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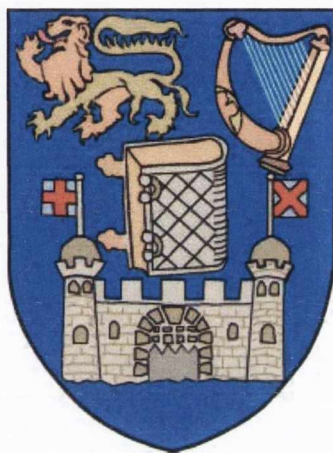
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Synthetic and Spectroscopic Studies of Novel Nonplanar Tetrapyrrolic Macrocycles



Submitted by

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B. A. (Mod) in Chemistry

*A thesis submitted to the University of Dublin, Trinity College for the degree of
Doctor of Philosophy*



Thesis 9319

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Summary

The aim of this work was to develop a new synthetic route for the synthesis of hydroporphyrins and to investigate their photophysical properties. A second aim was to investigate the effect of protonation on the conformation of both porphyrins and hydroporphyrins.

A new pathway was discovered for the synthesis of 2-mono- and 2,3-disubstituted chlorins, and 5,10-disubstituted porphodimethenes (PDM) from *meso* tetrasubstituted porphyrin starting materials. Reaction of *meso* tetraalkylporphyrins with organolithium reagents afforded both mono- and disubstituted chlorins in good yields. Use of palladium-based catalysts ensured selectivity for the single or double addition product. By and large, reaction of *meso* tetraarylporphyrins with aryllithium reagents afforded an unconjugated 5,10-disubstituted PDM product. Yields were improved more than ten-fold compared to those previously reported in literature.

Formation of chlorins and particularly, porphodimethenes, results in significant distortions to the tetrapyrrolic macrocycle. 5,10-Disubstituted PDMs are a relatively under-investigated area of porphyrin chemistry. Thus, intensive UV-vis and ^1H NMR investigations were performed on two of these compounds. It was found that the effect of protonation on PDMs contrasted to the effect on porphyrins. Different acids were tested to investigate anion effects, and like porphyrins, PDM dications were found to coordinate to the acid anion. Significantly, the formation of an elusive monocation intermediate was verified. Although of much interest, this intermediate is rarely observed in porphyrin chemistry.

Porphyrin trimers, linked by a rigid triptycene moiety were prepared and chelated with zinc. Their potential for applications in host-guest chemistry was investigated with bidentate ligand using UV-vis spectroscopy. The cavity size of the trimeric systems could be altered by using different linker groups. UV-vis investigations showed differences in the binding properties of each trimeric system upon ligand coordination. The main outcome of this study showed concentration-dependent binding interactions. At lower concentrations of the bidentate ligand, both sandwich and external binding interactions were observed. However, at higher concentrations, two systems formed fully externally complexed ligand/trimer systems.

Publications

Sergeeva, N. N.; Shaker, Y. M.; Finnigan, E. M.; McCabe, T.; Senge, M. O: Synthesis of hydroporphyrins based on comparative studies of palladium catalyzed and non-catalyzed approaches. *Tetrahedron* **2007**, 63, 12454-12464.

Finnigan, E. M.; Giordani, S.; Senge, M. O.; McCabe, T.: Structural, spectroscopic and anion binding properties of 5,10-porphodimethenes, an unusual class of calixphyrins. *J. Phys. Chem. A* **2010**,

Conference Abstracts

Natalia N. Sergeeva, Eimear Finnigan, Vanessa Lopez Pablo and Mathias O. Senge; Palladium Catalysed Reactions in Porphyrin Chemistry: Centre for Chemical Synthesis and Chemical Biology “Recent Advances in Synthesis and Chemical Biology V” RCSI, Dublin, 15th December **2006**.

Natalia N. Sergeeva, Eimear Finnigan and Mathias O. Senge; Palladium catalysed reactions for the synthesis of hydroporphyrins: Book of Abstracts, The Eighteenth Lakeland Symposium on Heterocyclic Chemistry, Grasmere Village, Cumbria, UK, 10th-14th May **2007**, P12.

Natalia N. Sergeeva, Eimear Finnigan and Mathias O. Senge; Palladium catalysed reactions for the synthesis of hydroporphyrins: Book of Abstracts, 15th European Symposium on Organic Chemistry, University College Dublin, Ireland, 8th-13th July **2007**, P96

Eimear Finnigan and Mathias O. Senge; Studies towards the synthesis of hydroporphyrins: Chlorins porphodimethenes and porphyrin dications: 9th Annual Symposium on Supramolecular Chemistry in Ireland, Trinity College Dublin, Ireland, 13th March **2008**.

Eimear Finnigan, Silvia Giordani and Mathias O. Senge; Hydroporphyrins as conformationally designed tetrapyrrole receptors: Tetrapyrrole Discussion Group Meeting, Trinity College Dublin, Ireland, 12th-14th September **2008**.

Eimear Finnigan, Silvia Giordani and Mathias O. Senge; Organic Synthesis: Hydroporphyrins as conformationally designed tetrapyrrole receptors: 2nd EU CheMS Chemistry Congress, Torino, Italy, 16th-20th September **2008**. 1.O-S Poster no. 58.

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For my parents

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Abbreviations

Ar	aromatic
AsPh ₃	trphenylarsine
BF ₃ .OEt ₂	boron trifluoride etherate
Bipy	4,4'-bipyridine
BNCT	boron neutron capture therapy
br	broad
Bu	butyl
calcd	calculated
CDCl ₃	deuterated chloroform
CH ₂ Cl ₂	dichloromethane
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
dd	doublet-doublet
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
EtOAc	ethyl acetate
equiv.	equivalent
ES	electrospray
FB	free base
Hex	hexyl
HMBC	Heteronuclear Multiple Bond Correlation
HRMS	High resolution mass spectrometry
HSQC	Heteronuclear Single Quantum Coherence
Hz	Hertz
IUPAC	International Union of Pure and Applied Chemistry
<i>J</i>	coupling constant measured in Hertz
m	multiplet
MALDI	matrix-assisted laser desorption/ionisation
me	methyl
MeOH	methanol
mp	melting point
MS	mass spectrometry
<i>m/z</i>	mass-to-charge ratio

NBS	<i>N</i> -Bromosuccinimide
NCS	<i>N</i> -Chlorosuccinimide
NEt ₃	triethylamine
NLO	nonlinear optics
NMR	nuclear magnetic resonance
noe	nuclear overhauser effect
H ₂ OEP	2,3,7,8,12,13,17,18-octaethylporphyrin
PdCl ₂ (PPh ₃) ₂	dichlorobis(triphenylphosphine)palladium(II)
Pd ₂ (dba) ₃	tris(dibenzylideneacetone)dipalladium(0)
Pd ₂ (dba) ₃ .CHCl ₃	tris(dibenzylideneacetone)dipalladium(0).chloroform complex
Pd(OAc) ₂	palladium(II)acetate
Pd(PPh ₃) ₄	tetrakis(triphenylphosphine)palladium(0)
PDM	porphodimethene
PDT	photodynamic therapy
Ph	phenyl
ppm	parts per million
q	quartet
quin	quintet
rec'd	recovered
R _f	retention factor
RI	alkyl iodide reagent
RLi	organolithium reagent
ROESY	rotational nuclear Overhauser Effect Spectroscopy
rt	room temperature
s	singlet
S _E Ar	electrophilic aromatic substitution
S _N Ar	nucleophilic aromatic substitution
t	triplet
TBAF	tetra- <i>n</i> -butylammonium fluoride
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilane
H ₂ T(3-MeOP)P	5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin

H ₂ T(4-MeOP)P	5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin
H ₂ TEPP	5,10,15,20-tetrakis(1-ethylpropyl)porphyrin
H ₂ T <i>i</i> BuP	5,10,15,20-tetra <i>i</i> sobutylporphyrin
H ₂ TPP	5,10,15,20-tetraphenylporphyrin
UV	ultraviolet
v/v	volume to volume
vis	visible
δ	chemical shift measured in parts per million (ppm)
ε	molar absorption coefficient
λ	wavelength measured in nanometre (nm)

Chapter 1

Introduction

1.1 Structure and basic properties of porphyrins

The class of organic compounds collectively known as porphyrins are found abundantly in nature. They are involved in oxygen transport (haem)¹ and storage (myoglobins),²⁻⁷ and electron transport (cytochrome c),⁸⁻¹¹ whereas their reduced forms play a fundamental part in photosynthesis (chlorophylls)¹²⁻¹⁶ and oxygen reduction (oxidases).¹⁷ The porphyrin structure was first proposed by Küster in 1912 and confirmed by Fischer in 1929 when he succeeded in synthesising protohaem.¹⁷ They comprise four pyrrole rings linked by one bridging carbon atom, to form a large macrocycle of twenty carbon atoms and four nitrogen atoms. The porphyrin macrocycle contains 22 conjugated π -electrons, only 18 of which are involved in the delocalisation pathway of the aromatic system, as can be seen in Figure 1.1. Thus, according to Hückel's Rule for aromaticity,^{18,19} with $[4n + 2]$ π -electrons, where $n = 4$, porphyrins are aromatic compounds. Porphyrins have several distinguishing characteristics resulting from their aromaticity. For example, the main absorption band in the spectra of porphyrins, the Soret band, has a very high extinction coefficient which is characteristic of the macrocyclic conjugation. Additionally, X-ray crystallography has revealed the planarity of the nucleus which is a basic requirement for aromatic character.¹

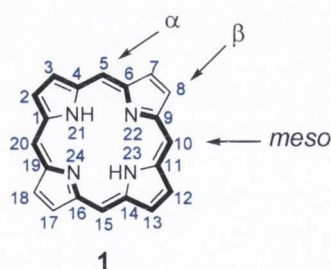


Figure 1.1. Unsubstituted porphyrin macrocycle with IUPAC nomenclature and designation of atoms.

There are four different types of atoms on the porphyrin macrocycle; the four pyrrole nitrogen atoms (numbered 21-24); the bridging methine carbon atoms, numbered 5, 10, 15 and 20 called the *meso* carbon atoms; the α -pyrrole atoms, numbered 1, 4, 6, 9, 11, 14, 16 and 19; and the β -pyrrole atoms are numbered 2, 3, 7, 8, 12, 13, 17 and 18. The β - and *meso* positions, at the porphyrin periphery, are available to undergo numerous addition and substitution reactions. The electronic properties of the porphyrin determine which of the two sites are activated.²⁰ Addition to the α -position is rare, however such

occurrences result in ring-opening i.e. bilane formation. Each of the two central pyrroline nitrogen atoms (N-22 and N-24) are capable of accepting a proton to form a porphyrin dication and the two N-H atoms (21 and 23) are capable of losing a proton to form the dianion. The porphyrin dianion has the potential to form metalloporphyrins.²¹ The main function of porphyrins in nature is to chelate metals, forming complexes that subsequently play an integral role in numerous biochemical processes.^{1,17}

As just 18 of the 22 conjugated π -electrons are incorporated into the delocalisation pathway, one or two of the peripheral β - β' double bonds are available to undergo addition reactions to form chlorins **2**, bacteriochlorins **3** and isobacteriochlorins **4**, without substantial loss of aromaticity (Fig 1.2). (IUPAC nomenclature will be followed throughout with the exception of the nomenclature proposed for chlorins [2,3-dihydro-21*H*,23*H*-porphyrin] which will be disregarded in favour of 2,3-dihydro-22*H*,24*H*-porphyrin). In **3** the reduced pyrrole rings are opposite each other, whereas in **4** they are adjacent to one another. Addition to the *meso* position of **1** causes an interruption in the macrocyclic conjugation to form phlorins **5**, with one sp^3 -hybridised *meso* carbon centre, porphodimethenes **6** with two, and porphomethenes **7** with three.²² Porphyrinogens **8** do not contain any sp^2 -hybridised *meso* carbon atoms, with the result that they lack the highly conjugated double bond structure found in porphyrins, are colourless and do not fluoresce in solution.

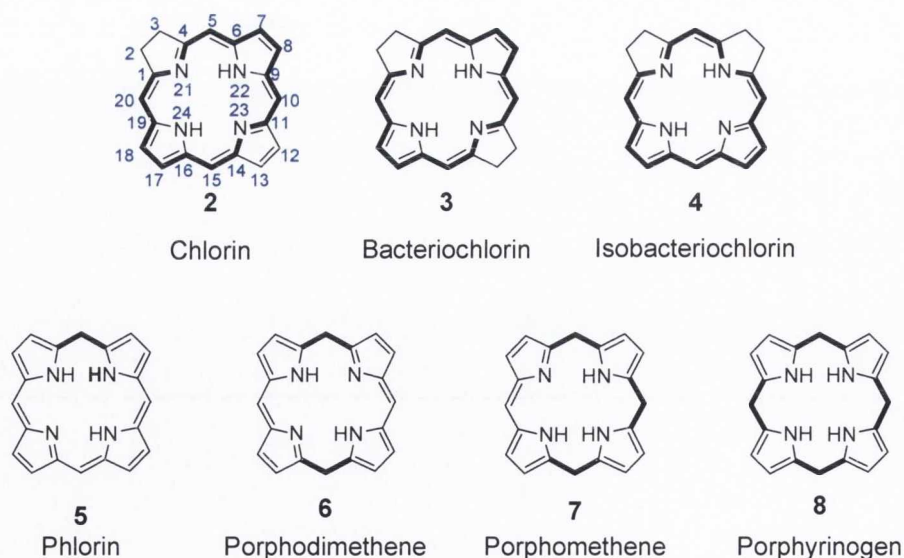


Figure 1.2. Aromatic (top) and non-aromatic (bottom) hydroporphyrins.

In recent years, porphyrinogens have become more commonly known as calix[4]pyrroles. Porphyrinogens were originally named as they were observed as intermediates in the (bio)synthesis of porphyrins.²³ However, their analogy to calix[4]arenes has led researchers to reclassify these macrocycles.²⁴ Nowadays, the non-aromatic hydroporphyrins are commonly called calix[4]pyrins, as they possess a mixture of sp^2 - and sp^3 -hybridised bridging *meso* carbon atoms i.e. they are a hybrid of *calixpyrroles* and *porphyrins*.²²

1.2 Synthesis of porphyrin compounds

Porphyrins play an important role in nature where they are involved in numerous biochemical processes. The majority of naturally occurring porphyrins are β -substituted. However, the syntheses of *meso* substituted porphyrins are considerably more attractive than those of the β -substituted derivatives as they can be easily prepared in a one-pot, two step reaction.²⁵ This has led to the development of more diverse and elaborate chemistry for the *meso* substituted class of porphyrins. They have no direct biological counterparts, however, they have found widespread applications in multiporphyrin assemblies,²⁶ materials chemistry,²⁷ catalysis,²⁸ photodynamic therapy (PDT),²⁹⁻³² electrochemical sensors³³ and molecular recognition.³⁴

1.2.1 Classes of *meso* substituted porphyrins

Synthetic control over the substitution pattern on the porphyrin periphery enables porphyrins to be designed and tailored for specific applications. Figure 1.3 shows the different degrees of substitution that *meso* substituted porphyrins can possess. These are: 1) monosubstitution, A-type porphyrins; 2) disubstitution comprising two symmetric, A_2 - and two unsymmetric AB-type porphyrins; 3) trisubstitution comprising A_3 -, symmetric and unsymmetric A_2B - and ABC-type; and 4) tetrasubstitution comprising seven types: A_4 , A_3B , *cis* and *trans* A_2B_2 and A_3BC , and ABCD.²³

