terms of the extent of blue shifting may be explained in terms of the orientation of the molecular dipole of NPs with respect to MPc-nanoparticle axis as discussed before for other dye systems [203], hence the pronounced differences in the spectra of Pc complexes 15 (peripherally-substituted) and 17 (non-peripherally substituted).

In **Figures 3.5A** and **3.5B**, the surface plasmon resonance of complexes **15** and **16** show slight red shifts of the SPR bands, 530 and 534 nm respectively, compared to the resonance bands of TOABr-AuNPs and complex **17**-AuNP at 525 nm. This red-shift is an indication of aggregation [**210**] as also shown by TEM.

Figure 3.6 shows the absorption, fluorescence excitation and emission spectra of complex **16**-AuNP. The excitation spectrum is similar to the absorption spectrum (except for the SPR band) and is the mirror image of the fluorescence emission spectrum. The proximity of the absorption and excitation spectra for the Pc and Pc-AuNP conjugate suggests that the nuclear configurations of the ground and excited states were similar and not affected by excitation in DMF. No fluorescence was observed (as expected) from the TOABr-AuNPs. The same was observed for conjugates of complexes **15** and **17** and results are shown in **Table 3.1**.



Figure 3.6: Absorbance (black), excitation (red) and emission (blue) spectra of 16-AuNP in DMF.

In order to confirm the chemical composition of the conjugate, complex **16**-AuNP was further studied by XPS analysis and compared with complex **16**. A one cycle etch was performed on the **16**-AuNP to remove any adsorbed O_2 on the surface of the samples. The overview of the XPS spectra of the conjugate, **Figure 3.7A(ii)** showed the expected presence of C, O, N, S, Au and Br in **16**-AuNP while the elements; Zn, C, N, O and S existed in complex **16**, **Figure 3.7A(i)**. The S atoms belong to the part of the Pc designed for attachment to the AuNPs via self-assembly. The XPS spectra, **Figure 3.7B(i)** (expanded wide scan of **Figure 3.7A)**, show sulfur peaks at 163 eV (corresponding to S $2p_{1/2}$ and S $2p_{3/2}$) as well as an S 2s peak at 227 eV related to the thioether groups in the Pc. The Zn 2p peak, **Figure 3.7A(i)**, expected at 1023 and 1043 eV had a very low intensity in the Pc (as the atomic percentage concentration is low) thus it could not be detected in

the conjugate, therefore information on chemical shifts and possible interactions through charge transfer at the interface with the metal nanoparticles could hardly be extracted from the Zn 2p data. The presence of the Au 4f and Br 3d peaks. Figures 3.7A(ii) and 3.7B(ii), at binding energies of 84 and 64 eV indicate the presence of the Au and the capping agent in the conjugate. The XPS results show evidence of metallic gold (Au⁰) as expected for gold nanoparticles. The presence of the Pc was already confirmed through UV/Vis and fluorescence spectroscopy, Figure 3.6. Perhaps the most telling piece of evidence is the high resolution N 1s spectra acquired for complex 16, AuNPs and 16-AuNP, Figure 3.8. Figure 3.8A shows the deconvolution of the N 1s peaks for the Pc. Three, possibly four, peaks are observed. Two main peaks were expected due to the pyrollic nitrogens of complex 16 and the N co-ordinated to the metal center Zn. For the AuNPs, the deconvolution of the N 1s peaks is shown in Figure 3.8B. Two peaks, with one main peak, are observed and this set of spectra is markedly different to the N 1s for the Pc. The one main peak is expected due to the loosely bound TOABr on the AuNP surface. Figure 3.8C shows the deconvolution of the N 1s peaks for the conjugate, 16-AuNP. Three main peaks are observed and this set of spectra is markedly different to the N 1s for the Pc. Two main peaks were expected due to the pyrollic nitrogens of the complex 16 and the N coordinated to the metal center Zn, while a third is expected for the TOABr loosely bound to the AuNP surface.



Figure 3.7: XPS spectra of (A) wide scan for (i) complex 16 and (ii) complex 16-AuNP and (B) expanded wide scan for (i) complex 16, (ii) 16-AuNP and (iii) AuNP (the latter only in B)



Figure 3.8: High resolutions XPS scans for (A) complex 16 (B) AuNPs and (C) 16-AuNP

3.3 Remarks on chapter

Zinc phthalocyanines and their gold nanoparticle conjugates were successfully synthesized and characterized by various spectroscopic techniques. All phthalocyanine complexes gave spectroscopic data indicating high purity and in accordance with the predicted structures.

4. Photophysical and photochemical parameters

The photophysical and photochemical properties of the synthesized MPcs are discussed. For the MPcs, comparisons are made with respect to the presence of different substituents, substitution positions and interactions with AuNPs in the phthalocyanine-gold nanoparticle conjugates. The photophysical and photochemical parameters of complexes 15 and 17 were determined in toluene whereas those of complex 16 were in DMF because the complex was insoluble in toluene. Complexes 15 and 17 were compared to each other to study the effect of the substitution position (α/β) and complex 16 was compared to unsubstituted ZnPc. In these studies, it was therefore impossible to compare the three Pc complexes due to the employment of different solvents. The reason for the use of different solvents was provided in the experimental section.

4.1 Fluorescence spectra, quantum yields and lifetimes

4.1.1 Phthalocyanine derivatives

The nature and the environment of a fluorophore determine its fluorescence lifetime and quantum yield. 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 the fluorescence quantum yield (Φ_F).

Using a comparative method, the fluorescence quantum yields (Φ_F) of the Pcs, **Table 4.1**, were determined. The fluorescence quantum yields of complexes **15**, **16** and **17** are shown in **Table 4.1**. The value for complex **16** is significantly larger than that of unsubstituted ZnPc [**167**], and

also larger than for MPc complexes in general, [204] showing that the coumarin substituent enhances fluorescence in ZnPc complexes as suggested in the introduction, **Table 4.1**. The yields for complexes 15 and 17 are shorter than what is typical of Pcs [99], but such low Φ_F have been observed in toluene [205].

Complex	Solvent	$\Phi_{\rm F}$	$ au_{\mathrm{F}}^{a}\left(\mathrm{ns} ight)$	Φ_{T}	$ au_{\mathrm{T}}(\mu s)$	$\tau_0 (ns)$	Φ_{Δ}
15	Toluene	0.053	$2.24 \pm 0.02 (100\%)$	0.68	108	42	0.44
15-AuNP	Toluene	0.007	1.90 ± 0.02 (81%) 0.85 ± 0.03 (19%)	-	-	264	0.78
16	DMF	0.36	2.32. ± 0.01 (100%)	0.33	19	6	0.21
16-AuNP	DMF	0.11	2.15. ± 0.03 (88 %) 0.56 ± 0.04 (12 %)	-	-	19	0.41
17	Toluene	0.03	2.40 ± 0.01 (100 %)	0.51	50	68	0.33
17-AuNP	Toluene	0.003	0.88 ± 0.03 (74 %) 2.17 ± 0.04 (26 %)	-	-	275	0.54

 Table 4.1: Photophysical and photochemical data of phthalocyanine-gold nanoparticle

 conjugates

^a abundances in brackets

Fluorescence lifetimes (τ_F) were determined using the time correlated single photon counting (TCSPC) technique. The decay component spectrum of complex **17** was obtained from a

monoexponential fit, **Figure 4.1**, with a single lifetime, **Table 4.1**. Similar results were obtained for complexes **15** and **16**, **Table 4.1**.



Figure 4.1: Fluorescence decay curves of complex 17 (black) and complex 17-AuNP (blue) in toluene. Insert = TRES analysis of 17-AuNP in toluene.

4.1.2 Phthalocyanine-gold nanoparticle conjugates

Phthalocyanines are quenched by close proximity of AuNPs and a decrease in fluorescence quantum yields and fluorescence lifetimes has been reported [**31,196**]. It has also been reported that when a fluorophore is excited in the presence of a nearby metal it interacts with the free

electrons from the metal surface and modifies the fluorescence behavior by altering the electric field around the molecule [206]. This effect can either increase or decrease the fluorescence lifetimes depending on the geometry or distance between the metal and molecule [207]. The fluorescence quantum yields of the Pcs were significantly larger than those of the Pc-AuNP conjugates, **Table 4.1**.

The low Φ_F for the Pc-AuNP conjugates was attributed to the heavy atom effect of Au and Br of the TOABr-AuNPs, which encourages intersystem crossing to the triplet state and also due to the known quenching of Pc fluorescence by AuNPs which has been observed for ZnPc complexes substituted with long chain thiol groups [78]. The fluorescence decay curves of complexes 17 and 17–AuNP in toluene measured by TCSPC are shown in Figure 4.1.

The decay curves of **17** and **17**–AuNP were obtained from a monoexponential and a biexponential fit respectively, suggesting two different emitting species for the latter. The Pc–AuNP conjugate had a faster decay than the Pc. The lowering of the phthalocyanine lifetime has been suggested [**31**] to arise from the close packing of phthalocyanines on the gold nanoparticle surface or from the interaction between phthalocyanines and gold nanoparticles. Thus, the two lifetimes for the Pc–AuNP complexes, **Table 4.1**, may correspond to the differently packed Pc complexes onto the gold nanoparticle surfaces.

Time-resolved emission spectroscopy (TRES) was conducted to determine the origin of the two lifetimes obtained for **17**-AuNP conjugates in **Table 4.1**. TRES results were in qualitative and quantitative agreement with TCSPC measurements and the biexponential correlation model provided an adequate fit to the data indicating the presence of two emitting species in the conjugate. The wavelength-dependent data from the TRES analysis, **Figure 4.1** (insert), showed
peaks with wavelengths, at 706 and 708 nm. The latter is at the same wavelength as the emission peak for **17**–AuNP (**Table 3.2**). The slight difference in the wavelengths is attributed to different packing of Pc molecules on the AuNPs. A plausible explanation for our findings is that there may be two different conjugation systems due to different orientation and packing of Pc molecules on the AuNPs surfaces.

Fluorescence radiative lifetimes (τ_0) are directly related to absorption coefficients and excited state lifetimes (τ_F) and are used to explain the decrease in lifetime of Pcs in the presence of AuNPs. τ_0 values were estimated from the fluorescence quantum yield (Φ_F) and lifetime (τ_F) using **Equation 4.1** [**208**]:

$$\tau_0 = \tau_F / \Phi_F \tag{4.1}$$

Large τ_0 values have been obtained for various Pcs [209] and hence the large values obtained for complexes 15 and 17 in Table 4.1 were anticipated. The spectral behavior of fluorophores is sensitive to their environment. When a fluorophore is excited in the proximity of a metal, it interacts with the free electrons from the metal surface and modifies the fluorescence behavior by altering the electric field around the molecule [206]. This effect can either enhance or decrease the fluorescence lifetimes depending on the geometry or distance between the metal and the molecule [207]. The molecule can therefore be viewed as an oscillating dipole in which the lifetime will increase when the oscillating dipole is not in line with the reflected field and decreases in τ_0 observed in the presence of the gold nanoparticles suggests an uncorrelated field between the MPcs and AuNPs. The fluorescence quenching of both complexes could also be due

to electron or energy transfer, enhanced intersystem crossing, or enhanced internal conversion in Pc-AuNP conjugates [**31,33**].