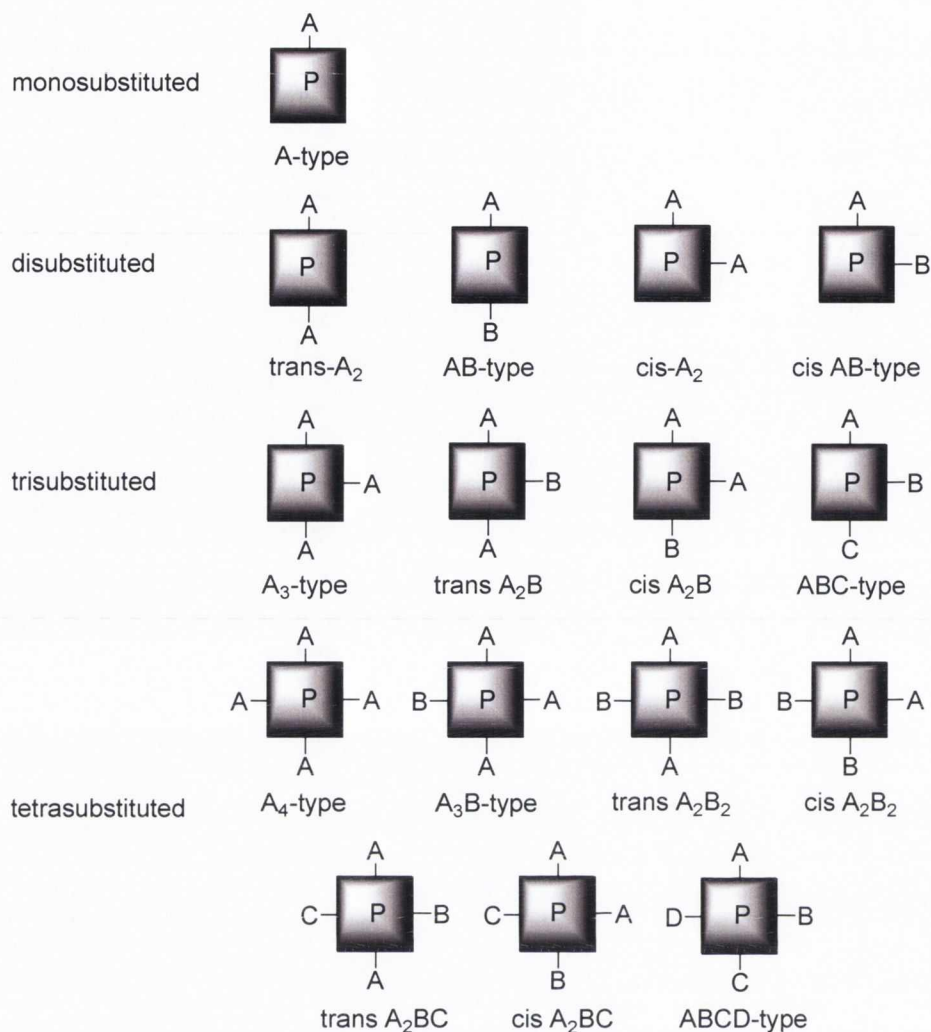
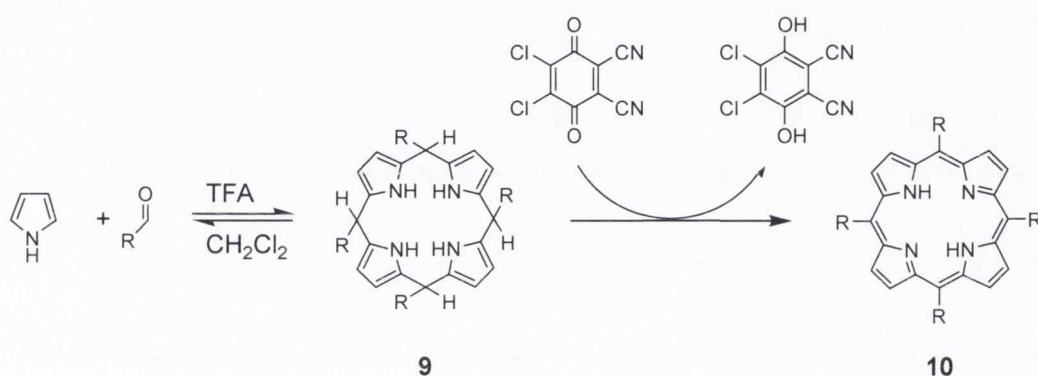


Figure 1.3. Schematic representation of possible *meso* substitution patterns.

1.2.2 Synthesis of *meso* substituted porphyrins

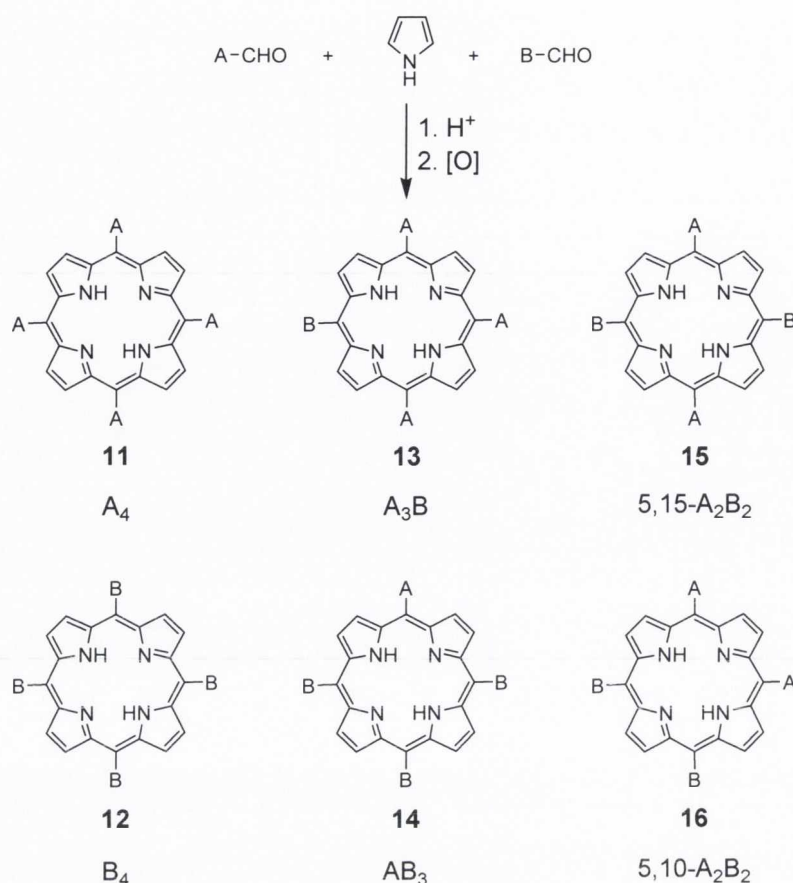
Rothemund first synthesised the parent compound, porphine **1**, and other *meso* tetrasubstituted porphyrins from condensation of aldehyde and pyrrole.³⁵ He later went on to modify this procedure,³⁶ however, high temperatures and high concentrations were required. In addition, no oxidant was added to the reaction, resulting in contamination by chlorin **2** (10-20%) in the reaction mixture. Yields were between 7.5-9%. The Adler Longo method was developed in 1967.³⁷ Refluxing propionic acid was used to dissolve

the aldehyde and pyrrole and crystalline porphyrins were directly obtained from the reaction mixture. Yields reached more than 20% for many aldehydes, however 2-10% chlorin impurity was still present. Also, when the porphyrin did not crystallise from the crude reaction mixture, isolation of the product proved difficult. The Lindsey method was developed in 1987 and is now the most commonly used method (Scheme 1.1).²⁵ It involves a one-pot reversible reaction of pyrrole and aldehyde at room temperature to form a tetrasubstituted porphyrinogen (calix[4]pyrrole) **9**. The addition of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) irreversibly oxidises **9** to the corresponding aromatic porphyrin **10**.



Scheme 1.1. Lindsey method for the synthesis of *meso* substituted porphyrins.²⁵

Mixed aldehyde condensation reactions are commonly employed to gain access to porphyrins bearing two different *meso* substituents. The reaction of pyrrole with two different aldehydes yields, in principle, a set of six porphyrins (Scheme 1.2): The two parent porphyrins, **11** and **12**; and four hybrid porphyrins **13-16**. This method was first used to prepare monohydroxy- and monopyridylporphyrins³⁸ and gained popularity for the preparation of a wide variety of porphyrins bearing two different types of substituents.^{39,40}

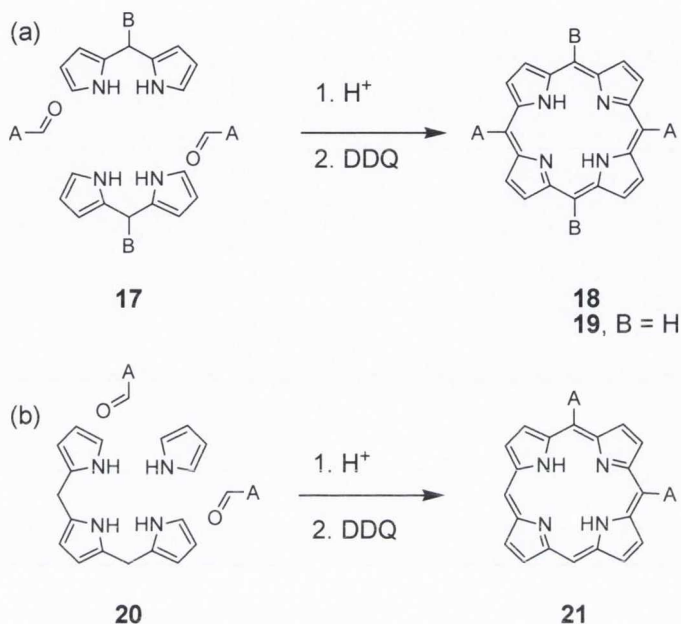


Scheme 1.2. The six porphyrins derived from a mixed condensation reaction of two different aldehydes A and B with pyrrole.

Often, the desired product from a mixed aldehyde condensation is either of the A_3B -type porphyrins **13** and **14**. The yield of this fraction is optimised theoretically by reaction of a 4:3:1 ratio of pyrrole/aldehyde A/aldehyde B.²³ However, the yield also depends on the actual reactivities of the two aldehydes and the ease of separation from the mixture of porphyrins⁴¹ therefore different ratios are sometimes used.⁴² The products in the reaction mixture can possess very similar polarities, making chromatographic purification difficult, particularly when the 5,10- or 5,15- A_2B_2 -isomer is the desired product.⁴³

Due to the difficulties in isolating the desired products from a mixed-aldehyde condensation reaction, several other synthetic routes have been investigated for the formation of differently *meso* substituted porphyrins. The [2+2] MacDonald condensation between a 1,9-diformyl- and a 1,9-diunsubstituted dipyrromethane or its 1,9-dicarboxylic acid in the presence of an acid catalyst was developed for the syntheses

of β -substituted porphyrins.⁴⁴ Procedures were developed for the synthesis of *meso* substituted porphyrins based on this [2+2] approach. Reaction of a dipyrromethane **17** with an aldehyde affords *trans*-A₂B₂ **18** and A₂-porphyrins **19** (Scheme 1.3).⁴⁵ A variation of this, the [3+1] condensation of a tripyrrane **20** and an aldehyde can be used to make the 5,10-derivative **21** (Scheme 1.3).⁴⁶



Scheme 1.3. Synthetic routes to (a) 5,15-A₂B₂- (and A₂-) porphyrins *via* a [2+2] MacDonald-type condensation reaction and to (b) 5,10-A₂-porphyrins *via* a [3+1] condensation reaction of tripyrrane and an aldehyde.

Porphyrins with free *meso* positions are synthetic precursors for numerous reactions including nucleophilic and electrophilic substitution reactions, and subsequently, palladium-catalysed cross coupling reactions such as Heck, Suzuki and Sonogashira reactions.

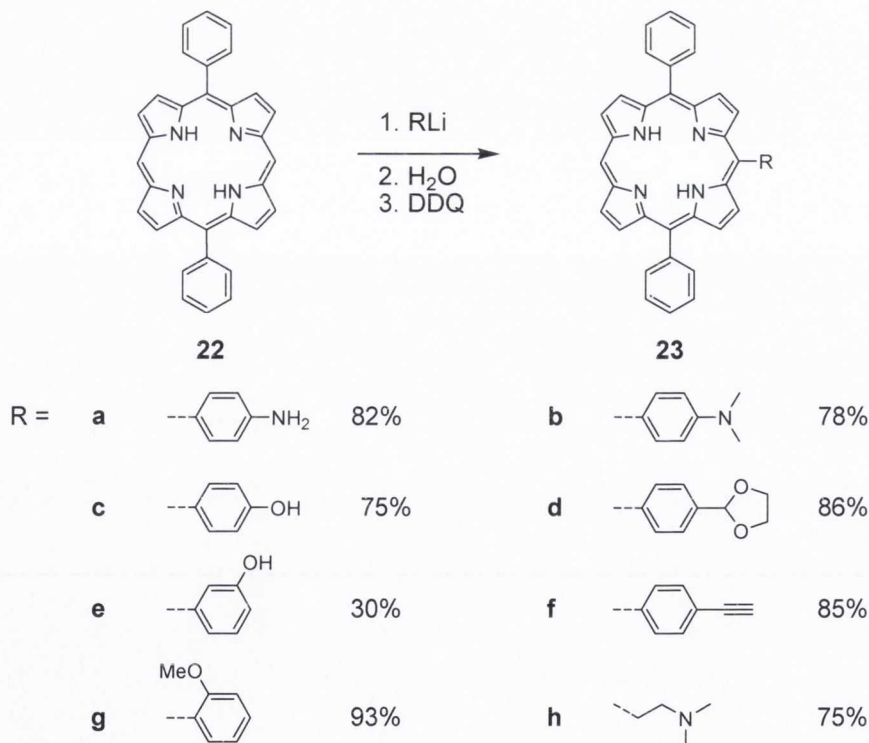
1.3 Reactivity of porphyrin compounds

Porphyrins are essentially aromatic molecules and as such, are expected to undergo the characteristic reactions of these compounds, i.e. electrophilic substitution reactions such as Vilsmeier formylations, nitrations, halogenations and acylations; nucleophilic reactions such as those with organometallic reagents; and oxidation and reduction reactions.

1.3.1 Nucleophilic reactions at the *meso* position with organolithium reagents

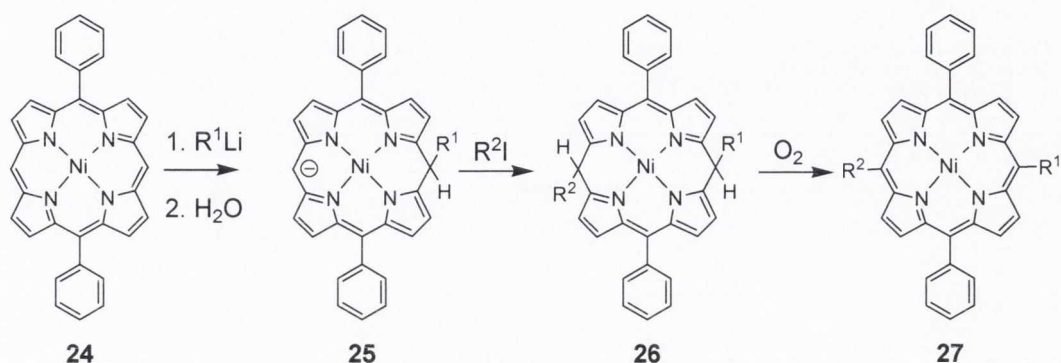
Porphyrins bearing substituents in the 5,15-positions are useful precursors for the synthesis of functionalised porphyrins. Highly functionalised asymmetric 5,10,15,20-tetrasubstituted porphyrins are required for catalysis, nonlinear optics (NLO), molecular recognition and photosensitisers.

Porphyrins react with nucleophiles such as Grignard and organolithium reagents at the *meso* or β -positions. However, most of these reactions require prior activation of the macrocycle with electron withdrawing groups⁴⁷⁻⁵⁷ or high valent metals.^{58,59} Notably, Senge *et al.* successfully synthesised unsymmetrically substituted porphyrins from unactivated porphyrin starting materials *via* a nucleophilic substitution reaction.^{60,61} A range of functionalised porphyrins were synthesised in yields up to 86% through the reaction of an organolithium reagent with 5,15-diphenylporphyrin **22** (Scheme 1.4). An excess of organolithium reagent was used (10-15 equiv.) to ensure high yields of the desired products and to prevent the formation of ring-opened side products. Using this method, a range of A₂B-type porphyrins **23a-h**, bearing highly reactive centres were easily prepared.



Scheme 1.4. Synthesis of unsymmetric A₂B-porphyrins *via* reaction with organolithium reagents.

Detailed mechanistic studies of the reaction with an organolithium reagent and (5,15-diphenylporphyrinato)Ni(II) **24** revealed the formation of a Meisenheimer-type complex. The negative charge was partly located at the 20-position of the nickel(II) porphyrin after addition of the organic nucleophile to the 10-position.⁶² It was found that this porphyrin anion **25** reacted directly with electrophiles such as alkyl iodide to yield A₂BC-type porphyrins **27** *via* the formation of porphodimethenes **26** (Scheme 1.5).



Scheme 1.5. One-pot, two step reaction for the synthesis of A₂BC-type porphyrins.

1.3.2 Carbon-carbon coupling reactions

Over the past decades palladium-catalysed reactions have proven to be one of the most adept and versatile metal-mediated transformations in organic chemistry.⁶³ Due to the facile performance of these reactions they have been extensively used in porphyrin chemistry with great success. Direct nucleophilic substitution of a halogen atom at an sp²-centre is not readily achievable due to the inaccessibility of the carbon-halide antibonding orbital. Metal-mediated cross-coupling methodology developed largely by Suzuki,⁶⁴ Sonogashira,⁶⁵ Kumada,⁶⁶ Negishi,⁶⁷ Heck,⁶⁸ and Stille^{69,70} has become an important tool in modern organic chemistry to facilitate formation of carbon-carbon bonds between aryl or alkenyl halide substrates and a variety of alkyl, aryl and vinyl organometallic reagents. A typical cross-coupling pathway involves oxidative addition of an aryl halide to a transition metal catalyst, followed by ligand exchange to give the complex. Finally, reductive elimination of the product regenerates the active catalyst. A wide range of palladium(0) catalysts, or precursors can be used for the above reactions. Tetrakis(triphenylphosphine)palladium(0) is most commonly used but bis(triphenylphosphine)palladium(II) chloride, palladium(II) acetate, triphenylphosphine, or other phosphine ligands are also effective, since they are stable to air and are readily reduced to the active palladium(0) complex. This methodology is directly applicable to a wide

variety of porphyrin synthetic schemes. Three palladium catalysed reactions will be discussed in this thesis.

A. Suzuki cross coupling

In the Suzuki coupling reaction an aryl or vinyl boronic acid are coupled with an aryl or vinyl halide using a palladium(0) catalyst (Figure 1.4).

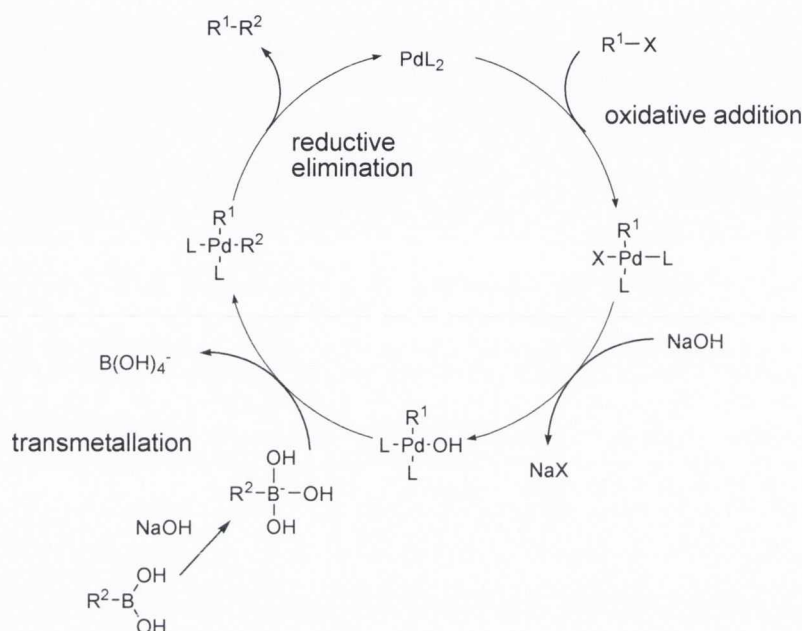
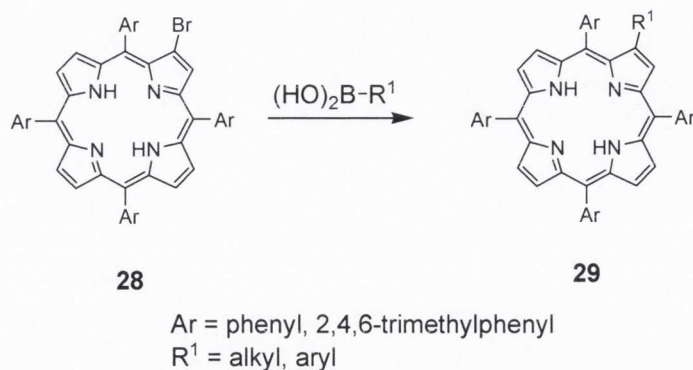


Figure 1.4. Catalytic cycle for the Suzuki-Miyaura reaction.⁷¹

The first report of a Suzuki cross-coupling reaction on a porphyrin was for the β -position of a porphyrin (Scheme 1.6). A series of β -aryl,⁷² and later β -alkyl^{73,74} porphyrins **29** were prepared from the reaction of β -bromoporphyrin **28** with various *p*-substituted arylboronic acids and alkylboronic acids. Yields were between 55 and 88%. Since then, this reaction has also been developed for *meso p*-bromophenylporphyrins with yields up to 79%,⁷⁵ and by Shi *et al.* for *meso* bromoporphyrins⁷⁶ for the synthesis of unsymmetrically substituted *meso* phenylporphyrins. Yields reported were between 24-78%.



Reagents and conditions: K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, toluene, 1-7 days.

Scheme 1.6. Suzuki cross coupling of β -bromoporphyrin with alkyl- and arylboronic acids.

Additionally, Hyslop *et al.* applied this methodology to boronylporphyrins i.e. a boronic ester was attached to the porphyrin.⁷⁷ This approach was later employed by Osuka *et al.* for the synthesis of covalently linked porphyrin dimers and trimers using one haloporphyrin and one boronylporphyrin.⁷⁸

B. Sonogashira Reaction

The Sonogashira reaction involves the coupling of a terminal alkyne with an aryl or vinyl halide (1.2).⁶⁵ It proceeds under basic conditions and generally requires the use of a copper iodide co-catalyst (Figure 1.5).

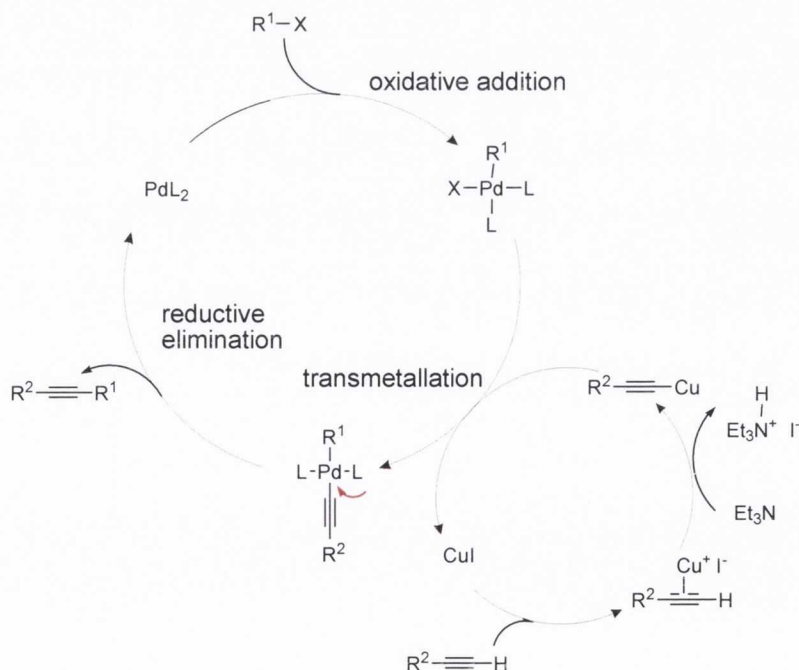
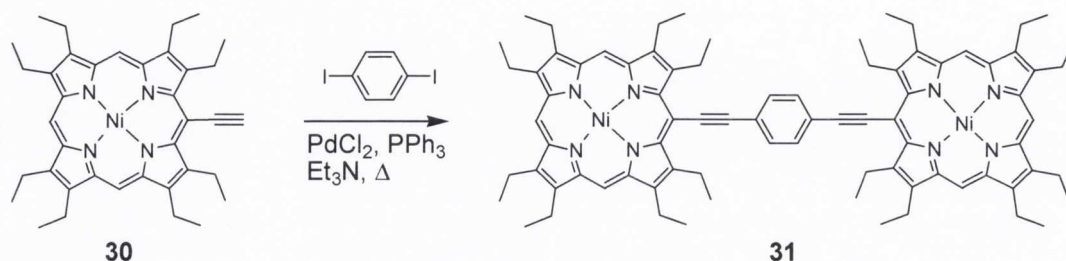


Figure 1.5. Catalytic cycle for the Sonogashira reaction.⁶⁵

This reaction was first applied to a porphyrin by Arnold and Nitschinsk (Scheme 1.7). A covalently-linked porphyrin dimer **31** was obtained from the reaction of a 5-ethynyl porphyrin **30** with 1,4-diiodobenzene in 60% yield.⁷⁹ Since then the Sonogashira reaction has also been applied to β - and *meso* halogenated porphyrins to yield various alkynyl substituted porphyrins.^{55,80}



Scheme 1.7. Synthesis of covalently-linked porphyrin dimer *via* a Sonogashira coupling reaction.

Sonogashira reactions are commonly used for the synthesis of multiporphyrin arrays (Fig. 1.4) as they provide the rigid, covalently-linked framework light-harvesting systems require to mimic photosynthesis.⁸¹⁻⁸³

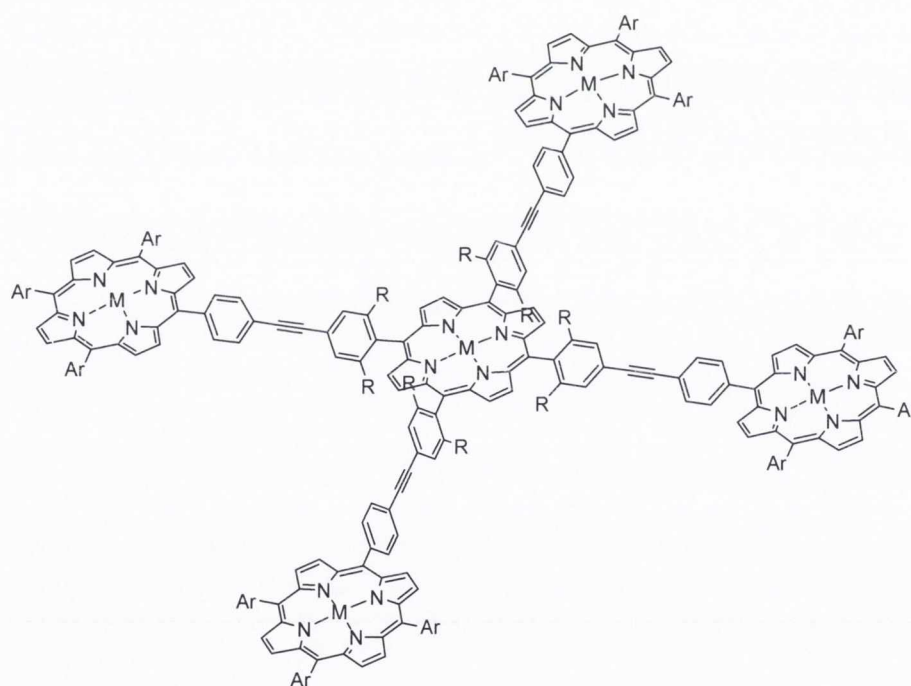


Figure 1.6. Structure of a multiporphyrin array synthesised by Lindsey and co-workers *via* Sonogashira coupling conditions.⁸¹

C. Heck Reaction

The Heck reaction is the palladium-catalysed coupling of a haloarene or haloalkene with an alkene.⁸⁴

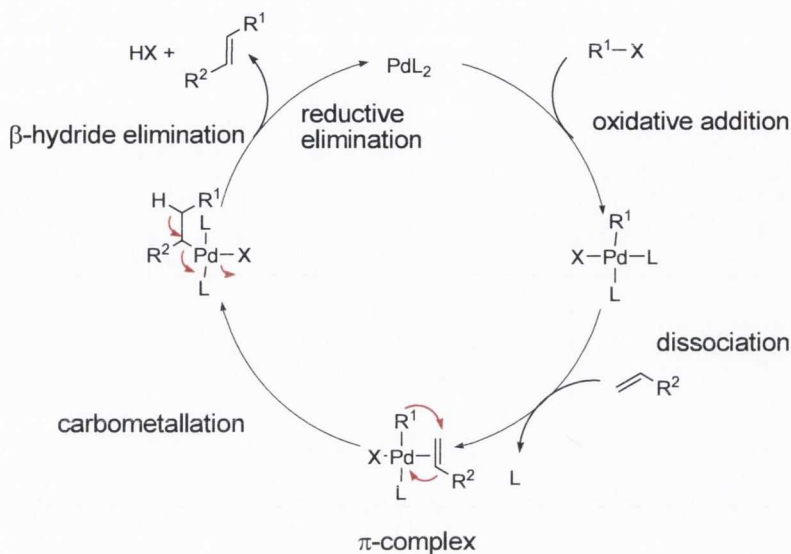
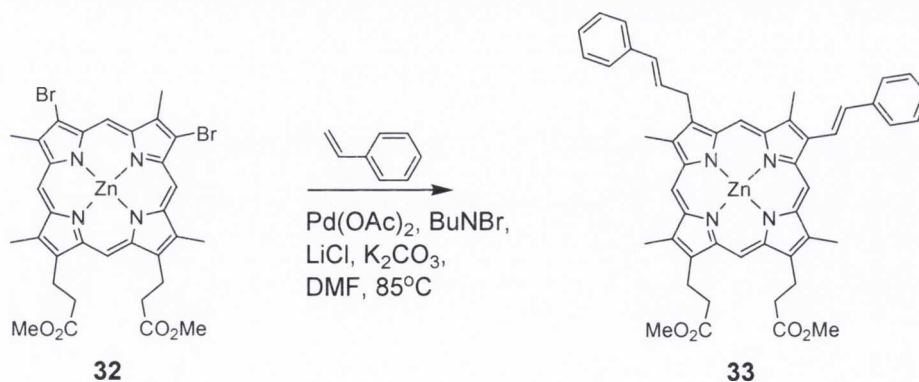


Figure 1.7. Catalytic cycle for the Heck reaction.⁸⁴

Heck reactions provide a useful method for introducing ethenyl substituents to the β -positions of porphyrins in high yields. Gauler and Risch reported synthesis of a 3,8-distyrylporphyrin **33** in 87% yield from bromoporphyrin **32** (Scheme 1.8).⁸⁵



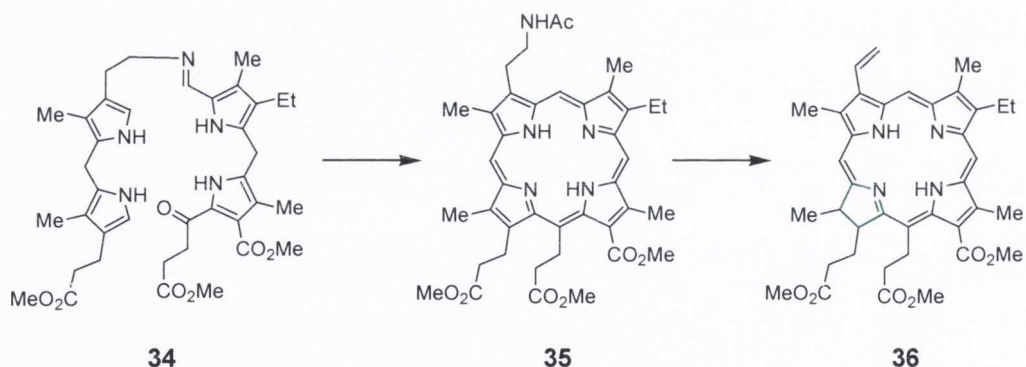
Scheme 1.8. Introduction of ethenyl moiety *via* a palladium-catalysed Heck reaction.

1.4 Chlorins; 2,3-dihydroporphyrins

Chlorins are very similar to porphyrins in that they both are highly conjugated tetrapyrrolic macrocycles. However, one pyrrole ring in a chlorin is saturated across the β -positions. Different physicochemical properties result from this altered symmetry and path of conjugation. An obvious visible difference is that chlorins absorb strongly in

both the red and blue region (resulting in their green colour) whereas porphyrins mainly absorb in the blue region (and are therefore purple). Chlorins have a lower oxidation potential which makes them suitable as excited state reductants. Because of these features, along with several others, chlorins have found multiple applications as photosensitisers in photodynamic therapy (PDT)^{29,31,86} and boron neutron capture therapy (BNCT),^{87,88} and as models for photosynthetic reaction centres.⁸⁹⁻⁹² The development of new synthetic routes to chlorins has not matched their obvious appeal over porphyrins. This is due to the difficulty in obtaining their requisite building blocks and has resulted in porphyrins being used in preference to chlorins. Thus the full potential of chlorins will not be realised until reasonable methodologies for their syntheses are developed.