4.2 Triplet state quantum yields and lifetimes

4.2.1 Phthalocyanine derivatives

The triplet quantum yield is the measure of the fraction of absorbing molecules that undergo intersystem crossing to the triplet state. The ability of an excited state phthalocyanine to go from the singlet state to the triplet state is a prerequisite for it to generate singlet oxygen from ground state molecular oxygen. The efficiency of a phthalocyanine as a photosensitizer is determined by its triplet state quantum yield (Φ_T) and lifetime (τ_T) and these were determined by laser flash photolysis in argon saturated solutions of the Pc complexes in toluene or DMF. Table 4.1 gives the triplet state parameters, Φ_T and τ_T , of complexes 15, 16 and 17. Figure 4.2 shows the triplet decay curve of complex 15, which is similar to those of the other complexes. All triplet decay curves showed first order kinetics. Triplet state quantum yields of 0.68, 0.33 and 0.51 were obtained for complexes 15, 16 and 17 respectively. Φ_T was larger for complex 15 at 0.68 than for complex 17 at 0.51 suggesting quenching at α substitution. For complex 16 in DMF $\Phi_{\rm T}$ = 0.33, is smaller than Φ_T of ZnPc in DMF at 0.58 [191], showing the quenching effect of the coumarin substituent. The triplet state lifetime (τ_T), **Table 4.1**, was longer for the peripherally substituted complex 15 ($\tau_T = 108 \ \mu s$) than the non-peripherally substituted complex 17 ($\tau_T = 50 \ \mu s$). This result contradicts the fact that high Φ_T corresponds to low τ_T . The short lifetime obtained for complex 16 ($\tau_T = 19 \mu s$) was anticipated due to its enhanced fluorescence quantum yield. However, these yields offer a good possibility of singlet oxygen generation.



Figure 4.2: Triplet state decay curve of complex 15 in toluene. Excitation wavelength: 695 nm

4.2.2 Phthalocyanine-gold nanoparticle conjugates

Table 4.1 shows that no triplet state parameters were determined for the phthalocyanine-gold nanoparticle conjugates. This result may be attributed to a short triplet lifetime as a result of the heavy atom effect of Br and Au in the TOABr-AuNPs. However, the singlet oxygen quantum yield of the conjugates could still be determined as will be shown below.

4.3 Singlet oxygen quantum yields

4.3.1 Phthalocyanine derivatives

Singlet oxygen is formed via energy transfer between the triplet state of a Pc and ground state molecular oxygen. Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen including; triplet excited state energy and lifetime, ability of substituents and solvents to quench the singlet oxygen and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen. Singlet oxygen quantum yields (Φ_{Δ}) were determined in toluene or DMF using DBPF as a chemical quencher and zinc phthalocyanine as the standard. The disappearance of DPBF at 416 nm was monitored using a UV/Vis spectrometer, **Figure 4.3**. The singlet oxygen quantum yields, **Table 4.1**, obtained for complexes **15**, **16** and **17** were 0.44, 0.21 and 0.33. No changes in the Q-band were observed in **Figure 4.3**, confirming that the Pc complex was not degraded during the studies.



Figure 4.3: Degradation of DPBF in the presence of complex 17 in toluene. Time interval: 5

s.

4.3.2 Phthalocyanine-gold nanoparticle conjugates

Phthalocyanine-gold nanoparticle conjugates also exhibited the ability to generate singlet oxygen, Figure 4.4, with higher singlet oxygen quantum yields compared to Pcs alone, Table 4.1. The singlet oxygen quantum yields were significantly enhanced with yields of 0.78, 0.41 and 0.54 for complexes 15-AuNP, 16-AuNP and 17-AuNP. No changes in the Pc-AuNP spectra were observed in Figure 4.4, confirming that the Pc-AuNP complex was not degraded during the studies. The Pc-AuNP conjugates generate singlet oxygen with significantly higher quantum vields than the Pc alone. Table 4.1, due to the presence of the gold atoms and in part due to the bromine atom from an association with the phase transfer agent, TOABr. This results in an increase in the energy transfer to the triplet state through enhanced spin-orbit coupling via the heavy atom effect [33]. When comparing Φ_{Δ} value of complex 16 ($\Phi_{\Delta} = 0.21$) to ZnPc ($\Phi_{\Delta} =$ 0.56) the yield is much lower for the former, **Table 4.1**, corresponding to its high fluorescence quantum yield. For complexes 15 and 17, the yields are relatively high in the absence and presence of gold nanoparticles. Even though the singlet oxygen quantum yield of complex 16alone ($\Phi_{\Delta} = 0.21$) is low, the presence of AuNPs significantly enhances this value ($\Phi_{\Delta} = 0.41$), thus making its use as a photosensitizer feasible.



Figure 4.4: Spectral changes during the degradation of DPBF in toluene using 17-AuNP. Time interval: 10 s.

4.4 Remarks on chapter

The photophysical and photochemical properties of phthalocyanine and phthalocyanine-gold nanoparticle conjugates were determined. The effects of the gold nanoparticles on the spectral characteristics of the phthalocyanines varied with substitution position (α/β). Interaction of MPcs with nanoparticles led to significant fluorescence quenching. However, the interaction between the gold nanoparticles and phthalocyanines does not restrict the formation of excited singlet and triplet states and hence the formation of singlet oxygen. The ability to generate singlet oxygen makes these complexes suitable for phototransformation of environmental pollutants either in solution or on solid supports. In further work, these photoactive molecules will be incorporated in electrospun fibers and characterized as discussed in the next chapter.

5. Electrospun polymer fibers

This chapter reports on the microscopic, spectroscopic, photophysical and photochemical properties of phthalocyanine and phthalocyanine-gold nanoparticle functionalized electrospun polymer fibers.

5.1 Influence of electrospinning conditions on morphology of polymer fiber

Electrospun polymer fibers are of industrial and scientific interest due to their long lengths, small diameters, porosity and high surface area per unit volume. Although electrospinning is a relatively simple process, many variables affect fiber quality, thus adding complexity to the method and making process optimization tedious. The structure and morphology of the electrospun polymer materials are determined by a synergetic effect of solution, process and ambient parameters. Development of useful electrospun polymer fiber applications requires a thorough knowledge of the parameters that govern the electrospinning process and their effect on the resultant fibers. In this work prior to functionalization of polymer fibers with phthalocyanines or phthalocyanine-gold nanoparticle conjugates, the effect of some electrospinning conditions (polymer concentration, conductivity, viscosity, solvent ratio, relative humidity) on fiber diameter and morphology were investigated using polycaprolactone (PCL) as a model polymer. In this study, we determine which parameters have the greatest effect on fiber diameter and are best for controlling the final morphology of the as-spun fibers for the development of multi-functional polymer fibers.

5.1.1 Effect of polymer viscosity and conductivity on fiber morphology

Polymer solution properties such viscosity and conductivity play a significant role in the electrospinning process and the resultant fiber diameter and morphology. The electrical property

of the solution, surface tension and viscosity will determine the amount of stretching of the solution. The molecular weight of the polymer represents the length of the polymer chain, which in turn has an effect on the viscosity of the solution since the polymer length will determine the amount of entanglement of the polymer chains in the solvent. **Table 5.1** shows that solution viscosity and conductivity are directly proportional to the polymer concentration and the higher the polymer concentration, the larger the resulting fiber diameter. Our results are in agreement with findings by other researchers [**212**].

 Table 5.1: Effect of polymer solution viscosity and electrical conductivity of different

 polycaprolactone (PCL) concentrations.

Polymer concentration (wt%)	Viscosity (cP)	Conductivity (mS/cm)	Fiber diameter (nm)
13	2307	0.287	315 ± 80
15	4071	0.301	400 ± 74
17	5384	0.168	525 ± 88

5.1.2 Effect of polymer concentration at various humidity conditions on fiber morphology

The humidity of the electrospinning environment may have an influence on the polymer solution during electrospinning as it determines the rate of evaporation of the solvent in the polymer solution. Results in **Table 5.2** show a trend that clearly indicates an increase in fiber diameter with increasing % relative humidity (RH). This is consistent with what has been reported before [**213,214**]. However, increasing the humidity from 20 % RH to 70% RH had no significant effect on fiber morphology as shown in **Figure 5.1**.

Table 5.2: The average fiber diameter (nm) as a function of polymer concentration and relative humidity, solvent ratio 50:50 AA:FA.

Polymer concentration (wt%)	20% RH	50% RH	70% RH
13	310 ± 50	392 ± 80	430 ± 40
15	337 ± 45	400 ± 74	413 ± 98
17	459 ± 22	525 ± 88	531 ± 89

RH: 20%RH: 50%RH: 70%13Image: Simple state stat

Figure 5.1: SEM images of 13, 15 and 17 wt% PCL electrospun at different relative humidities.

5.1.3 Effect of solvent ratios on polymer solutions viscosity and conductivity

Polycaprolactone was dissolved in solvent mixtures with different ratios of formic acid (FA) which acts as a solvent for the polymer and acetic acid (AA) which is a non-solvent but is required for electrospinning to occur. The effect of solvent ratios on polymer conductivity, viscosity and fiber diameter is shown in **Table 5.3**.

Solvent ratio (AA:FA)	Viscosity (cP)	Conductivity (mS/cm)	Fiber diameter (nm)
1:9	2849	0.218	392 ± 104
5:5	4595	0.286	400 ± 74
7:3	5615	0.321	1162 ± 254

 Table 5.3: Effect of solvent ratios on polymer solutions viscosity and conductivity

Results show an increase in polymer conductivity, viscosity and fiber diameter with an increase in AA concentration. This observation might be explained by a combined effect of the dielectric constants and the surface tension of the solution. Formic acid has a relatively high dielectric constant resulting from its high polarity which largely determines the charge distribution in the jet, whereas acetic acid has a much lower dielectric constant. The higher the formic acid content, the higher the dielectric constant and viscosity and the more the electric field pulls at the polymeric solution. It was observed that a decreasing surface tension resulting from increasing conductivity facilitated the formation of steady Taylor cones at higher viscosity resulting in large fiber diameters.

5.1.4 Effect of solvent ratios in polymer solutions and humidity conditions

Results in **Table 5.4** show a clear trend of an increase in fiber diameter at high FA content. This can be attributed to the fact that formic acid is the solvent used to dissolve the polymer. Reduction in its content in the solvent mixture resulted in an unforeseen high concentration of the polymer in solution leading to the larger fiber diameters observed for solvent ratios 7:3 and 9:1. In the case of solvent ratios, these results do show that humidity has a large effect on fiber morphology as no clear trends or definitive comparisons could be made with regards to fiber diameter for low formic acid contents.

Table 5.4: The average fiber diameters (nm) as a function of solvent ratio and relative humidity, PCL concentration at 13 wt%.

Solvent ratio AA:FA	20% RH	50% RH	70% RH
1:9	230 ± 40	315 ± 104	413 ± 100
5:5	310 ± 50	392 ± 80	430 ± 98
7:3	1162 ± 254	528 ± 186	520 ± 130
9:1	863 ± 190	570 ± 254	653 ± 254

Thus by optimizing the above electrospinning conditions, suitable electrospun polymer fibers functionalized with phthalocyanines and phthalocyanine-gold nanoparticle conjugates possessing appropriate morphology can be obtained. Such functionalized fibers can then be characterized and applied in the photodegradation of environmental pollutants which are the core aims of this work.

5.2 Characterization of electrospun polymer fibers functionalized with zinc phthalocyanines and their physico-chemical behavior

This section discusses the characterization of phthalocyanine and phthalocyanine-gold nanoparticle functionalized fibers. **Figure 5.2** shows a diagrammatic representation of the electrospinning of pure and functionalized polymer fibers. Polystyrene was used for conjugation to complexes **15** and **16**, whereas poly(methyl methacrylate) (PMMA) was used for conjugation to complex **17**. As explained before, PMMA was found to be unsuitable for photocatalytic applications due to poor mechanical strength and its tendency to form a gel in water, eventually leading to the leaching out of the Pc and Pc-AuNP complexes. Due to these reasons, polystyrene (PS) was chosen as the polymer of choice for complexes **15** and **16**.