Routes to chlorin syntheses are as elaborate as Woodward's classical synthesis of chlorin *e*₆ trimethyl ester, a precursor of chlorophyll, and as simple as hydrogenation of a synthetic or naturally occurring porphyrin. The final steps of Woodward's total synthesis involved a MacDonald-type reaction followed by transformation of a porphyrin **35** to yield the chlorin product **36** (Scheme 1.9).⁹³



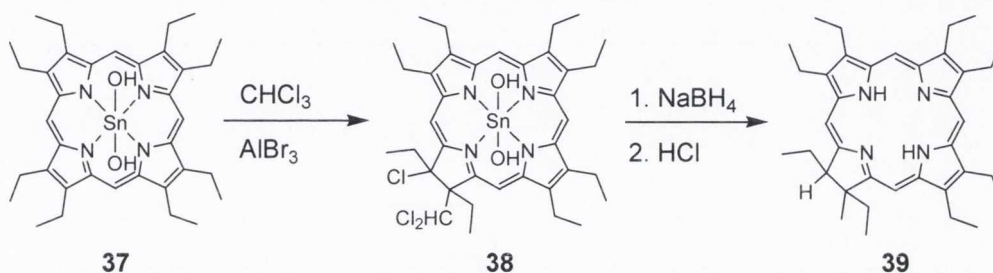
Scheme 1.9. Final steps of Woodward's total synthesis of chlorin *e*₆ trimethyl ester.

In recent years, these methods have been widely developed and now include: [2+2] MacDonald-type condensations of dipyrromethane precursors,^{94,95} Diels Alder reaction,⁹⁶⁻⁹⁸ reduction with diimide,⁹⁹ oxidation with osmium tetroxide^{100,101} and 1,3-dipolar cycloaddition¹⁰²⁻¹⁰⁵ on the peripheral double bonds of porphyrins.

Carbenes can attack the porphyrin at β -pyrrole positions to produce cyclopropanechlorins.¹⁰⁶ Porphyrins can also be reduced to give hydroporphyrins.¹⁰⁷ However, reductions work best when the porphyrin is metallated with Fe(III), Mn(III)

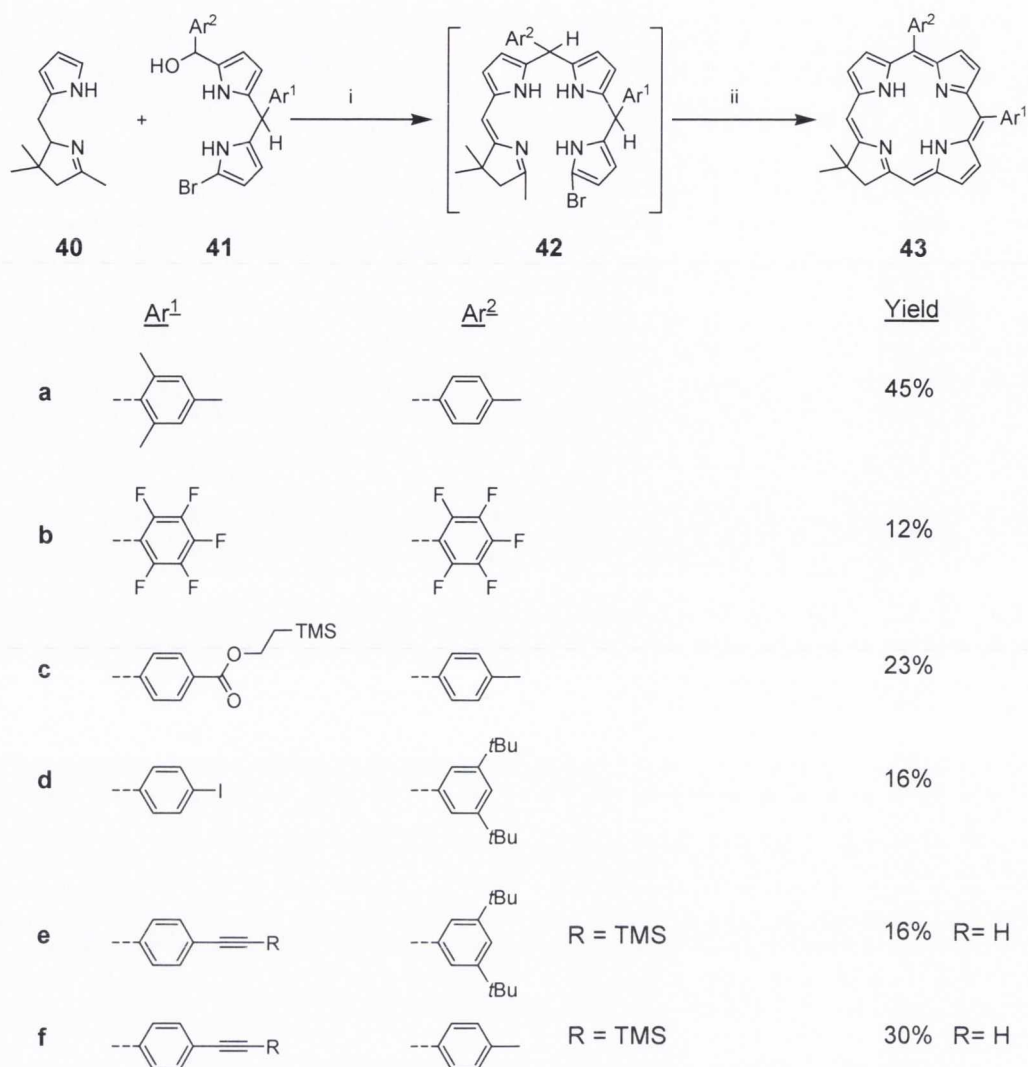
or Sn(IV), so as to decrease the electron density on the macrocycle and to make it more susceptible to reduction.²⁰

Electrophilic addition reactions tend to occur at the peripheral β - β' positions in the macrocycle which possess more double bond character (Section 1.1). For example, chlorin formation was achieved by reacting the tin(IV) dihydroxide complex **37** in the presence of AlBr_3 to yield the chlorin **38**. Reduction with sodium borohydride and demetallation yielded a methylchlorin **39** (scheme 1.10).¹⁰⁸



Scheme 1.10. Chlorin formation *via* an electrophilic addition reaction.

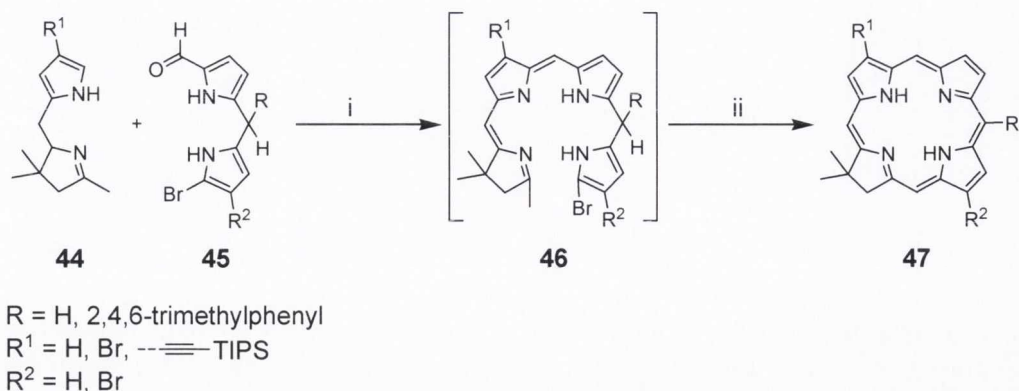
Lindsey *et al.* recently published a series of papers in which a number of chlorins were synthesised *via* a [2+2]-type condensation reaction.¹⁰⁹⁻¹¹¹ Two sets of dipyrroles were prepared, each comprising an “eastern half”, and a “western half”. In the first route, shown in Scheme 1.11, the reaction of the eastern half, a 9-bromodipyrromethane-1-carbinol **41**, and the western half, 1,3,3-trimethyltetrahydropyrroin **40**, proceeded in a two-step process, the first of which was a condensation to yield a 1-methyl-19-bromobilane derivative **42**.¹¹² The geminal dimethyl group of **40** ensured the stability of the reduced pyrroline ring, precluding adventitious dehydrogenation to the porphyrin. The second step, a metal-mediated oxidative cyclisation of the bilane **42**, yielded the desired chlorin **43**. A series of aromatic chlorins **43a-f** were prepared in yields between 12-45%.



Reagents and conditions: (i) TFA (10 mM), CH_3CN ; (ii) AgIO_3 , piperidine, $\text{Zn}(\text{OAc})_2$, toluene, 80°C , 2 h

Scheme 1.11. Synthesis of 3,3-dimethylchlorin *via* a bilane intermediate.

The second route proceeded in a similar fashion (Scheme 1.12). The eastern half comprised 9-bromodipyrromethane-1-carboxaldehyde **45** and the western half comprised a 1,3,3-trimethyltetrahydropyrrin **44** similar to that in Scheme 1.11. Overall yields were between 7 and 42% and allowed introduction of bromo- and ethynyl functionality onto the porphyrin periphery.¹¹²



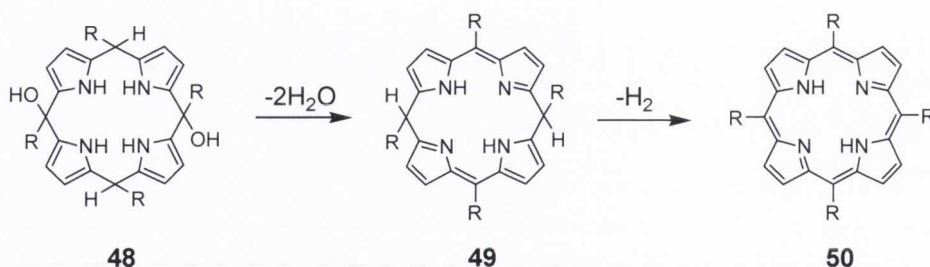
Reagents and conditions: (i) *p*-TsOH.H₂O, CH₂Cl₂/MeOH, rt, 30 min; (ii) AgOTf, Zn(OAc)₂, piperidine, reflux, 18-24 h

Scheme 1.12. Synthesis of 3,3-dimethylchlorin with β -functionality.

The above reactions provided an attractive method for the preparation of chlorins with no substituent or a single substituent on the *meso* carbon atoms. However, preparation of the eastern and western dipyrroles required two to three steps, so although the yields were acceptable, they had been determined from the dipyrrolic precursors. There are few reports of rational syntheses of chlorins from monopyrroles, and the 2,3-dihydroporphyrins are largely obtained by modification of naturally occurring chlorins or reduction of porphyrins and metalloporphyrins.

1.5 Porphodimethenes; 5,10- and 5,15-dihydroporphyrins

Porphodimethenes display different physicochemical properties than porphyrins. Only two of the *meso* positions are sp^2 -hybridised with the result that the conjugation in the macrocycle is interrupted. Porphodimethenes were first observed as intermediates in the (bio)synthesis of porphyrins. The acid catalysed condensation of pyrroles with aldehydes proceeds first to a porphyrinogen **48** and then *via* separate oxidation steps *via* a porphodimethene **49** to yield the desired porphyrin **50** (Scheme 1.13). It is believed that the chlorin by-product obtained from the Rothmund and Adler-Longo condensation methods (Section 1.2.2), forms as a result of a transformation of the porphodimethene intermediate **49**.¹¹³

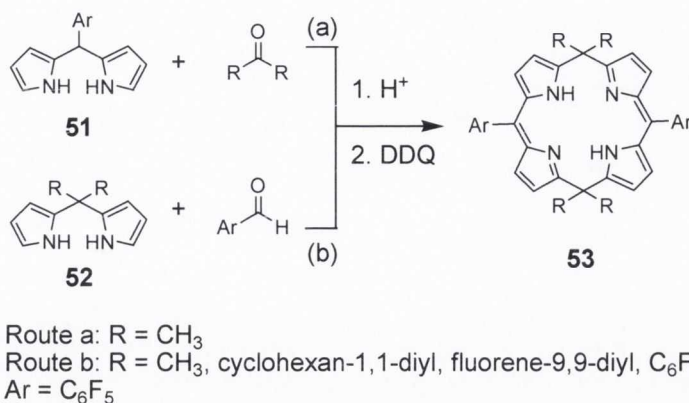


Scheme 1.13. Oxidation of porphyrinogen to porphyrin *via* hydroporphyrin intermediates.

Porphodimethenes also bear analogy to another class of tetrapyrroles, calixpyrroles. Calixpyrroles are unoxidisable porphyrinogens with all four *meso* positions sp^3 -hybridised. They have eight alkyl or aryl *meso* substituents, which prevent oxidation of the macrocycle to give the corresponding porphyrin. Calixpyrroles were first synthesised by Baeyer in the nineteenth century, but interest in these molecules only developed in the last two decades. Floriani and co-workers¹¹⁴⁻¹¹⁸ have investigated metallated calixpyrroles and more recently Sessler and co-workers¹¹⁹⁻¹²¹ examined the anion binding properties of these compounds. Porphodimethenes are often referred to as a hybrid of porphyrins and calixpyrroles and therefore have the potential to possess both the biological affinity of porphyrins and the anion binding properties of calixpyrroles.

Initially the only method for the synthesis of porphodimethenes was Buchler's method for the reductive alkylation of metalloporphyrins, however this procedure was limited to certain metalloporphyrins and was not compatible with all types of β -substituents. A number of alternative methods have been developed. These include a [2+2] MacDonald-like condensation reaction with a ketone,¹²²⁻¹²⁴ acid catalysed condensation of an oligopyrrole with acetone,^{22,125,126} and approaches based on the reaction of sterically hindered aldehydes with pyrrole.¹²⁷

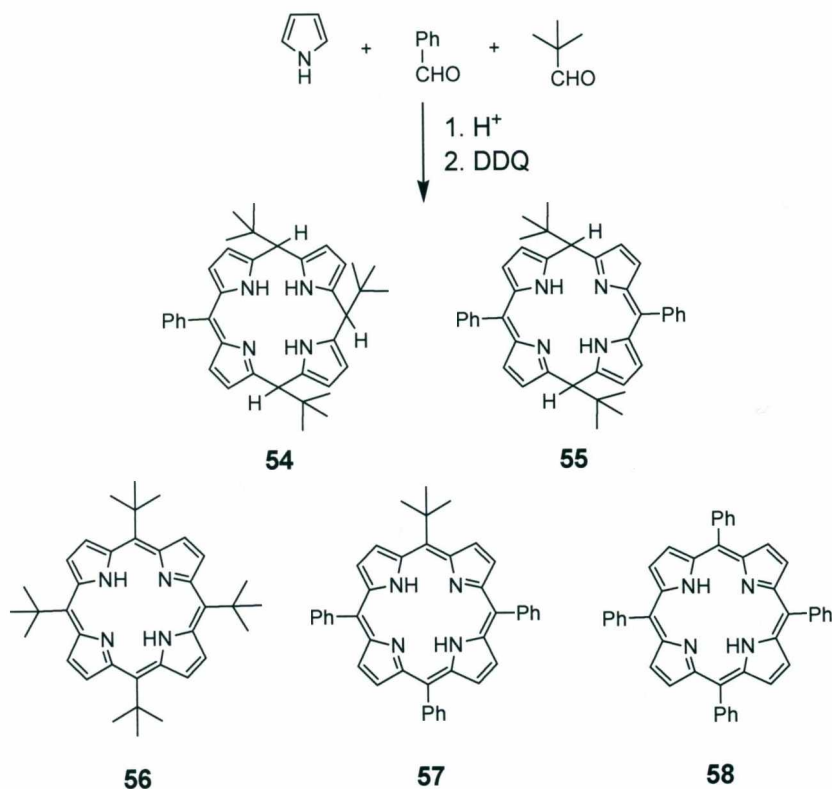
Král *et al.* employed a [2+2] condensation reaction (Scheme 1.14). Diaryl tetraalkyl porphodimethenes of type **53** were prepared by reaction of a 5-substituted dipyrromethane **51** with acetone.²² This method was later developed (route b) to allow for the placement of bulkier groups on the sp^3 -hybridised bridging carbons **52**.¹²⁸



Scheme 1.14. [2+2] Condensation approach to the synthesis of 5,15-porphodimethenes (calix[4]phyrin).

By altering the reaction conditions (longer reaction time, and using TFA), a higher yield was obtained for ring expanded calixphyrins. Both hexa- and octapyrroles were obtained: calix[6]phyrins and calix[8]phyrins respectively.