Figure 5.2: Diagrammatic representation of the electrospinning of non-functionalized and functionalized polymers.

5.2.1 Microscopic characterization

Two geometric properties of polymer fibers (fiber diameter and morphology) were assessed using SEM technique. The average diameters of the non-functionalized and functionalized electrospun fibers were determined using Cell^D software from Olympus. Both nonfunctionalized and functionalized PMMA and PS fibers consisted of continuous single fibers with defect-free fiber surfaces and controllable fiber diameters as shown in **Figure 5.3** and **Figure 5.4**.



Figure 5.3: SEM micrographs of (A) PS alone, (B) PS/15 and (C) PS/15-AuNP fibers.



Figure 5.4: SEM fiber mats of (A) PMMA, (B) PMMA/17 and (C) PMMA/17-AuNP.

The fiber diameters obtained for polystyrene alone ranged from $1780-2120 \text{ nm} (1.78-2.12 \mu \text{m})$. The fiber diameters obtained in this study were smaller than those obtained by Pai *et al.*, **[215]** using DMF as a solvent, instead of a solvent mixture of DMF:THF used in this study. This result was expected since Pai and co-workers **[215]** not only used a different solvent but a higher polymer concentration, 30 wt% instead of 25 wt% used in this work. This result is consistent with the theory which predicts that fiber diameter depends allometrically on solution viscosity **[213,214]**. **Table 5.5** shows the average diameters of PMMA and PS fibers functionalized with phthalocyanines and phthalocyanine-gold nanoparticles. In the case of non-functionalized PMMA fibers, the diameters ranged from 680-810 nm (0.68-0.81 μ m).

 Table 5.5: Average fiber diameter of electrospun polymer fibers functionalized with

 phthalocyanines and phthalocyanine-gold nanoparticle conjugates

Electrospun fiber	Average diameter/µm	Standard deviation
PS	1.82	0.31
PS/ 15	1.98	0.39
PS/ 15-AuNP	1.64	0.21
PS/16	2.82	0.75
PS/16-AuNP	2.04	0.33
PMMA	0.70	0.30
PMMA/17	0.71	0.40
PMMA/17-AuNP	0.53	0.60

PS/Pc and PS/Pc-AuNP solutions are more viscous than the polymer solution alone; probably due to the bulky Pc such that viscosity overcomes conductivity hence larger fiber diameters were obtained compared to the non-functionalized fibers. No significant effect on average fiber diameter of PMMA was observed after functionalization with Pc, **Table 5.5**. However functionalization of PMMA fibers with Pc-AuNP resulted in a significant decrease in average fiber diameter. Pcs are high charge density aromatic macromolecules and AuNPs increase conductivity which increases the extent of fiber stretching during electrospinning. The addition of gold nanoparticles resulted in a higher surface charge density of the solution jet, bringing more electric charges to the jet. As the charges carried by the jet increase, higher elongation forces are imposed to the jet under the electrical field, consequently leading to smaller fiber diameters; therefore polymer/Pc-AuNP has a smaller fiber diameter than polymer/Pc, **Table 5.5**. The formation of a polystyrene polymer containing unsubstituted ZnPc has been reported before [**127**]. The fiber morphology was found not to be depended on the nature of the MPc complex [**127**] or its substituents.

5.2.2 Spectroscopic characterization

5.2.2.1 Raman spectral characterization

The Raman spectral studies were done in order to ascertain the Van der Waals electronic interactions between the polymer (PS) and the phthalocyanines and to further confirm the presence of the Pc complexes in the fiber. Polystyrene was used for these studies due to its extensive aromatic system capable of π - π interaction with the Pc. Figure 5.5 shows the Raman spectra of PS and PS/16-AuNP. The peaks between 2500 and 3000 cm⁻¹ in the PS fiber Raman spectrum, were attributed to stretches due to the aromatic ring [216].



Figure 5.5: Raman spectra of PS fiber (black) and PS/16-AuNP (red).

Any electronic interaction between PS and Pc complexes in this study are most likely to involve the π -electrons of their aromatic systems. Observed changes in peak positions and/or splitting of the PS fiber bands in **Figure 5.5** in the PS/Pc-AuNP composite fiber suggest interaction between PS and Pc, which might be due to the π - π interaction of the PS and Pc aromatic systems.

5.2.2.2 X-ray diffraction spectral characterization

In nanofiber work, XRD methods are useful in studying the crystalline nature of fibers, changes in crystalline morphology as well as chain orientation in electrospun fibers. In this work, XRD was used to determine the presence of Pc and Pc-AuNP complexes in the fiber. Results in **Figure 5.6** show metastable amorphous PS fibers, consistent with the notion that electrospinning being a rapid process generally retards crystallite growth [**217**].



Figure 5.6: XRD diffraction patterns of complex 16 and electrospun PS fibers, PS/ZnTCMPc (PS/16) and PS/ZnTCMPc-AuNP (PS/16-AuNP)

XRD results confirmed incorporation of the complexes **16** and **16**-AuNP into the PS fibers with the Pc diffraction peak at 20° being present in the functionalized fiber with or without AuNPs. However, the influence of AuNPs could not be observed directly in **Figure 5.6**. The Pc alone showed a typical broad peak near $2\theta = 24.4^{\circ}$. This peak is close to the (002) reflection of carbon [**218**]. The broad nature of this peak underlines the substantial amorphous nature of Pc.

5.2.2.3 UV-visible spectral characterization

Polymeric matrices doped with phthalocyanines and gold nanoparticles show specific absorption in the UV-visible region owing to discrete energy levels and specific states of nanoparticles and Pcs. So, UV-Vis spectroscopy can be considered as a useful characterization technique for polymeric matrices containing Pcs and AuNPs. Figure 5.7 shows the electronic absorption spectra of polymer fibers functionalized with the Pc complexes 15, 16 and 17 and their AuNP conjugates in comparison with the spectra of the complexes in solution. The non-functionalized fibers showed no obvious absorption band. The spectra of the functionalized fibers were recorded from the fiber fixed on a glass slide. Figure 5.7 shows the electronic absorption spectra of the Pc complexes in solution exhibiting Q-band absorptions at 694, 684 and 710 nm for complexes 15, 16 and 17 respectively. There is significant broadening and blue shifting of the Qband in the peripherally substituted complexes, complexes 15 and 15-AuNP, Figure 5.7A, in the polymeric fiber and 16-AuNP, Figure 5.7B(ii). This broadening and shifting of the O band indicates aggregation. The strong π - π interaction due to stacking of the rings in PS/Pc and PS/Pc-AuNP fibers leads to broadening of the Q-band as observed in Figure 5.7A and 5.7B. The UV-Vis spectra of PS/Pc-AuNP, Figures 5.7A(ii), 5.7B(ii) and 5.7C(ii), show the characteristic surface plasmon resonance (SPR) band of AuNPs indicating successful incorporation of the phthalocyanine-gold nanoparticle conjugate in the polymeric matrix.



Figure 5.7: UV-Vis absorbance spectra of (A) 15 in toluene, (B) 16 in DMF and (C) 17 in toluene: (i) Pc alone (red) and polymer/Pc (black); (ii) Pc-AuNP (black) and polymer/Pc-AuNP (red)

5.3 Photophysical and photochemical behavior of phthalocyanine and phthalocyanine-gold nanoparticle functionalized polymer fibers

The photophysical and photochemical properties of phthalocyanine-functionalized polymer fibers have been reported to be maintained within the solid polymeric matrix [219]. In this work, the fluorescence behavior of functionalized polymer fibers was assessed as well as their photoactivity with the view of fabricating multi-functional fibers. **Table 5.6** gives the fluorescence and singlet oxygen quantum yields of Pcs and Pc-AuNPs in solution as well as their corresponding quantum yields estimated within the fiber matrices. This comparison study helps in clearer understanding of the fluorescence behavior and photoactivity of the complexes in solution and in polymeric matrices for successful fiber applications. The Φ_{Δ} values for functionalized fibers in **Table 5.6** are estimates due to light scattering. The singlet oxygen quantum yields of functionalized PMMA fibers could not be determined in water because of the instability of the polymer in aqueous media.

Complex	$\Phi_{ m F}$	Φ_{Δ}		Polymer
		Solution ^a	PS fiber (water)	
ZnPc	0.30 (DMF) [167]	0.56 (DMF)	0.14	PS
		0.58 (toluene)	b	PMMA
15	0.035	0.44 (toluene)	0.13	PS
15-AuNP	0.007	0.78 (toluene)	0.28	PS
16	0.36	0.21 (DMF)	0.09	PS
16-AuNP	0.11	0.41 (DMF)	0.15	PS
17	0.053	0.33 (toluene)	b	PMMA
17-AuNP	0.003	0.54 (toluene)	b	PMMA

Table 5.6: Fluorescence and singlet oxygen quantum yields of phthalocyanines and phthalocyanine-gold nanoparticle conjugates in solution and within solid polymer fibers

^a From Table 4.1 ^b value not determined

5.3.1 Fluorescence behavior of phthalocyanine and phthalocyanine-gold nanoparticle conjugates within polymeric matrices

The ability of the Pc complexes to fluoresce within the fiber matrix was examined using fluorescence microscopy by exciting the functionalized fibers in the Q-band region by a high-voltage mercury lamp, **Figure 5.8**. **Figure 5.8** shows the fluorescence images of complexes 16 and 16-AuNP in the PS fiber matrices. It was observed that the fluorescence emission was significantly more intense for PS/16 than PS/16-AuNP. This result was anticipated due to the

quenching nature of gold nanoparticles on Pc fluorescence. No fluorescence was observed for the non-functionalized fibers. **Figure 5.8** shows uniformity in emission intensity along all the fibers suggesting homogenous dispersion of complexes **16** and **16**-AuNP within the fiber matrix. The results in **Figure 5.8** show that fluorescence is maintained in the fiber and thus the ability of these fibers to fluorescence offers possibilities for potential application in gas sensing [**220**].



Figure 5.8: Fluorescence micrographs of (A) PS/16 and (B) PS/16-AuNP functionalized fibers.

5.3.2 Singlet oxygen generation behavior of functionalized fibers

The ability of the Pc and Pc-AuNP complexes to generate singlet oxygen within PMMA fiber matrices was determined using DPBF as a singlet oxygen quencher. Since functionalized PMMA fibers were unstable in aqueous media, hexane was used to determine the ability of complexes **17** and **17**-AuNP to generate singlet oxygen. **Figure 5.9** shows a typical degradation of DPBF in hexane when PMMA/**17**-AuNP composite fiber was used. No Φ_{Δ} values were calculated. Similar

changes were observed when PMMA/17 fiber was employed in the absence of AuNPs. This demonstrates that the MPcs within the fiber matrix are still capable of generating singlet oxygen.



Figure 5.9: Spectral changes during degradation of DPBF using PMMA/17-AuNP in hexane. Time interval: 30 seconds.

The fact that the Pc showed photoactivity within the fiber matrix suggests that not all the Pc molecules are completely encapsulated within the fiber but are found equally around the large exposed surface area of the fiber. The Pc did not leach out of the fiber into the solution as evidenced from the Q-band region of the sample solutions during photolysis. The complexes were also insoluble in hexane. This confirms once again the bound nature of the MPcs within the fiber matrix.

The generation of singlet oxygen in the functionalized fibers was also monitored using ADMA as a singlet oxygen quencher in aqueous media since the fibers are intended for application in photocatalysis. **Figure 5.10** shows the degradation profile of ADMA in solutions containing PS

fibers functionalized with complex 15-AuNP in water upon irradiation.



Figure 5.10: UV-Vis spectra changes observed on photolysis of ADMA in water with PS/15-AuNP. Time interval: 1 min.

Similar spectral changes were observed for PS/15, PS/16 and PS/16-AuNP. The absence of a Qband in the spectra is evidence that the Pc complexes did not leach out of the fiber since they were bound in the fiber matrix and are water insoluble. It is clear that the presence of the Pc complexes in the fiber matrix is essential for the production of singlet oxygen as no degradation of ADMA was observed under the same conditions when the PS fibers alone were used. The estimated singlet oxygen quantum yields obtained in the fibers, **Table 5.6**, are significantly lower than the Φ_{Δ} obtained in solution. This reduction in Φ_{Δ} in protic solvents has been observed [190] and has been explained to be as a result of interactions between the vibrational levels of the solvent molecules and the electronic or vibrational levels of singlet oxygen resulting in deactivation of the singlet oxygen in such solvents. This result can also be explained by the fact that there is an alteration of the Pc's photophysical and photochemical properties when constrained within the environment of a polymeric matrix, hence a direct correlation between the Pc complexes' behaviour in solution and in a solid fiber matrix cannot be feasible [**219**]. The results nonetheless, show that the photosensitizer-nanoparticle conjugates are efficient catalysts for the generation of singlet oxygen species.

Singlet oxygen quantum yields of complexes **15** and **16** were estimated to be 0.04 and 0.09 when used as solids (not in polymer fibers) for the degradation of ADMA in water. These low yields are most likely to be due to aggregation in aqueous media compared to when embedded on a fiber as has been reported before [**127**]. The Φ_{Δ} of the Pc-AuNP complexes could not be determined because the conjugates formed a cloudy suspension in water when used without a fiber support. These results show the importance of supporting the conjugates in a fiber matrix for successful photocatalytic applications using functionalized electrospun polymer fibers.

5.4 Surface area and porosity studies

Electrospun nanofibers are highly porous and therefore have very large surface-to-volume ratios, a property central to their application in filtration, chemical sensing, catalysis and tissue engineering. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were employed to determine surface area and porosity of the polymer nanocomposites, respectively. During electrospinning, pores on nanofibers are created when both water and solvent eventually evaporate. The BET surface areas, BHJ pore volumes and BHJ pore sizes of the nanocomposites are compiled in **Table 5.7**.

Sample	S_{BET}/m^2g^{-1}	Pore size/ nm	Total pore volume	Fiber diameter
			(cm ³ g ⁻¹)	(µm)
PS	60.6	33.4	0.50	1.82
PS/16	45.9	15.3	0.17	2.82
PS/16-AuNP	51.2	21.2	0.27	2.04

Table 5.7: Pore structure parameters of functionalized PS fibers

^a S_{BET}: BET Specific Surface Area

The surface area and pore structure parameters of PS are significantly higher than those of the functionalized fibers, **Table 5.7**. From the results in **Table 5.7**, it is believed that PS/Pc-AuNP is much more effective in increasing specific surface area and pore volume than PS/Pc. In this study, all electrospinning parameters were constant and hence any pore structure properties could be attributed to the strength of solvent-polymer interaction which would have an effect on solvent evaporation resulting in the control of pore structure. Based on the surface area and porosity data in **Table 5.7**, it was assumed that the fiber diameter, rather than fiber morphology contributes most to specific surface areas and porosity; hence PS fibers with the smallest fiber diameters had the largest values for the pore structure parameters and surface area. Such porous behavior of the polymeric nanomaterials would facilitate organic adsorption of organic pollutants from aqueous media, consequently accelerating their photodegradation over the catalyst [221,222]. This adsorptive property is an advantage to enforce heterogeneous photoactivity when Pc complexes are immobilized on a polymer fiber support. The porous structure and higher surface areas of PS functionalized fibers are thus beneficial to photoactivity via enhancing adsorption, which is a rate determining step in the heterogeneous photocatalytic reaction.

Therefore a combination of adsorption and heterogeneous photocatalysis makes photooxidation effective for the removal of organic pollutants in aqueous environments.

5.5 Thermal analysis

The thermal stability of the electrospun fibers was studied using thermal gravimetric analysis (TGA). **Figure 5.11** illustrates typical TGA thermograms of weight loss as a function of temperature at 150 – 550 °C. The difference in weight loss percentage between 150 and 350 °C, **Figure 5.11A**, between PS/Pc-AuNP, PS and PS/Pc is due to solvent loss. The degradation temperature was found to vary as a result of functionalization and **Figure 5.11** shows that the thermal stability of the functionalized fibers was higher than that of pure PMMA (**Figure 5.11A**) or PS (**Figure 5.11B**) and degradation temperature is significantly shifted to higher values on functionalization. These results indicate that there are interactions between the polymers and the Pc complexes and may be attributed to the possible hinderance effect of the Pc complexes on the mobility of the polymer chains. For polymer/Pc fibers, this increase in stability may be attributed to the higher thermal stability of Pcs and the higher thermal conductivity of gold nanoparticles compared to pure polymers as heat will be more diversely distributed in the composite fibers.



Figure 5.11: TGA thermograms of (A) PS (black), PS/16 (blue) and PS/16-AuNP (red) and (B) PMMA (black), PMMA/17 (blue) and PMMA/17-AuNP (red)

5.6 Remarks on this chapter

The photophysical and photochemical properties of phthalocyanine and phthalocyanine-gold nanoparticle conjugates incorporated in polymeric matrices were studied. The fluorescence behavior of the Pc and Pc-AuNP was maintained in composite fibers. The singlet oxygen generating abilities of the phthalocyanines and phthalocyanine-gold nanoparticle were maintained in the solid fibers, thus these polymeric fiber materials incorporating these complexes could be promising materials for the photo-conversion of environmental pollutants such as 4-chlorophenol and Orange G especially in aqueous media. These applications of functional fabric materials are discussed in the next chapter.

6. Phototransformation of environmental pollutants

This chapter reports on the application of Pc and Pc-AuNP functionalized fibers as photocatalysts for the phototransformation of the organic pollutants, 4-chlorophenol and Orange G.

6.1 Photocatalytic applications of functionalized fibers

Phthalocyanines can be employed as photocatalysts either in solution or in their solid state as well as when dispersed in solid support systems [103,223,224]. In this work, the use of electrospun polymer fibers functionalized with phthalocyanines and phthalocyanine-gold nanoparticle conjugates is explored for the degradation of environmental pollutants (4-chlorophenol and Orange G) in aqueous media. Functionalized electrospun fibers of polystyrene were found to be water-insoluble and porous, thus more promising in photocatalytic applications in aqueous systems, hence they were the polymer of choice.

6.1.1 Photodegradation of 4-chlorophenol

Electrospun polystyrene fibers functionalized with a phthalocyanine (PS/15) and a phthalocyanine-gold nanoparticle conjugate (PS/15-AuNP) were applied as examples for the photoconversion of 4-chlorophenol in aqueous media. The efficiency of the photoconversion of 4-CP with electrospun fibers functionalized with complexes 15 and 15-AuNP was compared with that of other Pc electrospun fiber supports that have been applied in the photoconversion of 4-chlorophenol.

Figure 6.1 shows the electronic absorption spectral changes observed upon the photooxidative degradation of 4-chlorophenol using the PS/15-AuNPs. When the pure PS polymer fiber alone was used as a control, no spectral changes of the aqueous 4-CP solution were observed indicating that the Pc complexes were responsible for the photodegradation. The fiber was suspended in solution in small pieces for these studies. Similar spectral changes were observed for PS/15. The 4-chlorophenol peaks at 243 and 297 nm decrease in intensity during irradiation in the presence of Pc or Pc-AuNP functionalized fibers suggesting conversion of 4-chlorophenol to its photolysis products. The products are known to be hydroquinone ($\lambda_{max} \sim 250$ nm) and benzoquinone ($\lambda_{max} \sim 227$ nm) are observed in Figure 6.1. The hydroquinone peak is not very pronounced in Figure 6.1. Our findings are in agreement with what has been reported in literature for the degradation of 4-chlorophenol in the presence of Pcs and other photosensitizers [127,224].



Figure 6.1: Electronic absorption spectra changes of $3.58 \times 10^{-4} \text{ mol } \text{L}^{-1}$ 4-chlorophenol in the presence of 10 mg PS/15-AuNP. The spectra were recorded at 5 min intervals.

The photodegradation of 4-CP using PS/15 and PS/15-AuNP showed first order kinetics, **Figure 6.2** for PS/15-AuNP, as observed by Kluson *et al* for the photodegradation of 4-chlorophenol using a sulphonated Al phthalocyanine [**225**].



Figure 6.2: Effects of initial concentration of 4-chlorophenol on its rate of degradation.
Concentrations were monitored at 243 nm. Starting concentrations (a) 2.72 x 10⁻⁴ mol L⁻¹,
(b) 3.58 x 10⁻⁴ mol L⁻¹ and (c) 4.36 x 10⁻⁴ mol L⁻¹. Amount of functionalized fiber: 10 mg PS/15-AuNP.

Reaction rates, rate constants and half-lives evaluated from **Figure 6.2** are listed in **Table 6.1**. The observed rate constant (k_{obs}), **Table 6.1**, decreased with an increase in concentration. The values of k_{obs} listed in **Table 6.1** for 4-CP transformation using PS/15-AuNP. The values in **Table 6.1** are larger than those reported using PS/ZnPc, PS/LuTPPc (TPPc= tetraphenoxy phthalocyanine) [127]. For 1.56×10^{-4} mol L⁻¹ 4-CP, k_{obs} values of 0.0006 min⁻¹ and 0.0231 min⁻¹ were obtained for PS/ZnPc and PS/LuTPPc respectively whereas 0.1146 min⁻¹ was obtained for PS/15-AuNP. The PS/15-AuNP showed greatly enhanced photocatalytic oxidation of 4-CP compared to PS/15 due to the effect of AuNPs on production of singlet oxygen as well as the increased surface area of the polymer fibers due to smaller fiber diameters. Pc-AuNP functionalized fibers have large surface area that would enhance the catalytic activity of the functional molecules immobilized on them.

Table 6.1: The rate, rate constant (k_{obs}) and half-life $(t_{1/2})$ of various initial concentrations of 4-chlorophenol using PS/15-AuNP. Values in brackets are when PS/15 was employed.

Concentration/ x 10 ⁻⁴	k _{obs} /min ⁻¹	Initial rate/ x 10 ⁻⁵	Half-life/ min
mol L ⁻¹		mol L ⁻¹ min ⁻¹	
1.56	0.1146 (0.0203)	1.99 (3.15 x 10 ⁻⁶)	6.05 (34.15)
2.72	0.0967 (0.0187)	2.62 (4.09 x 10 ⁻⁶)	7.17 (37.07)
3.58	0.089 (0.0172)	4.10 (4.58 x 10 ⁻⁶)	7.79 (40.30)
4.04	0.0734 (0.0162)	4.74 (4.86 x 10 ⁻⁶)	9.44 (42.79)
4.36	0.0542 (0.0149)	5.51 (4.97 x 10 ⁻⁶)	12.79 (46.52)
5.06	0.039 (0.0133)	6.84 (5.51 x 10 ⁻⁶)	17.77 (52.12)

The half-lives of the photodegradation of 4-CP, **Table 6.1**, by PS/15 and PS/15-AuNP, within the experimental concentrations, are quite comparable to the values reported for other chlorinated phenols, ~28-81 min for 2,4-dichlorophenol [121], ~30-68 min for 4-chlorophenol [127] but are shorter than those for PS/ZnPc (~1155-1824 min). The fact that the half-lives are within one hour of photo-irradiation for PS/15 and PS/15-AuNP suggests that the functionalized fiber is a promising fabric that could have real life application for removal of chlorophenols in aquatic systems.