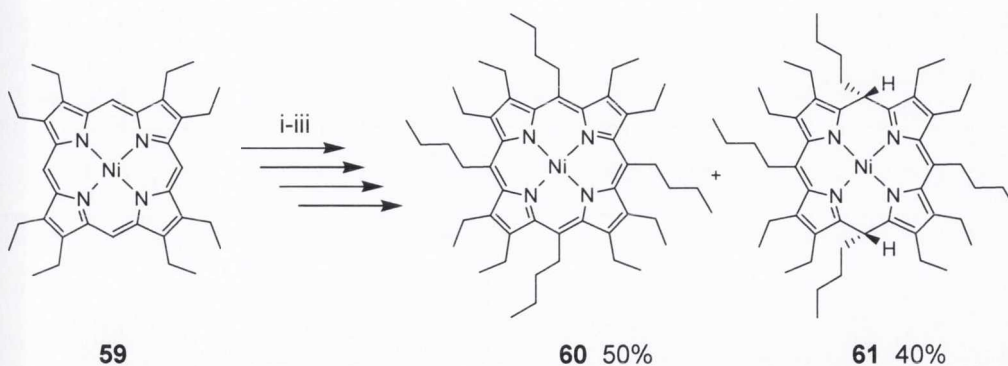
Senge and co-workers made use of steric constraints to synthesise several dihydroporphyrins.^{127,129} Occasionally, during the synthesis of sterically crowded porphyrins, a number of stable hydroporphyrins had been observed. Reaction of pyrrole, pivaldehyde and benzaldehyde (4:3:1 ratio) under Lindsey conditions,²⁵ with TFA as catalyst and DDQ as oxidant, yielded a set of five products **54-58**. Two of which were hydroporphyrins **54** and **55** (Scheme 1.15).



Scheme 1.15. Synthesis of sterically hindered porphyrins *via* a mixed aldehyde condensation reaction.

The formation of these hydroporphyrins was attributed to the steric demand of the *meso* substituents. Due to overcrowding at the porphyrin periphery, relief from macrocyclic strain was achieved by the formation of the corresponding porphodimethenes. sp^3 -Hybridised *meso* carbon atoms facilitated significant out-of-plane distortions of the pyrrole rings to minimise steric interactions of bulky *meso* substituents with β -pyrrole substituents.

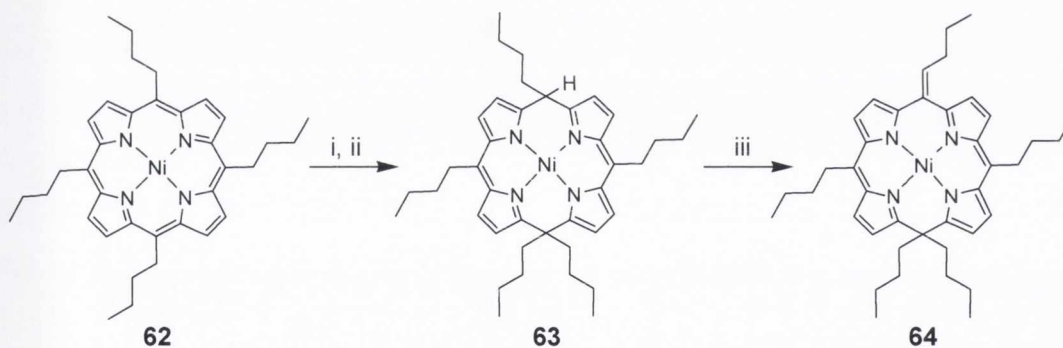
During investigations into the nucleophilic substitution reaction of a β -octasubstituted porphyrin with an organolithium reagent, Senge *et al.* observed oxidation-resistant hydroporphyrin side-products.^{61,130} After four cycles of nucleophilic substitution of (2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) **59** with *n*-butyllithium, the final reaction mixture included both the expected product **60** and a 5,15-dihydroporphodimethene **61** in 40% yield (Scheme 1.16).¹³¹



Reagents and conditions: (i) *n*-BuLi, THF, -70°C; (ii) H₂O; (iii) DDQ

Scheme 1.16. *meso* Functionalisation of Ni(II)OEP by nucleophilic substitution with organolithium reagents.

To understand the formation of the 5,15-porphodimethene **61**, the same reaction was performed with a tetra-*meso* alkylporphyrin **62**.⁶¹ Treatment with *n*-butyllithium at -100 °C followed by addition of water also yielded a 5,15-porphodimethene **63** in 90% yield. Upon treatment with DDQ, this oxidation resistant porphodimethene gave **64** in 80% yield (Scheme 1.17).



Reagents and conditions: (i) *n*-BuLi; (ii) H₂O (iii), DDQ

Scheme 1.17. Synthesis of a 5,15-porphodimethene with an exocyclic double bond from a tetra-*meso* alkylporphyrin.

1.6 Porphyrin dications; 22,24-dihydroporphyrins and nonplanarity

The two pyroline nitrogen atoms bearing lone pairs of electrons can be protonated easily with acids such as trifluoroacetic acid. The most striking feature of porphyrin dications is their deviation from planarity which makes them ideal model systems for nonplanar porphyrins.

Even though planarity is a feature of aromaticity, the porphyrin macrocycle is conformationally flexible and is capable of adopting nonplanar conformations.¹³²⁻¹³⁴ It is widely agreed that the conformation of a tetrapyrrolic macrocycle plays a role in controlling their biological properties in photosynthetic reaction centres,^{135,136} photosynthetic antenna systems,¹³⁷ factor F₄₃₀ from methyl reductase,^{138,139} vitamin B₁₂ and vitamin B₁₂-dependent enzymes¹⁴⁰ and haem proteins.¹⁴¹ In porphyrin dications, the distortion is caused by steric crowding in the porphyrin core and often results in out-of-plane tilting of the macrocycle.^{142,143}

Other methods for the synthesis of nonplanar porphyrins include: metallation; interruption of the aromatic system (phlorin or porphodimethene formation) and extensive substitution on the porphyrin periphery.¹⁴⁴ Depending on the type, location and number of substituents used, different types of distortions result.

Scheidt and Lee¹⁴⁵ suggested four different out-of-plane distortion modes to be used in order to describe porphyrin conformation (Fig. 1.5). Saddled and ruffled conformations are found most frequently. In saddle distorted macrocycles (a), the pyrrole rings are alternately displaced above and below the mean plane while the *meso* carbons largely remain in-plane. In ruffled porphyrins (b), often found in macrocycles chelated with small metals, the metal-nitrogen bond shortening causes a twisting about this bond which results in alternating displacement of the *meso* carbons above and below the plane. Domed conformations (c) are most frequently found in porphyrins metallated with five-coordinate metal atoms. The axial ligand forces the metal ligand out of the plane of the macrocycle, which in turn, displaces the macrocyclic atoms in the opposite direction. In wave conformations (d), two atoms of the *meso* or β -position are displaced alternately above and below the mean plane of the central 4N core. Normally, dications formed with CF₃COOH, H₂SO₄, HClO₄ and HX (where X = F, Cl, Br, I), exhibit a saddle distortion and are hydrogen bonded to the counter ion.^{143,146-149} The degree of distortion can also depend on the nature of the anion.

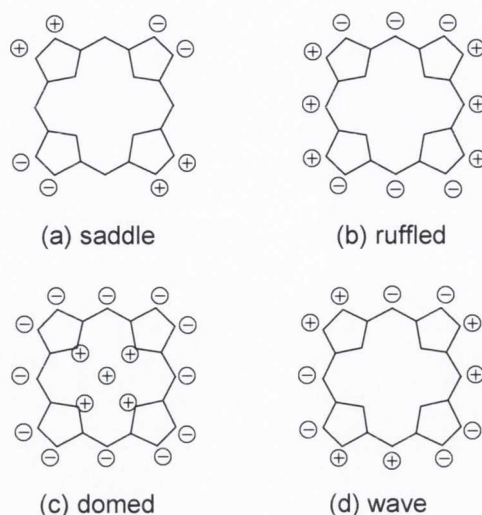


Figure 1.8. Illustration of the four main distortion modes observed for the porphyrin macrocycles. Only the most significant displacements are shown. (+) indicates displacements above the mean plane of the central 4N core and (-) indicates displacements below the mean plane core.

Porphyrins also display in-plane deformations. These include stretching of the *meso* carbon bonds (*m-str*), stretching in the direction of the nitrogen atoms (*N-str*), doubly degenerate deformations in x and y directions [*trn(x)* and *trn(y)*], a macrocycle breathing deformation (*bre*) and pyrrole rotation (*rot*).¹³³

The photophysical properties of nonplanar porphyrins differ significantly from their planar analogues. In the UV-vis spectra, the main absorption band, or Soret band, is shifted to longer wavelengths, whereas, in the fluorescence spectra, there are large spacings between the fluorescence and long wavelength absorption maxima, i.e. a large Stokes shift.¹⁵⁰

1.7 Coordination Chemistry of Porphyrins

Porphyrins are famous for their versatile metal coordination properties. They form complexes with most metallic elements in the periodic table, most of which are capable of binding additional axial ligands (Figure 1.6). Axial coordination alters the spectroscopic, electrochemical, structural and photophysical properties of metalloporphyrins.¹⁵¹

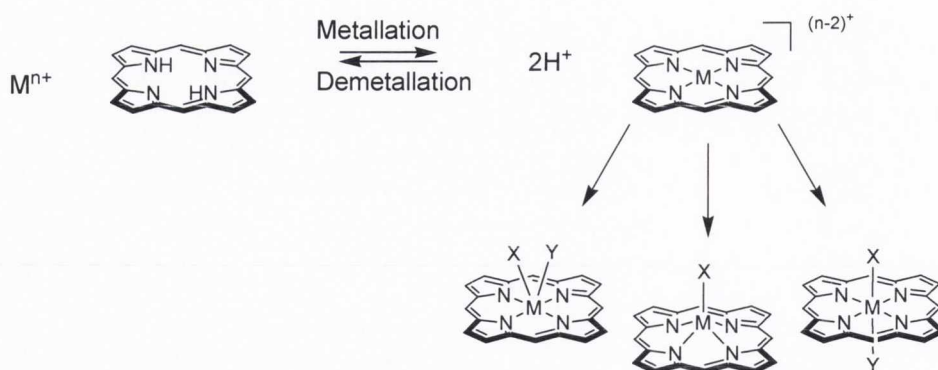


Figure 1.9. Schematic representation of porphyrin metallation with common axial coordination types.

Whereas the fundamental purpose of understanding the effects of axial ligation on the electronic spectra of iron porphyrins is a frequent goal, iron porphyrins are not easily analysed. This is because their d orbitals are only partially filled and there are uncertainties in relation to their coordination numbers, spin states and oxidation states.¹⁵² Therefore, simpler synthetic porphyrins are used to model more complex biological systems.¹⁵³⁻¹⁵⁸ Zinc porphyrins are preferred as model compounds for investigations into axial ligation.¹⁵¹ They are easy to prepare and are readily studied by ^1H NMR. The metal is unambiguously in the 2+ oxidation state and four coordinate zinc porphyrins will only accept one axial ligand to form five coordinate complexes. Since their electronic configuration is d^{10} , there are no empty d orbitals involved in the bonding. Nappa *et al.* revealed that the changes seen in the UV-vis spectra of the model zinc systems, were seen in more complex metalloporphyrins also.¹⁵²

Zinc porphyrins are also widely used in the assembly of multiporphyrin arrays. Multiporphyrin assemblies provide insight into naturally occurring tetrapyrrolic aggregates that perform key processes in bacterial photosynthetic reaction centres, light harvesting antennae complexes and electron transfer processes in proteins containing several haem groups. Artificial light harvesting antennae require multiple chromophore units that are well organised in space. Attractive synthetic strategies exploit the formation of coordination bonds, multiple hydrogen bonds or both. Zinc porphyrins readily coordinate to basic nitrogen ligands and have been widely used to probe the scope of noncovalent chemistry for controlling structure and reactivity.

1.8 Objectives

Many synthetic studies have been directed towards the synthesis of β - and *meso* substituted dihydroporphyrins, because of the biological relevance of the former, and the potential anion binding properties of the latter. However, the synthetic routes available are low in yield and not applicable to a wide variety of tetrapyrroles.

The aim of this work was to develop a new synthetic approach that would afford both 2,3- and 5,10-dihydroporphyrin regioisomers in one step, selectively and in good yields from *meso* tetrasubstituted porphyrin starting materials. *Meso* tetraalkyl- and tetraarylporphyrins were investigated. A palladium-based catalyst was employed to aid in the regioselectivity of the hydroporphyrin product. A second aim was to apply this methodology to the synthesis of functionalised hydroporphyrins, in particular, macrocycles bearing amino residues. These hydroporphyrins were prepared with investigations into their anion binding properties in mind.

While 5,15-porphodimethenes (PDMs) have been known for decades, their 5,10-regioisomers are a relatively new discovery, and thus remain an under-investigated class of tetrapyrroles. Porphodimethenes, or calix[4]phyrins as they are becoming increasingly known as, have unique structural features which give rise to specific conformations. A series of spectroscopic investigations were performed to determine their photophysical properties and to investigate their anion binding capabilities. Comparisons with their conjugated porphyrin counterparts were also carried out.

A series of porphyrins with different degrees of substitution were examined. Crystal structures of their dication salts were prepared in order to determine the extent of conformational distortion imposed by the degree of substitution.

Finally, a series of porphyrin trimers were synthesised. These were linked by a triptycene molecule which acted as a rigid scaffold for the porphyrin molecules. Using Suzuki-Miyaura, and Sonogashira reactions, three classes of trimers were prepared. These were directly linked to the scaffold, ethyne-linked and phenylethyne-linked. Chelation of the porphyrin with a zinc metal provided a binding site to probe the host/guest properties of these multiporphyrin arrays.

Chapter 2

Studies towards the synthesis of hydroporphyrins

2.1 Syntheses of hydroporphyrins

Recently interest in hydroporphyrin chemistry, particularly in calix[4]phyrins, has grown due to the discovery of their applications in supramolecular and anion receptor chemistry.^{159,160} The development of new and flexible syntheses for hydroporphyrins that would allow for the creation of specific porphodimethenes and chlorins was needed.

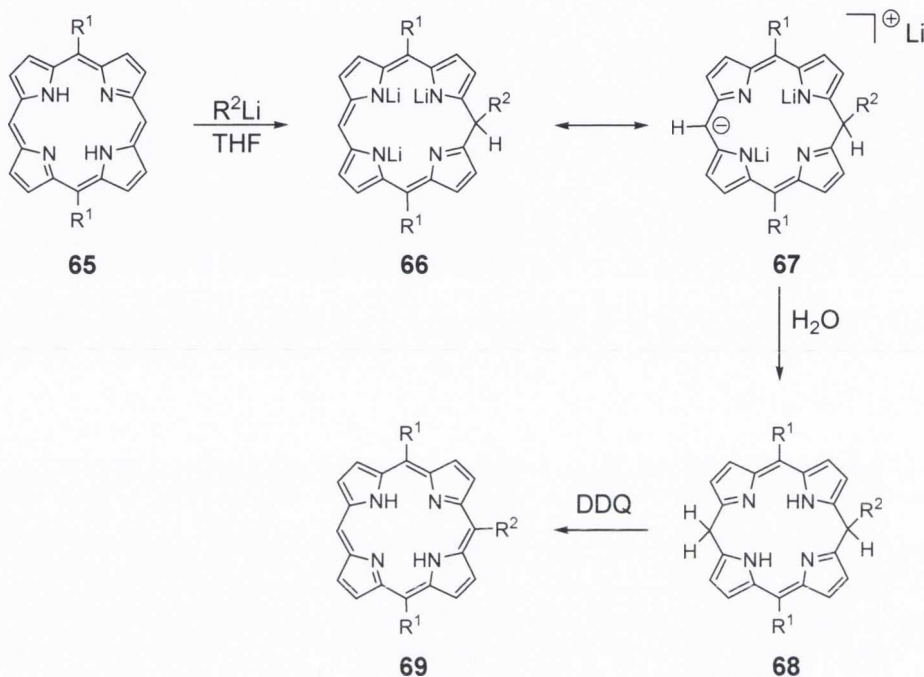
Numerous methods have been developed for the synthesis of mono- and disubstituted chlorins. They include reduction of porphyrins or metalloporphyrins,^{99,161-164} total synthesis and modification of natural chlorins. However, reduction of porphyrins or metalloporphyrins produces chlorins or bacteriochlorins that are readily re-oxidised. Total syntheses involve elaborate, multistep procedures and modification of natural chlorins can be limiting. Since the diimide reduction introduced by Whitlock *et al.* in 1969,⁹⁹ relatively few methods have been developed for the synthesis of *meso* tetraarylchlorin analogues from *meso* tetraarylporphyrins. Direct modifications of the tetrapyrrole have been achieved by the addition of carbenes and activated dienes or vicinal- β - β' -dihydroxylation.¹⁶⁵

Initially, porphodimethenes could only be prepared *via* Buchler's procedure which involved reductive alkylation at the *meso* position of metallated porphyrins.^{129,166-168} Alternative methods have been developed which allow both metallated and non-metallated PDMs to be synthesised. However these methods lacked regioselectivity, stability and/or good yields.^{22,123,125,127,169}

In 1962 Woodward proposed simple generalisations on the reactivity of porphyrins and chlorins based on valence bond considerations.¹⁷⁰ He predicted that the *meso* positions possessed greater electrophilic character than the β -pyrrolic positions. The two pyrroline units in porphyrins tend to achieve individual aromatic sextet of electrons, this then withdraws electron density from the neighbouring *meso* carbons, thus making them more electrophilic and more susceptible to reaction with nucleophiles such as organolithium reagents.