The Langmuir-Hinshelwood rate expression was used to describe the relationship between the initial rate of degradation of 4-chlorophenol and the corresponding initial concentration. This model, **Equation 6.1**, has successfully been applied to describe the kinetics of solid-liquid reactions, particularly heterogeneous photocatalytic degradation reactions [**226**]. A linear expression can conveniently be obtained by plotting the reciprocal of the initial rate against the reciprocal of the initial concentration, **Equation 6.1**:

$$\frac{1}{rate} = \frac{1}{k_a} + \frac{1}{k_a K C_0} \tag{6.1}$$

where k_a is the apparent reaction rate constant, *K* is the adsorption coefficient and C_0 corresponds to the initial concentration of 4-chlorophenol.

Plots of the inverse of initial rate $(rate)^{-1}$ versus the reciprocal of the initial concentration of 4chlorophenol $(C_0)^{-1}$, **Figure 6.3**, for PS/15-AuNP (as an example) were found to be linear with non-zero intercepts.



Figure 6.3: Plot of the inverse of initial reaction rate (rate⁻¹) vs. the reciprocal of the initial concentration of 4-chlorophenol for photooxidation using 10 mg PS/15-AuNP

The apparent reaction rate constants $(k_a) \min^{-1}$ and the adsorption coefficients (*K*) onto the PS fiber surfaces were calculated from **Figure 6.3** and the results are shown in **Table 6.2**. The apparent reaction rate constants (k_a) for 4-chlorophenol was found to be 5.41 x 10⁻² mol L⁻¹ min⁻¹ and the adsorption coefficients (*K*) onto the PS/15-AuNP fiber surfaces was found to be 0.231 mol⁻¹, **Table 6.2**.

For the PS/15 composite, the apparent reaction rate constant (k_a) for 4-chlorophenol was found to be 2.31 x 10⁻² mol L⁻¹ min⁻¹ and the adsorption coefficient (*K*) was found to be 0.54 mol⁻¹. The rate constants (k_a) improved in the presence of AuNPs. From **Table 6.2**, it can be observed that the heterogeneous catalytic system PS/15-AuNP displays greatly enhanced and efficient photoactivity for the degradation of 4-chlorophenol in the presence of visible light compared to the other systems. The Langmuir-Hinshelwood expression was also used to assess the extent adsorption of 4chlorophenol onto the functionalized fiber. The adsorption coefficients, **Table 6.2**, were less than one (K < 1), suggesting that adsorption of 4-chlorophenol is less favorable than desorption. The results presented in **Figure 6.3**, give an indication that the Langmuir-Hinshelwood kinetic model is an appropriate model in describing the photodegradation kinetics by a heterogeneous catalytic system based on Pc and Pc-AuNP complexes on an electrospun polymeric fiber support.

 Table 6.2: Langmuir-Hinshelwood parameters for photocatalysis of 4-CP using PS/15 or

 PS/15-AuNP fibers. Solvent = water

Complex	$k_a \pmod{L^{-1} \min^{-1}}$	K (mol ⁻¹)
PS/15	2.31×10^{-2}	0.540
PS/15-AuNP	5.41×10^{-2}	0.231
PS/LuTPPc	6.39×10^{-3}	0.81 [127]
PS/ZnPc	3.30×10^{-7}	$2.48 imes 10^3$ [127]

6.1.2 Photodegradation of Orange G

The UV-Vis spectra of the Orange G (OG) degradation with PS/15-AuNP functionalized fibers are shown in **Figure 6.4**. The spectrum consists of three main peaks at 259, 330 and 478 nm plus a shoulder peak at 421 nm. The peaks at 259 and 330 nm are assigned to the aromatic rings, whereas the peaks at 478 and 421 nm are assigned to the conjugated structure formed by the azo bond [**227-229**]. As the reaction proceeds, there is a dramatic decrease in the absorption peaks indicating destruction of the conjugated system and a disruption of the aromatic rings. In this study, the variation of absorption peak at 478 nm was applied to evaluate the kinetics of OG degradation. When the pure polystyrene polymer fiber alone was used as control, no spectral changes of the aqueous OG solution were observed.



Figure 6.4: Electronic absorption spectra changes of 1.66 x 10⁻⁴ mol L⁻¹ Orange G during visible light photocatalysis in the presence of 10 mg PS/15-AuNP. The spectra were recorded at 30 sec intervals.
The photodegradation of OG using PS/15 and PS/15-AuNP showed first order kinetics, **Figure** 6.5. Reaction rates, rate constants and half-lives were evaluated from **Figure 6.5** and are listed in **Table 6.3**. The observed rate constant (k_{obs}) decreased with an increase in concentration of the initial dye concentration. This is due to the decrease in the number of active sites on the catalyst surface by adsorption of the dye molecules on the catalyst surface.



Figure 6.5: Effects of initial concentration of Orange G on its rate of degradation.
Concentrations were monitored at 478 nm. Starting concentrations (a) 1.66 x 10⁻⁴ mol L⁻¹,
(b) 2.21 x 10⁻⁴ mol L⁻¹ and (c) 3.32 x 10⁻⁴ mol L⁻¹. Amount of functionalized fiber 10 mg.

The half-lives in **Table 6.3**, for PS/15 and PS/15-AuNP suggest that the functionalized fiber is a promising fabric that could have real life application for removal of azo dyes such as Orange G in aquatic systems. The relatively short reaction times would result in faster removal of pollutants from aquatic environments hence saving time. The use of functionalized fibers for the photo-conversion of OG, an azo dye showed much slower reaction kinetics, **Table 6.3** than those

of 4-chlorophenol, **Table 6.1**. Such slow photoconversion has been reported before for Orange G [**230**]. In all cases, the initial reaction rates increase with the initial concentration of the analyte, consistent with basic reaction kinetics laws.

Table 6.3: The rate, rate constant (k_{obs}) and half-life $(t_{1/2})$ of various initial concentrations of Orange G using PS/15-AuNP. Values in brackets are when PS/15 was employed.

Concentration/ x 10 ⁻⁴	k _{obs} /min ⁻¹	Initial rate/ x 10 ⁻⁴	Half-life/ min
mol L ⁻¹		mol L ⁻¹ min ⁻¹	
1.11	0.0162 (0.0098)	1.07 (2.56 x 10 ⁻⁵)	42.78 (70.73)
1.66	0.0155 (0.0087)	1.54 (3.83 x 10 ⁻⁵)	44.72 (79.67)
2.21	0.0082 (0.0075)	1.97 (5.10 x 10 ⁻⁵)	84.53 (92.42)
2.78	0.0058 (0.0069)	2.72 (6.42 x 10 ⁻⁵)	129.51 (100.46)
3.32	0.0032 (0.0059)	3.18 (7.67 x 10⁻⁵)	216.61 (117.48)
3.81	0.0018 (0.0051)	3.33 (8.43 x 10 ⁻⁵)	385.08 (135.91)
4.42	0.0012 (0.0043)	4.39 (9.21 x 10 ⁻⁵)	577.62 (161.20)

The Langmuir-Hinshelwood rate expression was also used to describe the relationship between the initial rate of degradation of Orange G and the corresponding initial concentration. Plots of the inverse of initial rate (rate)⁻¹ versus the reciprocal of the initial concentration of Orange G (C_0)⁻¹, **Figure 6.6**, for PS/15-AuNP (as an example) were found to be linear with non-zero intercepts.



Figure 6.6: Plot of the inverse of initial reaction rate (rate⁻¹) vs. the reciprocal of the initial concentration of Orange G for photooxidation using 10 mg PS/15-AuNP

The apparent reaction rate constant (k_a) for Orange G was found to be 4.39 x 10⁻¹ mol L⁻¹ min⁻¹ and the adsorption coefficient (*K*) onto the PS/15-AuNP fiber surfaces was found to be 0.228 mol⁻¹, **Table 6.4**. For the PS/15 composite, the apparent reaction rate constants (k_a) for Orange G was found to be 1.69 x 10⁻² mol L⁻¹ min⁻¹ and the adsorption coefficients (*K*) was 0.59 mol⁻¹. An adsorption phenomenon plays an important role in the photocatalytic degradation of pollutants like azo dyes in the aqueous phase. In the case of heterogeneous photocatalytic systems involving functionalized electrospun fibers, the Langmuir-Hinshelwood expression was also used to assess the extent adsorption of Orange G onto the functionalized fiber. The adsorption coefficients were less than one (*K* < 1), suggesting that adsorption of Orange G is less favorable than desorption. The rate constants improved in the presence of AuNPs.

 Table 6.4: Langmuir-Hinshelwood parameters for photocatalysis of OG using PS/15 or

 PS/15-AuNP fibers. Solvent = water

Complex	k _a (mol L ⁻¹ min ⁻¹)	K (mol ⁻¹)
PS/15	1.69 × 10 ⁻¹	0.59
PS/15-AuNP	4.39×10^{-1}	0.228

The results presented in **Figure 6.6**, give an indication of that the Langmuir-Hinshelwood kinetic model is an appropriate model in describing the photodegradation kinetics of OG by a heterogeneous catalytic system based on phthalocyanine complexes on a polymeric fiber support. Thus in this work the OG was not just transferred from the solution onto the solid functionalized fiber by adsorption, but was also mineralized to other products.

6.2 Product analysis

The catalytic products of 4-chlorophenol were identified with high performance liquid chromatography (HPLC), **Figure 6.7**. The degradation profile of 4-chlorophenol, **Figure 6.7B**, showed significant degradation. A standard consisting of hydroquinone, benzoquinone and 4-chlorophenol was used for the identification of degradation products. Using the standards' retention times; hydroquinone (HQ, at 5.9 min), benzoquinone (BQ, at 7.8 min) and 4-chlorophenol (4-CP, at 19.3 min), **Figure 6.7A**; two degradation products were identified as hydroquinone and benzoquinone according to their retention times. The profile also shows that the photocatalysis was not complete since 4-CP is still present but that it is possible to degrade 4-CP to less harmful products.



Figure 6.7: Chromatograms taken at 350 nm of (A) the standards (hydroquinone (HQ), benzoquinone (BQ) and of 4-CP) and (B) the 4-CP degradation products.

It has been reported [231] that the formation of benzoquinone is mainly due to the reaction of singlet oxygen with 4-CP (Type II mechanism, Scheme 6.1), while the formation of hydroquinone and other dimeric products are explained by electron transfer reactions involving the phthalocyanine or phthalocyanine-gold nanoparticle conjugate, oxygen and 4-chlorophenol (Type I mechanism, Scheme 6.1). The PS functionalized fibers are capable of degrading both 4-CP and OG via both Type I and Type II mechanisms which start with the photogeneration of singlet oxygen and radicals, respectively, by the immobilized phthalocyanine complexes.



Scheme 6.1: Mechanism of photooxidation of 4-chlorophenol

The degradation products of OG could not be identified unequivocally, but the UV-Vis spectra did not show any new peaks, **Figure 6.4**. OG degradation products that have been reported in literature include substituted phenols, nitroso compounds and aromatic hydroxyl amines **[232**].

6.3 Remarks on chapter

In this work, electrospun polystyrene fibers incorporating phthalocyanines and phthalocyaninegold nanoparticle conjugates were used for the photoconversion of a phenolic compound, 4chlorophenol and an azo dye, Orange G. These electrospun fibers were found to be promising materials for photocatalytic conversion of organic pollutants.

7. General Conclusions and Future prospects

7.1 General Conclusions

The syntheses and spectroscopic characterization of arylthio zinc phthalocyanine complexes conjugated to gold nanoparticles have been reported in this work. Changes in photoinduced processes, photophysical and photochemical properties of the MPcs confirmed successful conjugation of the AuNPs to the phthalocyanines. The photophysical and photochemical properties were enhanced as a result of interaction with gold nanoparticles. The phthalocyanine and phthalocyanine-gold nanoparticle conjugates were found to be photoactive and promising photosensitizers for the conversion of the environmental pollutants, 4-chlorophenol and Orange G. The phthalocyanine and phthalocyanine-gold nanoparticle conjugates were incorporated into polymer fibers and characterized using various spectroscopic and microscopic techniques. Results suggested that the phthalocyanine and phthalocyanine-gold nanoparticle conjugates were embedded and uniformly dispersed within the polymeric fiber matrices.

The photophysical and photochemical properties of the phthalocyanine and phthalocyanine-gold nanoparticle conjugates incorporated in electrospun polymer fiber matrices were also assessed. The fluorescence properties and singlet oxygen generation ability of the phthalocyanine complexes were maintained in the polymer fibers. These polymeric fiber materials incorporating phthalocyanine and phthalocyanine-gold nanoparticle conjugates were thus promising fabric materials in developing multi-functional nanomaterials for applications in photocatalysis.

7.2 Future prospects

The use of electrospun fibers functionalized with phthalocyanine and phthalocyanine-gold nanoparticle conjugates for solving environmental problems is promising. However a correlation study between the spectroscopic behavior and the spatial arrangement of phthalocyanines on gold nanoparticle surfaces is essential for the understanding of the conjugates' photophysical and photochemical properties. For a comparative study of phototransformation of environmental pollutants, a mixture of pollutants to mimic a real life environment would be ideal. Since the functionalized electrospun fibers are photoactive, there is a possibility of applications in PDT, gas sensing, tissue engineering and as anti-microbial nanofabrics.

References

- [1] M. Faraday, Phil. Trans. R. Soc. Lond., 1857, 147, 145
- [2] G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G.H.M. Calis, W.A. Vandervelden, Chemische Berichte-Recueil, 1981, 114, 3634
- [3] M. Giersig, P. Mulvaney, Langmuir, 1993, 9, 3408
- [4] M. Pelton, J. Aizpurua, G. Bryant, Laser & Photon. Rev. 2, 2008, 3, 136
- [5] P.K. Jain, X. Huang, I.H. El-Sayed, M.A. Sayed, Acc. Chem. Res., 2008, 41, 1578
- [6] E. Hutter, J.H. Fendler, Adv. Mater., 2004, 16, 1685
- [7] P.P. Edwards, J.M. Thomas, Angew. Chem. Int. Ed., 2007, 46, 5480
- [8] M. Chen, D.W. Goodman, Acc. Chem. Res., 2006, 39, 739
- [9] M.-C. Daniel, D. Astruc, Chem. Rev., 2004, 104, 293
- [10] T. Murakami, K. Tsuchida, Mini Rev Med Chem, 2008, 8, 175
- [11] S.H. Hsu, H.J. Yen, C.L. Tsai, Artif. Organs., 2007, 31, 854
- [12] A.C. Enriquez, I.A.R. Espejel, E.A. Garcia, M.E. Diaz-Gracia, Anal. Bioanal. Chem, 2008, 391, 807
- [13] X. Huang, I.H. El-Sayed, W. Qian, M.A. El-Sayed, J. Am. Chem. Soc., 2006, 128, 2115
- [14] B.V. Enüstün, J. Turkevich, J. Am. Chem. Soc., 1963, 85, 3317

[15] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, J. Chem. Soc., Chem. Commun, 1994, 7, 801

[16] M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, R. W. Murray, Langmuir, 1998, 14, 17

[17] C.J. Ackerson, P.D. Jadzinsky, R.D. Kornberg, J. Am. Chem. Soc, 2005, 127, 6550

[18] M. Aslam, L. Fu, M. Su, K. Vijayamohanan, V.P. Dravid, J. Mater. Chem, 2004, 14, 1795

[19] L. A. Porter, D. Ji, S.L. Westcott, M. Graupe, R.S. Czernuszewic, N.J. Halas, T.R. Lee, Langmuir, 1998, 14, 7378

[20] Y. Shon, C. Mazeitelli, R.W. Murray, Langmuir, 2001, 17, 7735

[21] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, Chem. Rev., 2005, 105, 1103

[22] P. Mukherjee, R. Bhattacharya, N. Bone, Y. K. Lee, C. R. Patra, S. Wang, L. Lu, C. Secreto,P. C. Banerjee, M. J. Yaszemski, N. E. Kay, D. Mukhopadhyay, J. Nanobiotechnol., 2007, 5, 4

[23] W. Eck, G. Craig, A. Sigdel, G. Ritter, L. J. Old, L. Tang, M. F. Brennan, P. J. Allen, M. D. Mason, ACS Nano, 2008, 2, 2263

[24] I. H. El-Sayed, X. H. Huang, M. A. El-Sayed, Nano Lett., 2005, 5, 829

[25] T. Zhang, P. Chen, Y. Sun, Y. Xing, Y. Yang, Y. Dong, L. Xu, Z. Yang, D. Liu, Chem. Commun., 2011, 47, 5774

- [26] S. Guo, Y. Huang, Q. Jiang, Y. Sun, L. Deng, Z. Liang, Q. Du, J. Xing, Y. Zhao, P. C.Wang, A. Dong, X.-J. Liang, ACS Nano, 2010, 4, 5505
- [27] S. Park, K. Hamad-Schifferli, ACS Nano, 2010, 4, 2555
- [28] L. Calzolai, F. Franchini, D. Gilliland, F. Rossi, Nano Lett., 2010, 10, 3101
- [29] C.-C. You, R. R. Arvizo, V. M. Rotello, Chem. Commun., 2006, 2905
- [30] M. E. Aubin- Tam, K. Hamad-Schifferli, Langmuir, 2005, 21, 12080
- [**31**] A. Kotiaho, R. Lahtinen, A. Efimov, H-K. Metsberg, E. Sariola, H. Lehtivuori, N.V. Tkachenko, H. Lemmetyinen, J. Phys. Chem. C, 2010, 114, 162
- [32] V.P. Chauke, E. Antunes, W. Chidawanyika, T. Nyokong, J. Mol. Cat. A: Chem. 2011, 335, 121
- [33] D.C. Hone, P.I. Walker, R. Evans-Gowing, S. FitzGerald, A. Beeby, I. Chambrier, M.J. Cook, D.A. Russell, Langmuir, 2002, 18, 2985
- [34] N. Masilela, T. Nyokong, J. Photochem. Photobiol. A: Chem., 2011, 223, 124
- [35] Leznoff, C.C.; Lever, A.B.P., Eds., Phthalocyanines: Properties and Applications, Vols. 1-4;VCH Publishers (LSK) Ltd.: Cambridge, 1989, 1993, 1996
- [**36**] McKeown, N.B., Ed. Phthalocyanine Materials. Synthesis, Structure and Function; Cambridge University Press: Cambridge, 1998
- [**37**] Kadish, K.M.; Smith, K.M., Guillard, R., Eds. The Porphyrin Handbook, Vol. 15; Academic Press: San Diego, 2003

- [38] A. Braun, J. Tscherniac, Chem. Ber., 1907, 40, 2709
- [39] H. De Diesbach, E. von der Weid, Helv. Chem. Acta, 1927, 10, 886
- [40] A.G. Dandridge, H.A. Drescher, J. Thomas, GB Patent, 3221691928
- [41] R.P. Linstead, J. Chem. Soc., 1934, 1022
- [42] C.E. Dent, R.P. Linstead, A.R. Lowe, J. Chem. Soc., 1934, 1033
- [43] J.M. Robertson, J. Chem. Soc., 1935, 615
- [44] J.M. Robertson, R.P. Linstead, C.E. Dent, Nature, 1935, 135, 506
- [45] J.M. Robertson, J. Chem. Soc., 1936, 1195
- [46] J.M. Robertson, I. Woodard, J. Chem. Soc., 1937, 219
- [47] J.M. Robertson, I. Woodard, J. Chem. Soc., 1940, 36
- [48] T. Patrice in Photodynamic therapy (Eds. D.P. Häder, G. Jori) European Society for Photobiology, Cambridge, 2003, 4-8
- [**49**] P. Gregory, High-Technology Applications of Organic Colourant, Plenum Press, New York, 1991, 7-273
- [50] F. Mosser and A.L. Thomas, The Phthalocyanines, Eds., CRS Press: Boca Raton, F.L. 1983
- **[51]** I. Okura in: Photosensitization of Porphyrins and Photosensitization of Porphyrins and Phthalocyanines, Gordon and Breach publishers, Germany (2001)

[52] T. Nyokong in N₄-macrocyclic metal complexes: electrocatalysis, electrophotochemistry, and biomimetic electrocatalysis (Eds. J.H. Zagal, F. Bedioui, J-P. Dodelet) Springer, 2006, Chpt.
7. ISBN0-387-28429

[53] Dini, D., and Hanack, M., in: Kadish, K.M., Smith, and K.M., Guilard, R. (Eds.) (2003) The Porphyrin Handbook: Physical Properties of Phthalocyanine-based Materials, vol. 17, Academic Press: USA; 22-31

[54] D. Wörhle, L. Kreienhoop and D. Schlettwein in Phthalocyanines: Properties and Applications, eds., A.P.B. Lever and C.C. Leznoff, VCH Publishers, New York, 1996, Vol. 4.