Organolithium reagents have been proven to be excellent reagents in porphyrin chemistry as they react readily with *meso* carbon atoms to form unsymmetric porphyrins in very good yields.^{46,61,62,131,171-174} Organolithium reagents attack the

porphyrin *via* an S_NAr reaction (Scheme 2.1). The initial reaction of the organic nucleophile, RLi , with the free *meso* carbon in A_2 -type free base porphyrins **65** yields the phlorin-type intermediate **66**, which is converted to an anionic species **67**. Hydrolysis of **67** with water gives a 10,20-dihydroporphyrin **68**. Subsequent oxidation with DDQ yields the A_2B -type *meso*-substituted porphyrin **69**.



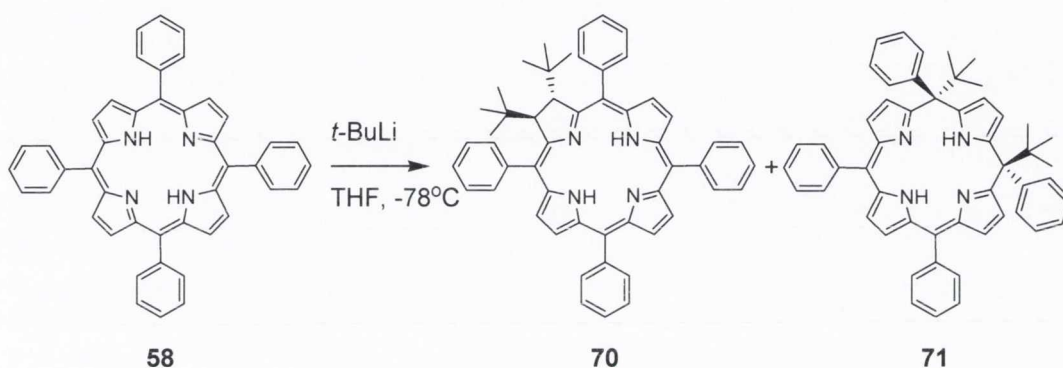
Scheme 2.1. The general mechanism for the nucleophilic substitution reaction of free base porphyrins using organolithium reagents.

Previous work carried out with 5,15-disubstituted porphyrins found that reaction of 5,15-diphenylporphyrin or 5,15-dibutylporphyrin with sterically undemanding reagents like phenyl- or *n*-butyllithium yielded the 5,10,15-trisubstituted porphyrin in quantitative yields.¹⁷⁴ However, the analogous reactions with more sterically demanding organolithium reagents led to a reduced yield of the trisubstituted product and the formation of multiple side products that were not isolable, i.e. reaction at the β -position became a competing reaction.

Together with reactions involving organometallic reagents, C-C bonds are commonly formed *via* transition metal catalysed cross coupling reactions. These two methods have been combined in numerous reactions. Organocopper reagents and vinyl halides were combined to form alkenes.¹⁷⁵ Vinyl halides and Grignard reagents were reacted with iron catalysts by Kochi *et al.*^{176,177} and with nickel catalysts by Corriu *et al.*¹⁷⁸ and

Kumada and Tamao.¹⁷⁹ As nickel catalysts were not appropriate for reaction with organolithium reagents, numerous workers employed palladium as a suitable catalyst.

Krattinger and Callot carried out intensive work on the synthesis of phlorins (5,21-dihydroporphyrins)^{162,164,180,181} which led them to investigate the synthesis of hydroporphyrins from unactivated porphyrin starting materials. Using organolithium reagents, the formation of both chlorins **70** and 5,10-PDMs **71** was reported (Scheme 2.2). However, low yields coupled with no regioselectivity in the formation of chlorins and/or PDMs meant that further studies into the synthesis of hydroporphyrins *via* this method were not attractive.



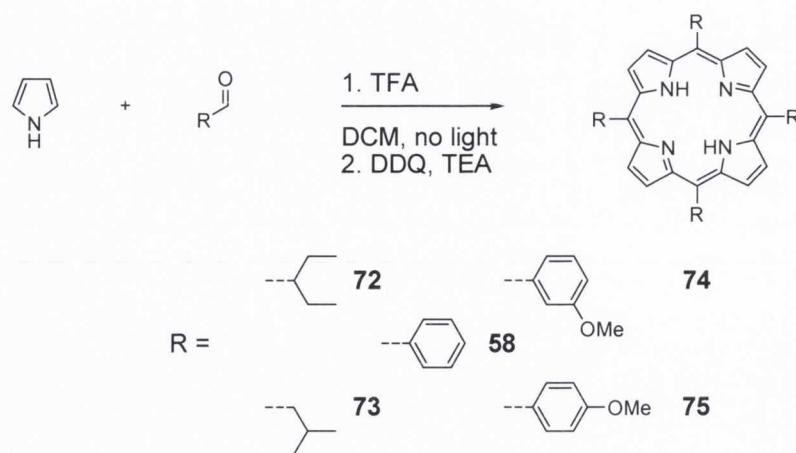
Scheme 2.2. Reaction of H₂TPP **58** with *t*-BuLi.

By adapting Krattinger and Callot's method and introducing palladium-based catalysts, it was found that the yields of both chlorins and porphodimethenes could be improved.

2.2 Synthetic methods

2.2.1 Synthesis of *meso* tetrasubstituted porphyrins

Meso tetrasubstituted porphyrins were prepared using the standard Lindsey method.²⁵ Symmetric porphyrins (A₄-type porphyrins) were easily synthesised in moderate yields (up to 40%) using pyrrole and the respective aldehyde (Scheme 2.3). Due to the wide availability of aldehydes, a range of A₄-type porphyrins could be prepared without the need for elaborate multistep syntheses. In the present work, the *meso* positions were substituted with both alkyl and aryl groups, but possibilities included both heterocyclic and aromatic groups, along with other porphyrins (bis-porphyrins).

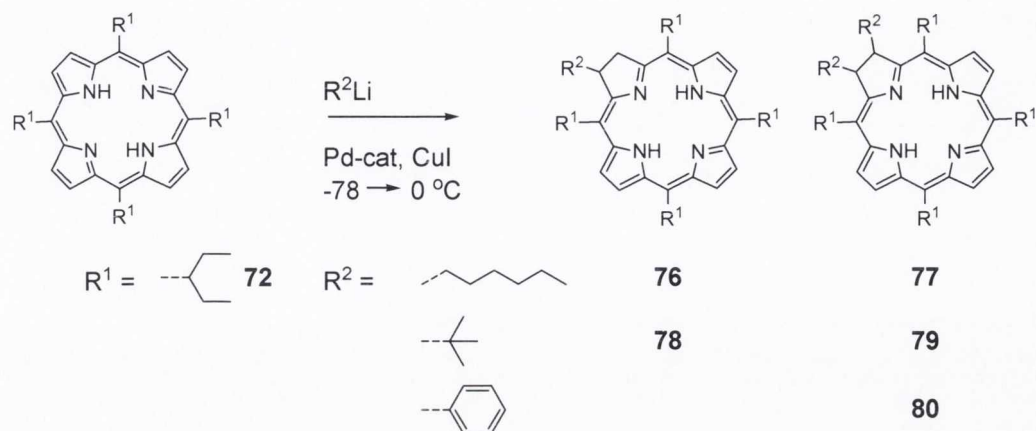


Scheme 2.3. Synthesis of *meso* tetrasubstituted porphyrins from pyrrole and aldehyde.

Using *meso* tetraalkylporphyrins, 5,10,15,20-tetrakis(1-ethylpropyl)porphyrin (H_2TEPP) **72** and 5,10,15,20-tetra(*isobutyl*)porphyrin (H_2TiBuP) **73** and *meso* tetraarylporphyrins, 5,10,15,20-tetraphenylporphyrin (H_2TPP) **58**, 5,10,15,20-tetrakis(3-methoxy)phenylporphyrin ($\text{H}_2\text{T}(3\text{-MeOP})\text{P}$) **74** and 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin ($\text{H}_2\text{T}(4\text{-MeOP})\text{P}$) **75**, a series of reactions with both alkyl- and aryllithium reagents were performed.

2.2.2 Synthesis of hydroporphyrins

The reactivity of free base porphyrins strongly depended on the nature of the *meso* substituents.²⁰ Solubility, steric and electronic effects could influence the outcome of a particular reaction. A new method was developed for the preparation of 5,10-porphodimethenes and mono- and disubstituted chlorins. By combining a palladium based catalyst and a copper(I) co-catalyst with alkyl- or aryllithium reagents, access to these hydroporphyrins was achieved.¹⁸² Investigation into the reaction behaviour of a series of *meso* tetrasubstituted porphyrins showed that a range of hydroporphyrins could be synthesised. In the case of *meso* tetraalkylporphyrins, the palladium catalyst proved crucial in minimising side products, and in certain cases, showed selectivity for either the mono- or disubstituted chlorin depending on the structure of the catalyst.



Comp'd	R^2	Catalyst	2-mono-chlorin	2,3-di-chlorin	S.M. rec'd
72	<i>n</i> -Hexyl	$Pd(PPh_3)_4$	< 1% 76	14% 77	56%
72	<i>t</i> -Butyl	$Pd_2(dba)_3 \cdot CHCl_3$	10% 78	21% 79	30%
72 *	<i>t</i> -Butyl	$Pd_2(dba)_3$		31% 79	
72	<i>n</i> -Hexyl	$Pd_2(dba)_3 \cdot CHCl_3$	Inseparable mixture		
72	Phenyl	$Pd(PPh_3)_4$		6% 80	
72	Phenyl	$Pd_2(dba)_3 \cdot CHCl_3$	Inseparable mixture		

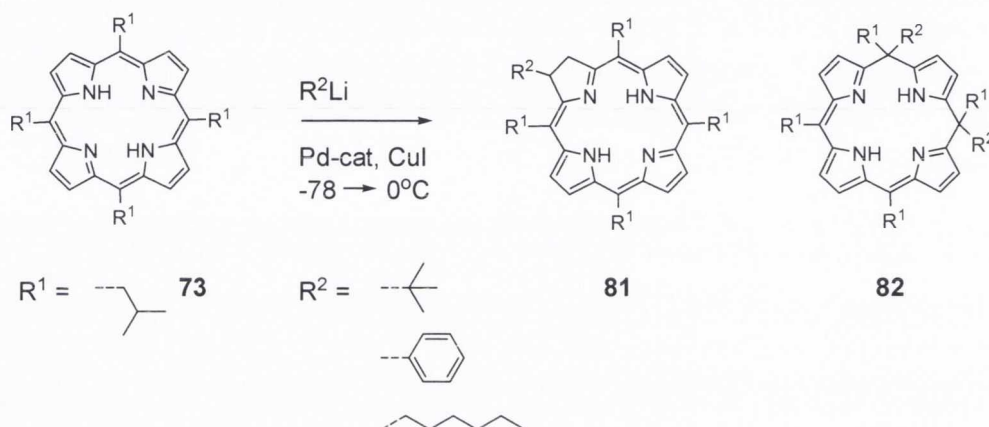
Figure 2.1. Reaction of 5,10,15,20-tetrakis(1-ethylpropyl)porphyrin **72** with RLi and Pd-based catalysts.

5,10,15,20-Tetrakis(1-ethylpropyl)porphyrin **72** reacted smoothly with alkyllithium reagents in the presence of $Pd(PPh_3)_4$ or $Pd_2(dba)_3 \cdot CHCl_3$ and CuI to form both the 2-mono and 2,3-disubstituted chlorins in low yields (Fig. 2.1). The less sterically demanding organolithium reagent, *n*-hexyllithium, gave the double addition product, **77**, as the major product (1:14 ratio, mono:disubstituted chlorin) when $Pd(PPh_3)_4$ was used. With *t*-butyllithium and $Pd_2(dba)_3 \cdot CHCl_3$ a higher proportion of the single addition product **78**, was isolated (1:2 ratio). Given that 56% of starting material was recovered from the former reaction whereas 30% was recovered from the latter, overall conversion to products was lower in the former set of conditions than the later. Within our group, the reaction with *t*-butyllithium was also carried out with $Pd_2(dba)_3$. The double addition hydroporphyrin **79** was isolated in 31% yield as the sole product. Largely, the dibenzylidene-based palladium catalysts yielded isolable hydroporphyrins when they

* Work carried out by Dr. N. N. Sergeeva

were reacted with *t*-butyllithium, whereas $\text{Pd}(\text{PPh}_3)_4$ was the preferred catalyst in reactions with phenyllithium.

The reaction between **72** and phenyllithium with $\text{Pd}(\text{PPh}_3)_4$, was slow to proceed. Upon gentle heating (40°C), a complex mixture of products was obtained from which the 2,3-disubstituted chlorin **80** could be isolated in 6% yield. In changing the catalyst to $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$, three new compounds formed, two of which were green in colour (TLC) indicating chlorin formation. Attempts at purification failed with multiple decomposition products forming. It was therefore, impossible to further characterise these fractions.



Comp'd	R^2	Catalyst	2-mono chlorin	5,10-PDM
73 *	<i>t</i> -Butyl	$\text{Pd}_2(\text{dba})_3\text{CHCl}_3$	17% 81	16% 82
73 *	<i>t</i> -Butyl	$\text{Pd}_2(\text{dba})_3$	43% 81	12% 82
73	<i>t</i> -Butyl	$\text{Pd}(\text{PPh}_3)_4$	Inseparable mixtures	
73	<i>n</i> -Hexyl	$\text{Pd}(\text{PPh}_3)_4$	~ 22% chlorin	
73	Phenyl	$\text{Pd}_2(\text{dba})_3\text{CHCl}_3$	No reaction	
73	Phenyl	$\text{Pd}(\text{PPh}_3)_4$	Inseparable mixtures	

Figure 2.2. Reaction of 5,10,15,20-tetra(*iso*-butyl)porphyrin **73** with RLi and Pd-based catalysts.

5,10,15,20-Tetra(*iso*-butyl)porphyrin **73** was reacted with *t*-butyl-, *n*-hexyl- and phenyllithium. Using $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ the 2-monosubstituted chlorin **81** and the 5,10-disubstituted porphodimethene **82** were isolated in 16 and 17% yield respectively. With $\text{Pd}_2(\text{dba})_3$ the yield of the chlorin **81** improved to 43%, whereas that of **82** was reduced

* Work carried out by Dr. N. N. Sergeeva

to 12%. Thus the structure of the palladium catalyst played a role in the regiochemistry of the resulting hydroporphyrin. When using *t*-butyllithium and $\text{Pd}(\text{PPh}_3)_4$, almost complete conversion of the starting material was achieved. One main new product was observed by TLC. This compound was unstable as after work up (treatment with saturated ammonium chloride and filtration through a layer of aluminium oxide) numerous fractions were observed by TLC. Purification was therefore not attempted.

Full conversion of the starting *meso* alkylporphyrin **73** was achieved in the reaction with *n*-hexyllithium and $\text{Pd}(\text{PPh}_3)_4$. However, a complex mixture of products was obtained, from which only ca. 20% of hydroporphyrin product was isolated. Due to decomposition of this product during work up, it could not be characterised by NMR spectroscopy. It was identified as a chlorin using UV-vis measurements. Reaction of **73** with phenyllithium and $\text{Pd}(\text{PPh}_3)_4$ was unsuccessful. The reaction either did not proceed or proceeded with less than 30% conversion. Only 2% of a chlorin product was isolated and identified using UV-vis spectroscopy. Another, more polar fraction was observed by TLC, however decomposition occurred during column chromatography so this fraction was not classified. In changing the catalyst to $\text{Pd}_2(\text{dba})_3 \text{CHCl}_3$, no reaction occurred and the starting porphyrin was recovered.