[55] D.Wöhrle, O. Suvorova, R. Gerdes, O. Bartels, L. Lapok, N. Baziakina, S. Makarov, A. Slodek, J. Porphyr. Phthalocya, 2004, 8, 1020

[56] M.S. Rodríguez-Morgade, G. de la Torre, T. Torres, in The Porphyrin Handbook, K.M. Kadish, R. Guillard, K.M. Smith (Eds.), Academic Press, Elsevier Science, Vol. 15, 2003, Chapter 99

[57] A. Louati, M.E.I. Meray, J.J. Andre, J. Simon, K.M. Kadish, M. Gross, A. Giraurdeau, Inorg. Chem., 1985, 24, 1175

[58] M. Hanack, D. Meng, A. Beck, M. Sommerauer, L.R. Subramanain, J. Chem. Soc. Chem. Commun., 1953, 58

[59] M. Sommerauer, C. Rager, M. Hanack, J. Am. Chem. Soc., 1996, 118, 10085

[60] E.V. Kudrik, E.M. Bauer, C. Ercolani, A. Chiesi-Villa, C. Rizzoli, A. Gaberkorn, P.A. Stuzhin, Mendeleev. Commun., 2001, 45

- [61] G. Schmid, M. Sommerauer, M. Hanack, Angew Chem. Int. Ed. Engl., 1993, 32, 1422
- [62] I. Chambrier, M.J. Cook, D.A. Russell, Synthesis, 1995, 1283
- [63] M.J. Cook, R. Hersans, J. McMurdo, D.A. Russell, J. Mater. Chem., 1996, 6, 149
- [64] M.J. Cook, Pure Appl. Chem. 1999, 71, 2145
- [65] Z. Li, M. Lieberman, Supramol. Science, 1998, 5, 485
- [66] Z. Li, M. Lieberman, W. Hill, Langmuir, 2001, 17, 4887
- [67] H. Ali, J.E. van Lier, Chem. Rev, 1999, 99, 2379
- [68] R. Bonnett, Chem. Soc. Rev, 1995, 24, 19
- [69] A.C. Tedesco, J.C.G. Rotta, C.N. Lurnardi, Curr. Org. Chem., 2003, 7, 187
- [70] B. Agboola, K.I. Ozoemena, T. Nyokong, Electrochim. Acta, 2006, 51, 4379
- [71] A. Aslı Esenpınar, M. Bulut, Dyes Pigm, 2008, 76, 249
- [72] R.D. George, A.W. Snow, J.S. Shirk, W.R. Barger, J. Porphyr. Phthalocya, 1998, 2, 1
- [73] H. Ogata, R. Higashi, N. Kobayashi, J. Porphyr. Phthalocya, 2003, 7, 551
- [74] G. Jones, W.R. Jackson, C.Y. Cho, W.R. Bergmark, J. Phys. Chem., 1985, 89, 294
- [75] B.Y. Wang, X.Y. Liu, Y.L. Hu, Z.X. Su, Polym. Int., 2009, 58, 703
- [76] Z-S. Wang, Y. Cui, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, Adv. Mater., 2007, 19, 1138
- [77] S. Forteath, E. Antunes, W. Chidawanyika, T. Nyokong, Polyhedron, 2012, 34, 114

- [78] N. Nombona. E. Antunes, C. Litwisnki, T. Nyokong, Dalton Trans, 2011, 40, 11876
- [79] S. Moeno, E. Antunes, T. Nyokong, J. Photochem. Photobiol A: Chem, 2011, 222, 342
- [80] M. Gouterman, in The Porphyrins, Part A. Physical Chemistry, D. Dolphin (Ed), Academic Press, New York, Vol 3, 1978, 1-165
- [81] J. Mack, M.J. Stillman, J. Am. Chem. Soc. 1994, 116, 1292
- [82] T. Nyokong, Z. Gasyna, M.J. Stillman, Inorg. Chem. 1987, 26, 1087
- [83] W.J. Schutte, M. Sluyters-Rehbach, J.H. Sluyters, J. Phys. Chem., 1993, 97, 6069
- [84] N. Kobayashi, S. Nakajima, H. Ogata, T. Fukuda, Chem. Eur. J. 2004, 10, 6294, 71
- [85] Y. Asano, N. Kobayashi, Tetrahedron Lett. 2004, 45, 9577
- [86] N. Kobayashi, A.B.P. Lever, J. Am. Chem. Soc., 1987, 109, 7433
- [87] A.R. Monahan, J.A. Brado, F.A. DeLuca, J. Phys. Chem. 1972, 76, 446
- [88] W.A. Nevin, W. Liu, S. Greenberg, M.R. Hempstead, S.M. Maruccio, M.M. Melnik, C.C. Leznoff, A.B.P. Lever, Inorg. Chem. 1987, 26, 291
- [89] E. Schnabel, H. Nöther, H. Kuhn, in Chemistry of Natural and Synthetic Colouring Matters,
- T.S. Gore, B.S. Joshi, S.V. Sunthankar, B.D. Tilak (Eds.), Academic Press, New York, 1962, pp 561-572
- [90] Z.A. Schelly, R.D. Farina, E.M. Eyring, J. Phys. Chem. 1970, 74, 617
- [91] H. Abramczyk, I. Szymczyk, G. Waliszewska, A. Lebioda, J. Phys. Chem. 2004, 108, 264

- [92] N. Kobayashi, H. Ogata, N. Nonaka, E.A. Luk'yanets, Chem. Eur. J. 2003, 9, 5123
- [93] A. Skorobogaty, T.D. Smith, G. Dougherty, J.R. Pilbrow, J. Chem. Soc., Dalton Trans, 1985, 651
- [94] M. Kasha, Radiat. Res., 1960, 20, 55; Z. Gaysna, N. Kobayashi, M.J. Stillman, J. Chem. Soc. Dalton Trans., 1989, 2397
- [95] A.W. Snow in: The Porphyrin Handbook, Vol. 17, K.M. Kadish, K.M. Smith, R. Guilard (Eds), Elsevier Science, New York, 2003
- [96] P. Suppan, Chemistry and Light, Royal Society, Cambridge, 1st ed., 1994
- [97] A. Jablonski, Z. Phys. 1935, 94, 38
- **[98]** P.W. Atkins, in Physical Chemistry, P.W. Atkins (Ed.), Oxford University Press, Oxford, 6th Edition, 1998, Chapter 17
- [99] K. Ishii, N. Kobayashi, in the Porphyrin Handbook, K.M. Kadish, K.M. Smith, R. Guilard,(Eds.) Elsevier Science, New York, 2003, Vol 16, Chapter 102
- [100] M.J. Stillman, A.J. Thomson, J. Chem. Soc. Faraday. Trans II, 1974, 70, 790
- [101] A.B.P. Lever, Adv. Inorg. Radiochem., 1965, 7, 27
- [102] L. Kaestner, M. Cesson, K. Kassab, T. Christensen, P.D. Edminson, M.J. Cook, T. Chambrier, G. Jori, Photochem. Photobiol. Sci., 2003, 2, 660
- [103] P. Tau, T. Nyokong, J. Mol. Catal. A: Chem., 2007, 273, 149
- [104] B. Agboola, K.I. Ozoemena, T. Nyokong, J. Mol. Catal. A: Chem., 2006, 248, 84

- [105] S. Fery-Forgues, D. Lavabre, J. Chem. Educ. 1999, 76, 1260
- [106] S.E. Maree, D. Phillips, T. Nyokong, J. Porphyr Phthalocya, 2002, 6, 17
- [107] X.F. Wang, T. Uchida, S. Minami, Appl. Spectrosc., 1991, 45, 560
- [108] G.J. Brakenhoff, M. Müller, R.I. Ghauharali, K. Visscher, Proc. SPIE, 1995, 2412, 115
- [109] H.C. Gerritse, R. Sanders, A. Draaijer, Proc SPIE, 1994, 2329, 260
- [110] A.G. Ryder, S. Power, T.J. Glynn, J.J. Morrison, Proc. SPIE, 2001, 4529, 102
- [111] P. Kubat, J. Mosinger, J. Photochem. Photobiol. A: Chem., 1993, 96, 93
- [112] M.C. Palumbo, N.A. Garcia, Toxicol. Environ. Chem., 1988, 17, 103
- [113] D. Wörhle, W. Spiller, G. Schneider, G. Schulz-Ekloff, J. Stark, J. Inf. Rec. Mats., 1994, 21, 1
- [114] D. Wörhle, G. Schneider, J. Stark, G. Schulz-Ekloff, J. Mol. Catal., 1992, 75, L39
- [115] R. Bonnet, in Chemical Aspects of Photodynamic Therapy, Gordon and Breach Science Publishers, Amsterdam, (2002)
- [116] M. Niedre, M.S. Patterson, B.C. Wilson, Photochem. Photobiol., 2003, 75, 382
- [117] P.B. Merkel, D.R. Kearns, J. Am. Chem. Soc. 1989, 97, 833
- [118] C.S. Foote, SPIE Institute Series, 1990, 6, 115
- [119] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Ref. Data., 1993, 22, 113

[120] C.S. Foote, In Singlet Oxygen, (eds H.H. Wasserman and R.W. Murray), Academic Press, New York, San Francisco, London, 1979, 139

[121] M.A. Zanjanchi, A. Ebrahimian, M. Arvand, J. Hazard. Mat., 2010, 175, 992

- [122] R. Słota, G. Dyrda, K. Szczegot, G. Mele, I. Pio, Photochem. Photobiol. Sci., 2011, 10, 361
- [123] L. Wu, A. Li, G. Gao, Z. Fei, S. Xu, Q. Zhang, J. Mol. Catal. A Chem., 2007, 269, 183
- [124] M. Alvaro, E. Carbonell, M. Esplá, H. Garcia, Appl. Catal. B, 2005, 57, 37
- [125] S.L. Wang, Y-F. Fang, Y. Yang, J-Z. Liu, A-P. Deng, X-R. Zhao, Y-P. Huang, Chinese Sci. Bull., 2011, 56, 969
- [126] R. Zugle, C. Litwinski, N. Torto, T. Nyokong, New J. Chem, 2011, 35, 1588
- [127] R. Zugle, E. Antunes, S. Khene, T. Nyokong, Polyhedron, 2012, 33, 74
- [128] R. Zugle, T. Nyokong, J. Macromol. Sci., Pure Appl. Chem. 2012, 49, 279
- [129] G. Larsen, R. Velarde-Ortiz, K. Minchow, A. Barrero, I.G. Loscertales, J. Am. Chem. Soc., 125, 1154
- [130] D. Li, T. Herricks, T. Xia, Appl. Phys. Lett., 2003, 83, 4586
- [131] D. Li, Y. Xia, Nano Lett, 2003, 3, 55
- [132] B. Carlberg, M.Z. Axell, U. Nannmark, J. Liu, H.G. Kuhn, Biomed. Mater., 2009, 4, 045004
- [133] D. Wöhrle, Macromol. Rapid. Commun., 2001, 22, 68

[134] D. Wöhrle and G. Schnurpfeil, in The Porphyrin Handbook, ed. K.M. Kadish, K.M. Smith and R. Guilard, Academic Press, San Diego, CA, 2003, vol. 17, pp.177-246

[135] N.B. McKeown, J. Mater. Chem., 2000, 10, 1979

[136] R. Zugle, T. Nyokong, J. Mol. Catal. A: Chem, 2013, 366, 247

[137] J. Mosinger, K. Lang, P. Kubát, J. Sýkora, M. Hof, L. Píštil, B. Mosinger Jr., J. Fluoresc., 2009, 19, 709

[138] S-L. Cheng, X-J. Huang, Z-K. Xu, Cellulose, 2011, 18, 1295

[139] Z. Guo, B. Chen, J. Mu, M. Zhang, P. Zhang, Z. Zhang, J. Wang, X. Zhang, Y. Sun, C. Shoo, Y. Liu, J. Hazard. Mater., 2012, 219-220: 156-163

[140] R. Zugle, T. Nyokong, J. Mol. Catal. A: Chem, 2012, 358, 49

[141] M.M. Demir, I. Yilgor, E. Yilgor, B. Erman, Polymer, 2002, 43, 3303

[142] V.N. Morozova, T.Y. Morozova, N.R. Kallenbach, Int. J. Mass Spectrom, 1998, 178, 143

[143] E.P.S. Tan, C.T. Lim, Appl. Phys. Lett., 2004, 84, 1603

[144] R. Inai, M. Kotaki, S. Ramakrishna, Nanotechnology, 2005, 16, 208

[145] M.Y. Li, Y. Guo, Y. Wei, A.G. MacDiarmid, P.I. Lelkes, Biomaterials, 2006, 27, 2705

[146] E.D. Boland, G.E. Wnek, D.G. Simpson, K.J. Pawlonski, G.L. Bowlin, J. Macromol. Sci.Pure Appl. Chem., 2001, 38, 1231

[147] X.F. Wang, I.C. Um, D.F. Fang, A. Okamoto, B.S. Hsiao, B. Chu, Polymer, 2005, 46, 4853