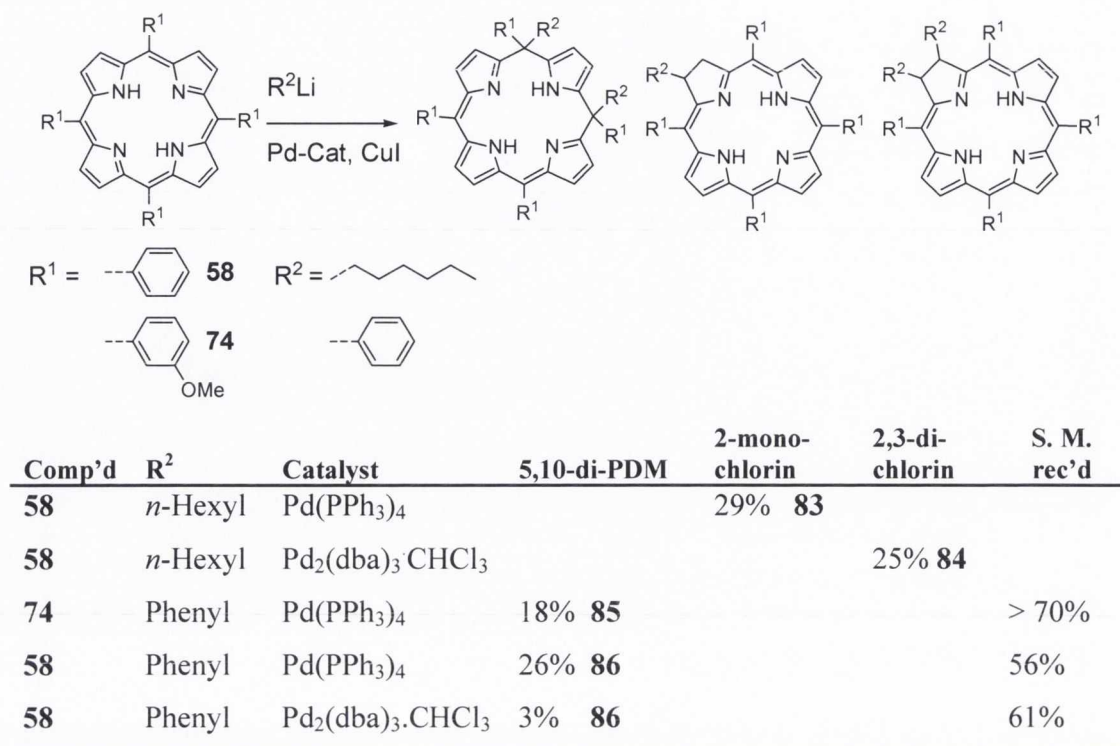
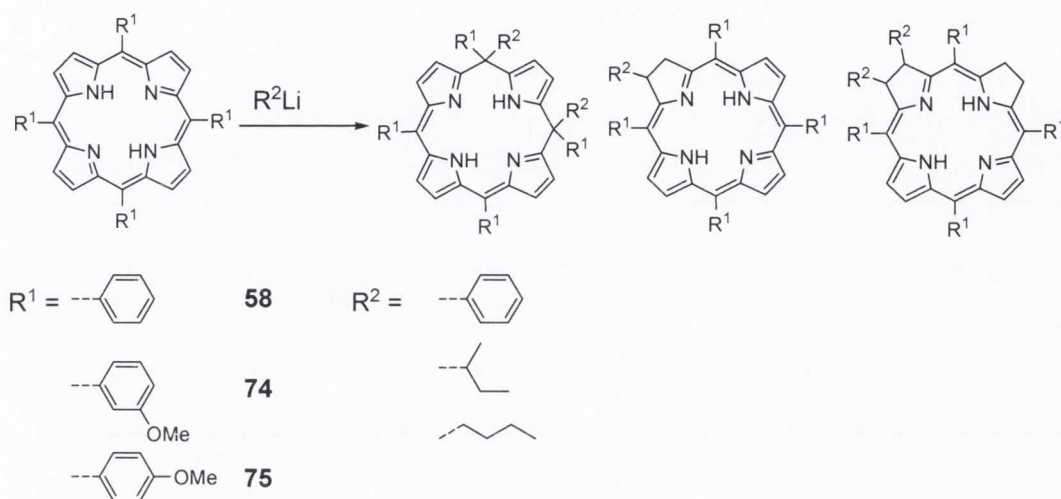


Figure 2.3. Reaction of 5,10,15,20-tetraarylporphyrins with RLi and Pd-based catalysts.

The reaction of 5,10,15,20-tetraphenylporphyrin **58** with the sterically unhindered *n*-hexyllithium led to the formation of chlorin products. Depending on the structure of the catalyst, the single or double addition product could be isolated, indicating the influence of the palladium catalyst on the reaction mechanism. The 2-monosubstituted chlorin, **83** was isolated from the reaction with $\text{Pd}(\text{PPh}_3)_4$, whereas the 2,3-disubstituted chlorin, **84** was obtained from the reaction with $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$. In this case, the product of the reaction could be specifically directed by the choice of catalyst.

In reacting *meso* tetraarylporphyrins with aryllithium instead of alkylolithium reagents, complete regioselectivity for the 5,10-disubstituted porphodimethene was observed, with no evidence of β -addition products. Yields for the reaction between *meso* tetrakis-(3-methoxy)phenylporphyrin **74**, phenyllithium and $\text{Pd}(\text{PPh}_3)_4$ were lower than those for the *meso* tetraphenyl derivative. However, conversion to products for both experiments was low, with 56% of **58** recovered and > 70% of **74**. Thus, the lower yield of **85** compared to **86** was consistent with the lower solubility of **74** compared to **58**. When the catalyst was changed to $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$, there was a decrease in both the yield of the hydroporphyrin **86** (3%) and conversion of the starting porphyrin (39%).

It is likely the porphodimethene products of the reactions above are formed due to the relief of steric strain achieved by their formation.^{183,184} The same reactions were thus carried out without palladium catalysts to investigate whether the catalysts were preventing the approach of the aryllithium reagents:



Comp'd	R^2	5,10-di-PDM	2-mono-chlorin	2,3-di-chlorin	S.M. rec'd
58	Phenyl	62% 86			12%
74	Phenyl	31% 85			43%
75	Phenyl	47% 87			40%
74	<i>sec</i> -Butyl		8% 88	18% 89	57%
74	<i>n</i> -Butyl		17% chlorin		30%

Figure 2.4. Reaction of 5,10,15,20-tetraarylporphyrins with RLi.

Yields of the PDMs improved without the palladium catalyst indicating the extra bulk around the activating site served to hinder the approach of the organolithium reagent in the *meso* tetraarylporphyrins (Fig. 2.4). Conversion to products reached 88% without the catalyst. The lower yields of the methoxyphenyl-derivatives were attributed to the lower solubility of **74** and **75** (60% conversion) compared to **58**. Reactions were thus carried out with *meso*-arylporphyrins and alkylolithium reagents without the use of a palladium catalyst.

Compound **74** was reacted with alkylolithium reagents, *sec*- and *n*-butyllithium. 43 and 70% of starting material was consumed respectively. The lower conversion in the former reaction was credited to the larger steric demands of the *sec*-butyl group. Complex mixtures were obtained from which hydroporphyrin products were difficult to

extract. Reaction of *meso* arylporphyrins with alkyllithium reagents yielded only the β -addition products. In reacting *meso* tetraalkylporphyrins with organolithium reagents the non-catalysed approach was largely unsuccessful as inseparable mixtures were frequently formed.

2.3 Reaction Mechanism

As highlighted in the introduction, palladium catalysed reactions are widely applied in porphyrin chemistry and are used on activated porphyrins to functionalise the periphery. Heck,⁸⁴ Suzuki,⁶⁴ Stille,⁶⁹ Kumada, Negishi^{185,186} and Sonogashira⁶⁵ have all successfully used palladium-based catalysts to develop new methods for the formation of carbon-carbon bonds. Palladium was introduced in the reaction between unfunctionalised porphyrins and organolithium reagents to activate the porphyrin towards nucleophilic attack.

High temperatures and harsh reaction conditions are required to insert palladium metal into the core of the porphyrin. We were confident that palladium did not activate the porphyrin in this manner.

As palladium has an affinity for π -electron systems, by coordinating to a double bond on the porphyrin, the macrocycle was activated towards nucleophilic attack (Fig. 2.5). Cu(I) was originally included in the system to promote the dissociation of the phosphine ligands from the palladium catalyst, thus promoting the reaction.^{187,188} However it was found that reaction with the palladium dibenzylidene complexes also required Cu(I). It was believed that an organo-copper complex, similar to a Gilman reagent, formed and subsequently associated with the palladium to synthesise the resulting hydroporphyrins. However, beyond this, we were hesitant to assign a model for the reaction.

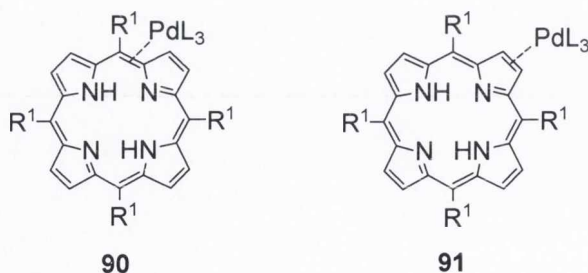


Figure 2.5. Proposed activation site of the palladium catalyst.

2.4 Spectroscopic properties of porphyrins and hydroporphyrins

2.4.1 UV-vis Spectroscopy

UV-vis spectroscopy is one of the most important characterisation tools in hydroporphyrin chemistry. Due to the distinctive and intense absorptions of many tetrapyrroles, and the large number of known spectra, this method is both sensitive and selective. The spectrum consists of two distinct regions. The Soret band appears in the near UV region between 390 and 425 nm and represents an allowed $\pi\text{-}\pi^*$ transition (Fig 2.6).¹⁷ The Q bands appear as a set of between two and four much weaker bands in the visible region between 480-700 nm. They occur due to quasi permitted $\pi\text{-}\pi^*$ transitions and show a vibrational fine structure. The pattern, number and/or intensity of the Q bands can give information about the substitution pattern on the porphyrin periphery, whether it is metallated or free base, and if it is metallated, the stability of the metal cation. Metal free porphyrins have four Q bands (Fig 2.6).

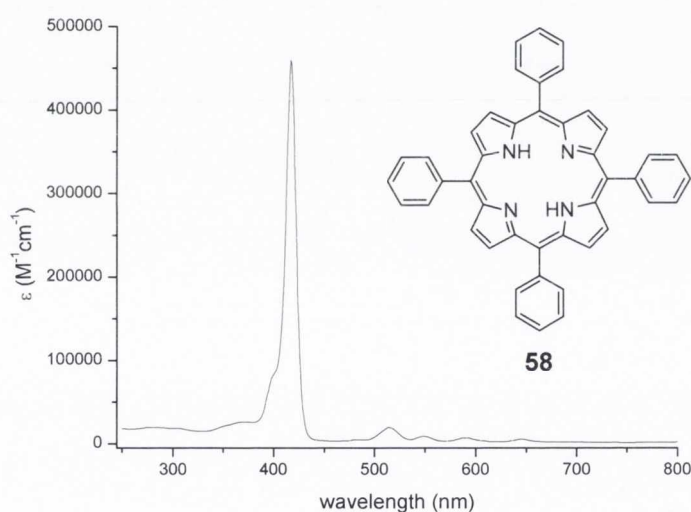


Figure. 2.6. UV-vis spectrum of H₂TPP **58** in dichloromethane (1×10^{-6} M).

As chlorins are also aromatic, their UV-vis spectra are very similar to those of porphyrins. Chlorins display a general bathochromic shift together with a more intense band in the visible region, typically at around 660 nm, which is due to the relaxation of the quasidegeneracy of the excited states. In the free base porphyrin system, the transition moments cancel each other out, whereas in the chlorin, this cancellation is incomplete. This leads to an increase in intensity of the Q band. This characteristic band is the most convenient way of identifying chlorins (Fig. 2.7).¹⁸⁹

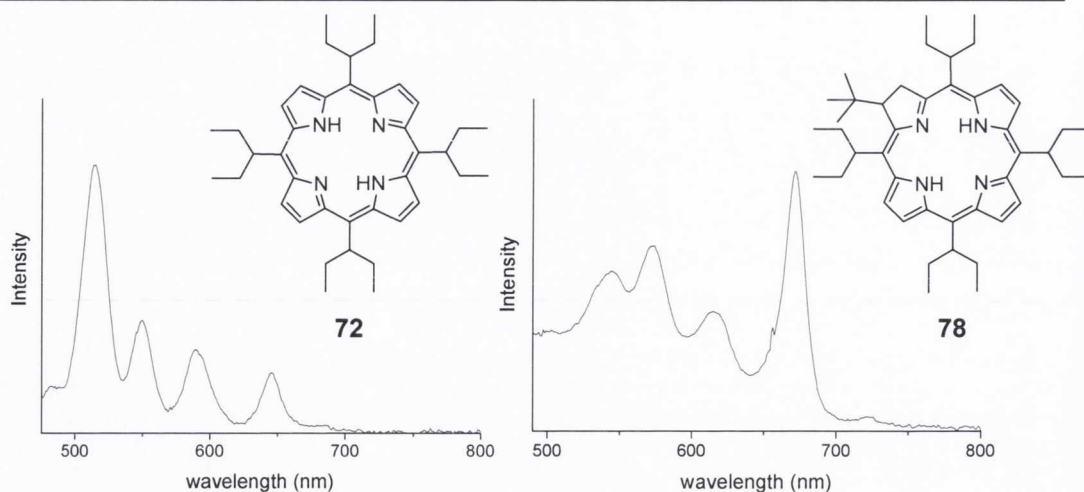


Figure 2.7. Q bands in the UV-vis spectra for free base porphyrin **72** and chlorin **78** recorded in dichloromethane.

Dramatic differences are seen in the UV-vis spectra of 5,10-porphodimethenes. As the macrocycle is no longer aromatic, the spectra do not possess the distinctive features of porphyrin and chlorin spectra. The UV-vis spectra of 5,10-PDMs comprise two absorption bands, one at ~ 350 nm and the other at ~ 550 nm.^{162,180} In 5,10-PDMs, the tetrapyrrole ring is divided into a tripyrrane unit and an isolated pyrrole unit (see insert in Fig. 2.12). The tripyrrane moiety is responsible for these two broad absorbances, with the absorption due to the isolated pyrrole unit being too weak to be measured.¹⁹⁰ The extinction coefficients of both absorption bands in the PDM spectrum were considerably reduced compared to those in the parent porphyrin **58**. This was attributed to the interrupted conjugation in the porphodimethene (Fig. 2.8).¹⁸⁹

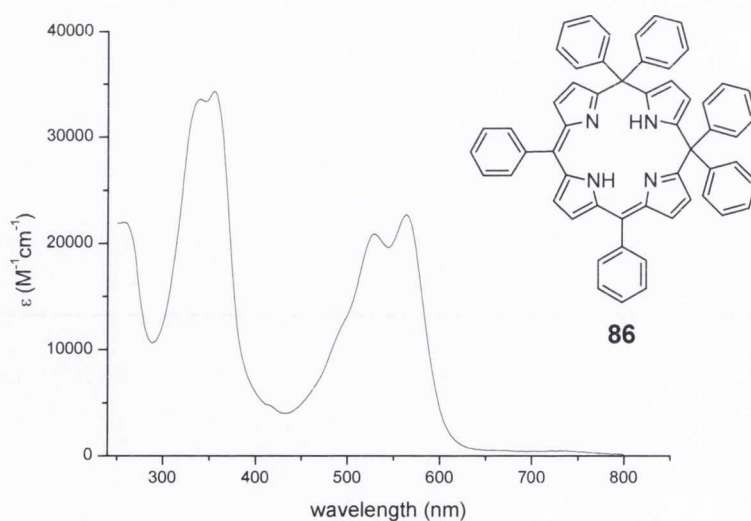


Figure 2.8. UV-vis spectra of 5,5',10,10',15,20-hexaphenylporphyrin **86** in dichloromethane ($1 \times 10^{-5}M$).

2.4.2 ^1H NMR Spectroscopy

The ^1H NMR spectra of porphyrins are very different from most other compounds. They are diamagnetic compounds, and as such, their chemical shift is strongly dependent upon the distance and orientation of the proton in relation to the delocalisation pathway of the π -electrons of the porphyrin. Protons above or inside the porphyrin macrocycle are in the shielding region of the ring current effect, whereas those in the plane of the macrocycle, but on the porphyrin periphery are in the deshielding region.¹⁹¹ This occurrence was readily apparent in the ^1H NMR spectra of free base porphyrins (Fig. 2.9). When compared to the chemical shifts of the protons in pyrrole, the N-protons in porphyrins displayed upfield shifts of ca. 11 ppm and the β -protons displayed downfield shifts of 5 ppm. In H_2TPP **58** there are four planes of symmetry. Consequently, one signal was observed for the eight β -pyrrole protons and one for the two N-protons. The β -protons, located on the porphyrin periphery, resonated at 8.85 ppm. The N-protons, in the core of the porphyrin, were shielded by the ring current and resonated upfield at -2.86 ppm. The *meta*- and *para*-protons of the phenyl ring displayed similar chemical shifts. This was attributed to steric hindrance which caused the phenyl groups to twist out of plane. Although the *meta*-protons were closer to the porphyrin, they were in a less deshielding region and appeared as a multiplet at 7.78 ppm.