- [148] A.I. Berlin, S.A. Vol´fson, V.G. Oshmyan, Principles of creation of composite materials, Khimiya, Moscow, 1990; J. Simon, J.J. Andre, Molecular semiconductors, Springer, Berlin, 1985
- [149] B. Nearingburg, A.L. Elias, Thermochimica Acta, 2011, 512, 247
- [150] H. Xia, H.J. Chung, C.-H. Sow, H.S-O. Chan, J. Nanosci. Nanotechnol, 2010, 10, 2409
- [151] R.R. Bhattacharjee, T.K. Mandal, 2007, J. Colloid Interface Sci, 307, 288
- [152] B. Guo, G. Han, M. Li, S. Zhao, Thin Solid Films, 2010, 518, 3228
- [153] F.H. Anka, S.D. Perera, C. Ratanatawanate, K.J. Balkus Jr, Mater Lett., 2012, 75, 12
- [154] H. Dong, E. Fey, A. Gandelman, W.E. Jones Jr, Chem. Mater., 2006, 18, 2008
- [155] S. Tang, C. Shao, Y. Li, R. Mu, J. Phys. Chem. Solids, 2007, 68, 2337
- [156] S-L. Cheng, X-J. Huang, Z-K. Xu, Cellulose, 2011, 18, 1295
- [157] D. Li, T. McCann, M. Gratt, Y. Xia, Chem. Phys. Lett., 2004, 394, 387
- [158] S. Marx, M.V. Jose, J.D. Andersen, A.J. Russell, Biosens. Bioelectron., 2011, 26, 2981
- [159] N. Mahanta, S. Valiyaveettil, Nanoscale, 2011, 3, 4625
- [160] S. Koh, M.V. McCullar, D.D. Focht, Appl. Environ. Microbiol., 1997, 63, 2054
- [161] G.W. Kohring, J.E. Rogers, J. Wiegel, Appl. Environ. Microbiol., 1989, 55, 348
- [162] F. Al-Momani, Environ. Eng. Sci., 2006, 23, 722

- [163] I.F. Cheng, Q. Fernando, N. Korte, Environ. Sci. Technol., 1997, 31, 1074
- [164] M.S. Ureta-Zanartu, P. Bustos, C. Berros, M.C. Diez, Electrochim. Acta, 2002, 47, 2399
- [165] T.A. Albanis, T.G. Danis, M.G. Kourgia, Environ. Technol. 1998, 19, 25
- [166] J.W. Lee, W.G. Shim, J.Y. Ko, H. Moon, Sep. Sci. Technol., 2004, 39, 2041
- [167] T. Shen, Z-I. Yuan, H-J. Xu, Dyes Pigm., 1989, 11, 77
- [168] W.Z. Tang, C.P. Huang, Water Res., 1995, 29, 745
- [169] Y. Ku, C.B. Hsieh, Ind. Eng. Res., 1992, 31, 1823
- [170] J. Giménez, D. Curcó, M.A. Queral, Catal. Today, 1999, 54, 229
- [171] M.P Ormada, J.L. Ovelleiro, J. Kiwi, Appl. Catal. B: Environ., 2001, 32, 157
- [172] K. Ozoemena, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. A: Chem., 2001, 139, 217
- [173] M.C. DeRosa, J.R. Crutchley, Coord. Chem. Rev., 2002, 233, 351
- [174] A. Ogunsipe, D. Maree, T. Nyokong, J. Mol. Struct., 2003, 650, 131
- [175] Christie R.M., Colour Chemistry. The Royal Society of Chemistry, Cambridge (UK)(2001)
- [176] C. Zhu, L. Wang, L. Kong, X. Yang, L. Wang, S. Zheng, F. Chen, F. Maizhi, H. Zong, Chemosphere, 2000, 41, 303
- [177] K.-T. Chung, G.E. Fulk, A.W. Andrews, Appl. Environ. Microbiol., 1981, 42, 641

- [178] H.M. Pinheiro, E. Touraud, O. Thomas, Dyes Pigm., 2004, 61, 121
- [179] J. Chang, C. Chou, Y. Lin, P. Lin, J. Ho, T.L. Hu, Water Res., 2001, 35, 2841
- [180] F. Sosath, Biologisch-chemische Behandlung von Abwässern der Textilveredelung mit ReaKtivfarbstoffen, VDI Fortschrittsberichte, Reihe Umweltverfahrenstechnik, 1999, 209
- [181] N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizbar, Sep. Purif. Technol., 2003, 31, 153
- [182] Y.M. Slokar, A.M.L. MareChal, Dyes. Pigm., 1998, 37, 335, 220
- [183] C. Galindo, P. Jacques, A. Kalt, Chemosphere, 2002, 48, 1047
- [184] B. Muktha, G. Madras, T.N.G. Row, U. Scherf, S. Patil, J. Phys. Chem. B, 2007, 1117994
- [185] P. Mahata, G. Madras, S. Natarajan, Catal. Lett, 2007, 115, 27
- [186] M. Sökmen, A. Özkan, J. Photochem. Photobiol. A: Chem, 2002, 147, 77
- [187] J. Sun, X. Wang, J. Sun, R. Sun, S. Sun, L. Qiao, J. Mol. Catal. A: Chem, 2006, 260, 241
- [188] C. Hachem, F. Bocquillon, O. Zahraa, M. Bouchy, Dyes Pigm, 2001, 49, 117
- [189] P. Tau, T. Nyokong, Dalton Trans, 2006, 4482
- [190] A. Ogunsipe, J.Y. Chen and T. Nyokong. New J. Chem., 2004, 28, 822
- [191] J. Kossanyi, D. Chahraoui, Int. J. Photoenergy, 2000, 2, 9
- [**192**] S.M. Bishop, A. Beeby, A.W. Walker, M.S.C. Foley, D. Phillips, J. Photochem. Photobiol. A: Chem. 1995, 90, 39

- [**193**] W. Spiller, H. Kliesch, D. Wörhrle, S. Hackbath, B. Roder, G. Schnurpfeil, J. Porphyr. Phthalocya, 1998, 2, 145
- [194] A. Ogunsipe, T. Nyokong, J. Photochem. Photobiol. A: Chem 2005, 173, 211
- [195] A. Aoudia, G. Cheng, V.O. Kennedy, M.E. Denney, M.A.J. Rodgers, J. Am. Chem. Soc., 1997, 119, 6029
- [196] R. Sardar, A.M. Funston, P. Mulvaney, R.W. Murray, Langmuir, 2009, 25, 13840
- [197] S.G. Murray, F.R. Hartley, Chem. Rev. 1981, 99, 365
- [**198**] A.W. Snow. Phthalocyanine aggregation. In *The Porphyrin Handbook*; Kadish, K. M., Guilard, R., Smith, K. M., Eds.; Academic Press: New York, 2002; Vol. 17, pp 129-173
- [199] K. S. Lokesh, V. Narayanan, S. Sampath, Microchim Acta, 2009, 167, 97
- [200] V. P. Chauke, Y. Arslanoglu, T. Nyokong, J. Photochem. Photobiol. A: Chem, 2011, 221, 38
- [201] T. Nyokong, H. Isago, J. Porphyr. Phthalocya, 2004, 8, 1083
- [202] T. Nyokong, in: J. Jiang (Ed.), Functional Phthalocyanine Molecular Materials, Structure and Bonding, vol. 135, Springer, New York, 2010, pp. 45–88.
- [**203**] N.R. Tiwari, A. Rathore, A. Prabhune, S.K. Kulkarni, Adv. Bioscie. Biotechnol., 2010, 1, 322
- [204] T. Nyokong, Coord. Chem. Rev., 2007, 251, 1707

[205] A. Ogunsipe, M. Durmuş, D. Atilla, A.G. Gürek, V. Ahsen, T. Nyokong, Synth. Met. 2008, 158, 839-847

[206] C.D. Geddes, J.R. Lakowicz, J. Fluoresc., 2002, 12, 121

- [207] J.R. Lakowicz, Y. Shen, S. D'Auria, J. Malicka, J. Fang, Z. Gryczynski, I. Grycznski, Anal. Biochem., 2002, 301, 261
- [208] C.D. Geddes, J.R. Lakowicz (Eds.), Topics in Fluorescence Spectroscopy, Springer, New York, 2005
- [209] Y. Kaneko, Y. Nishimura, N. Takane, T. Arai, H. Sakuragi, N. Kobayashi, D. Matsunaga,C. Pac, K. Tokumaru, J. Photochem. Photobiol. A, 1997, 106,177
- [210] J. Lakowicz, Anal. Biochem., 2001, 298, 1
- [211] J.R. Lakowicz, Anal. Biochem., 2005, 337, 171
- [212] Z-M. Huang, Y-Z. Zhang, M. Kotaki, S. Ramakrishna. Comp Sci & Tech, 2003, 63, 2223
- [213] J.M. Deitzel, J. Kleinmeyer, D. Harris, N.C. Beck Tan, Polymer, 2001, 42, 261
- [214] X.H. Qin, Y.Q. Wan, J.H. He, J. Zhang, J.Y. Yu, S.Y. Wang, Polymer, 2004, 45, 6409
- [215] C.L. Pai, M.C. Boyce, G.C. Rutledge, Macromolecules, 2009, 42, 2102

[216] D.W. Mayo, F.A. Miller and R.W. Hannah, *Course Notes on the Interpretation of Infrared and Raman Spectra*, John Wiley and Sons, Inc., New Jersey, 2004, Chapt. 5.

- [217] H. Fong, D.H. Reneker, J. Polym. Sci. B., 1999, 37, 3488
- [218] B.N. Achar, K.S. Lokesh, J. Organomet. Chem., 2004, 689, 2601

- [219] K. Lang, J. Mosinger, D.M. Wagnerova, Coord. Chem. Rev., 2004, 248, 321
- [220] S. Tang, C. Shao, Y. Liu, S. Li, R. Mu, J. Phys. Chem. Solids, 2007, 68, 2337.
- [221] Y. Huang, J. Li, W. Ma, M. Chen, J. Zhao, J. Yu, J. Phys. Chem. B 2004, 108, 7263
- [222] M. Cheng, W. Ma, J. Li, Y. Huang, J. Zhao, Y. Wen, Environ. Sci. Technol. 2004, 38, 1569
- [223] D. Gu, Q. Chen, X. Tang, F. Gan, S. Shen, K. Liu, H. Xu, Opt. Comm., 1995, 121, 125
- [224] M. Hu, Y. Xu, J. Zhao, Langmuir, 2004, 20, 6302
- [225] P. Kluson, M. Drobek, T. Strasak, J. Krysa, M. Karaskova, J. Rakusan, J. Mol. Catal., A Chem., 2007, 272, 213
- [226] D.D. Dionysiou, A.P. Khodadoust, A.M. Kern, M.T. Suidan, I. Baudin, J.-M. Laîné, Appl.Catal. B, Environ., 2000, 24, 139
- [227] J. Deng, J. Jiang, Y. Zhang, X. Lin, C. Du, Y. Xiong, Appl. Catal B., 2006, 84, 468
- [228] X.-R. Xu, X.-Z. Li, Sep. Purif. Technol., 2010, 72, 105
- [229] M. Muthukumar, M.T. Karuppiah, G.B. Raju, Sep. Purif. Technol. 2007, 55, 198
- [230] G. Thennarasu, S. Kavithaa, A. Sivasamy, Environ. Sci. Pollut. Res, 2012, 19, 2755

[231] E. Silva, M.M. Pereira, H.D. Burrows, M.E. Azenha, M. Sarakha, M. Bolte, J. Photochem.Photobiol. Sci. 2004, 3, 200

^[232] M.A. Meetani, M.A. Rauf, S. Hisaindee, A. Khaleel, A. AlZamly, A. Ahmad, RSC Adv., 2011, 1, 490