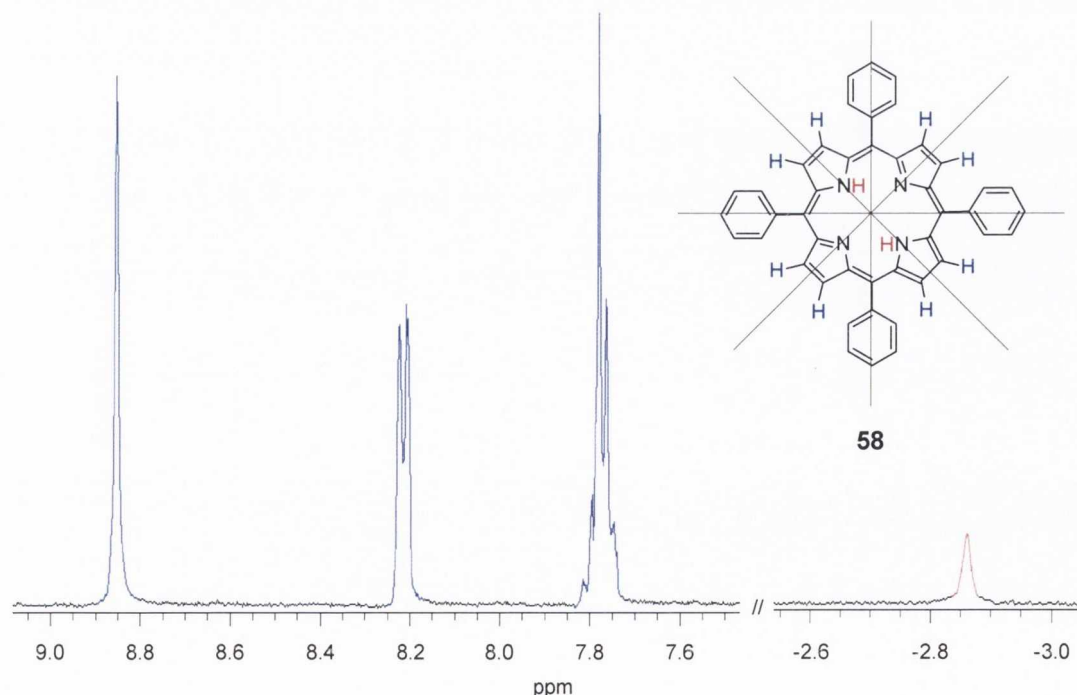


Figure 2.9. ^1H NMR spectrum of β - (blue) and N-protons (red) of H_2TPP **58** in CD_2Cl_2 .

Chlorins and porphodimethenes are isomers of one another and both possess two sp^3 hybridised carbon atoms which are absent from the free base porphyrin. Any structural modification to the porphyrin changes its ring current. Opposite shifts were observed for resonances of protons that were inside the ring versus those outside. In the hydroporphyrins, the lowered symmetry resulted in a downfield shift of the N-protons and an upfield shift of β -pyrrole protons. Shown in Figure 2.10 are the ^1H NMR spectra of *meso* tetraalkylporphyrin **72** and the corresponding 2,3-disubstituted chlorin **79**. In chlorins the macrocycle retained its aromaticity (Fig. 2.11) with the N-protons experiencing a downfield shift ($\Delta\delta = 2.47$ ppm) and the β -protons (β^7 -, β^8 -, β^{12} -, β^{13} -, β^{17} - and β^{18} -H) a slight upfield shift ($\Delta\delta = 0.77$ ppm). The lowered symmetry also resulted in a splitting of resonances. Instead of one signal for the β -protons, there were four: (4.7 [$\beta^{2/3}$ -H], 8.8 [$\beta^{7/18}$ -H], 9.1 [$\beta^{12/13}$ -H] and 9.2 [$\beta^{17/18}$ -H] ppm). The protons on the reduced pyrrole ring (β^2 - and β^3 -H) no longer participated in the delocalisation pathway so they were not influenced by the chemical anisotropy and appeared upfield at 4.7 ppm (not shown).

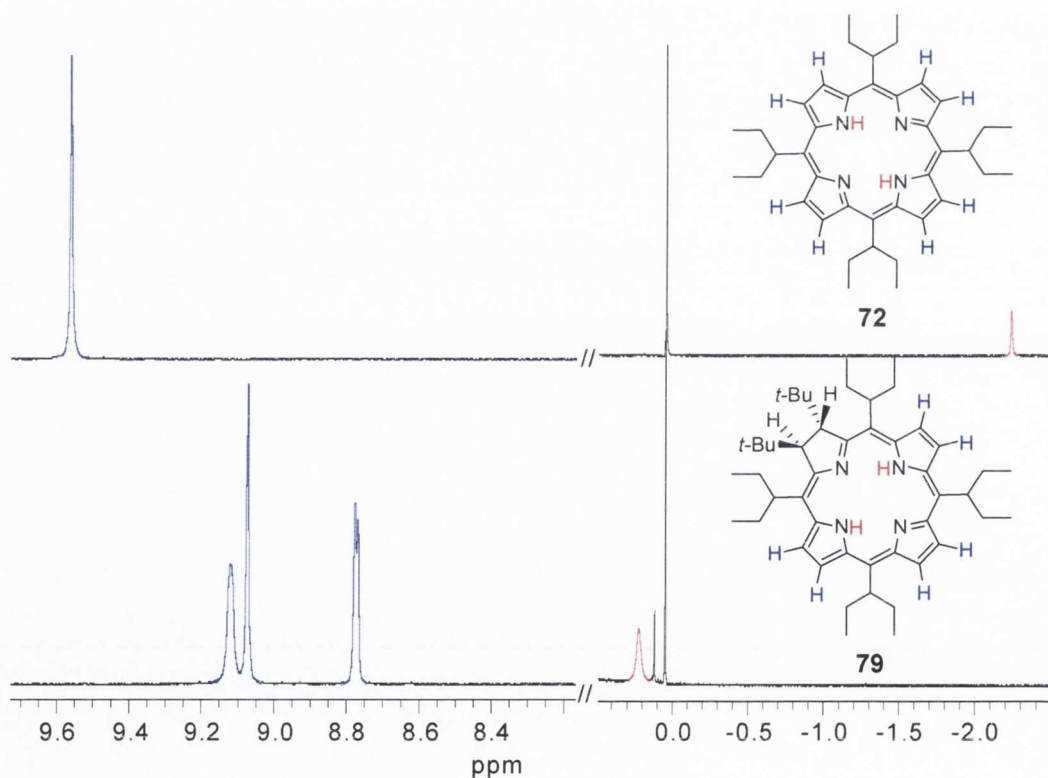


Figure 2.10. ^1H NMR spectrum of 5,10,15,20-tetrakis(1-ethylpropyl)porphyrin **72** (top) and 2,3-di-*tert*-butyl-5,10,15,20-tetrakis-(1-ethylpropyl)chlorin **79** with IUPAC numbering (bottom) recorded in CDCl_3 .

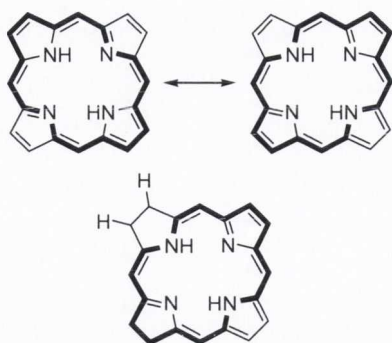


Figure 2.11. Delocalisation of the 18 π -electrons in free base porphyrins (above) and the preferred electron pathway for chlorins with the protons outside the pathway indicated (below).

Addition to the *meso* position of a porphyrin interrupted the conjugation of the macrocycle, which in turn, caused dramatic changes to the chemical shifts of the β - and N-protons. Previously the N-protons were in the shielding region of the aromatic porphyrin macrocycle, in porphodimethenes they came inside the deshielding region of the pyrrole rings. The change in chemical environment was reflected in the ^1H NMR spectra where an enormous chemical shift change of 14 ppm to 10.51 and 12.59 ppm was observed. The β -protons experienced an upfield shift from 8.85 to between 5.46 and 6.65 ppm (Fig 2.12).

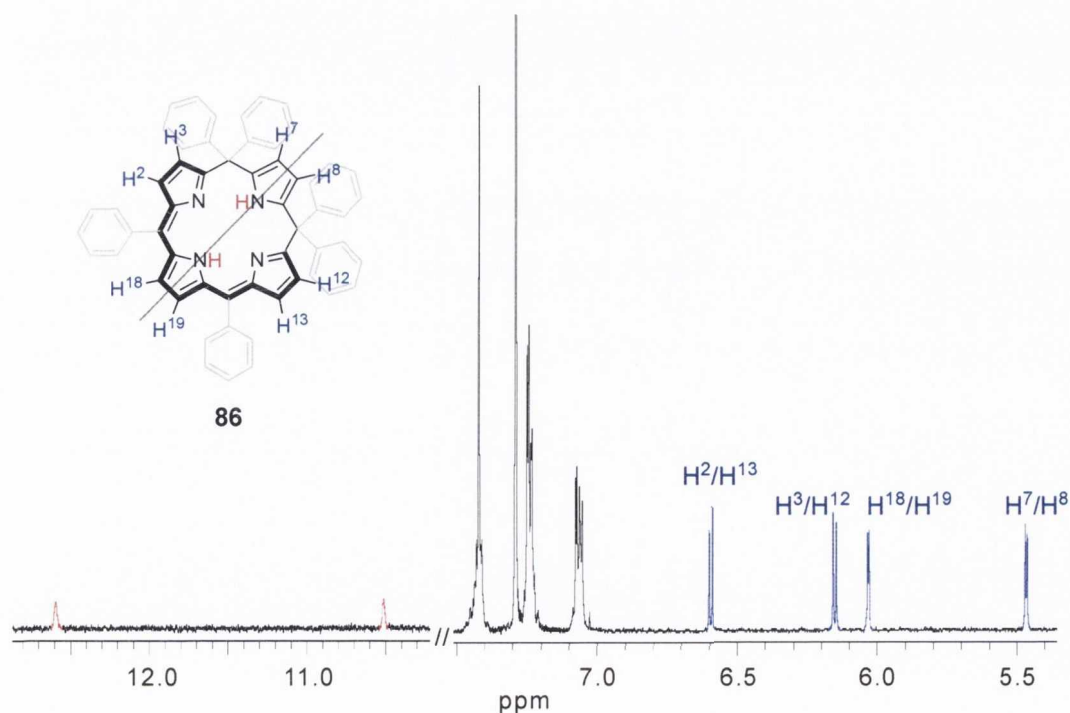


Figure 2.12. ^1H NMR spectrum of 5,5',10,10',15,20-hexaphenylporphyrin **86** recorded in CDCl_3 .

Similar to the 2,3-disubstituted chlorin, there was only one plane of symmetry in 5,10-disubstituted PDMs. The pyrrole protons were split into four sets of signals each with an integration value of two. In contrast to the chlorins, there were two signals for the PDM N-protons. This was due to the different chemical environments experienced by the two inner protons. The resonance furthest downfield at 12.59 ppm was associated with the tripyrrane region (highlighted in Fig. 2.12), whereas the resonance further upfield was attributed to the proton in the pyrrole region. The phenyl protons in porphyrins resonated at 7.81 and 8.28 ppm (Fig. 2.9). In 5,10-PDMs they appeared further upfield at 7.06, 7.24 and 7.42 ppm. The resonance furthest downfield at 7.42 ppm is related to the phenyl protons on C15 and C20. The phenyl protons on C5 and C10 appear as two multiplets. It was not possible to further assign these resonances.

Due to the obvious differences between the ^1H NMR spectra of porphyrins and those of 5,10-porphodimethenes, in depth investigations were carried out into the spectra of 5,10,15,20-tetrakis(4-methoxyphenyl)-5',10'-diphenylporphyrin **87**. A large amount of information on the structure of 5,10-disubstituted porphodimethenes was obtained from the ^1H NMR spectrum of this molecule (Fig. 2.13). The aromatic groups on the 5- and 10-positions were distinguishable in **87** whereas the higher symmetry element possessed by it over **85** meant the ^1H NMR spectra could be clearly interpreted.

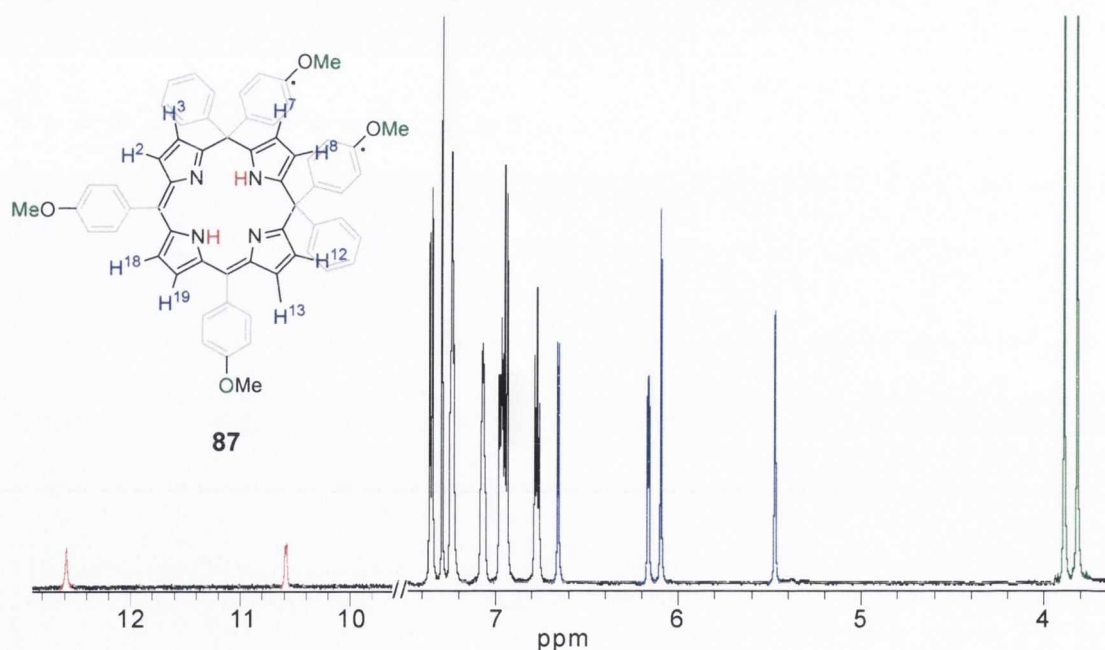


Figure 2.13. ^1H NMR spectrum of 5,10,15,20-tetrakis-(4-methoxyphenyl)-5',10'-diphenylporphyrin **87** recorded in CDCl_3 . Highlighted in red, blue and green are the N-, β -, and OCH_3 protons respectively.

NOESY, HMBC, HSQC and selective ROESY experiments were performed to investigate the influence of *meso* addition on the porphyrin macrocycle. As was noted with **86**, the N- and β -protons shifted in opposite directions which related to a decrease in aromatic ring current with hydroporphyrin formation. Each with coupling constants of $^3J = 8.4$ Hz, the doublets at $\delta = 6.94$ and 7.35 ppm were identified as being apart of the same spin system. As were the resonances at $\delta = 6.16$ and 6.65 ppm with $^3J = 4.6$ Hz. (Fig. 2.13 and 2.14).

Selective ROESY experiments were performed by exciting the methoxy resonances at $\delta = 3.81$ and 3.89 ppm. From this, the *meta*-phenyl protons on C20 and C5 were identified. Using H-H COSY (Fig. 2.14) and coupling constants, the chemical shifts of the *ortho* protons were determined. *Meta*- and *ortho*-protons on C5 (red) resonated at 6.77 and 6.96 ppm respectively. The corresponding protons on C20 (green) resonated at 6.94 and 7.35 ppm. In the parent porphyrin macrocycle, the *meta* protons resonated at 7.32 and the *ortho* at 8.15 ppm. The phenyl resonances on the sp^3 hybridised centre, C5, experienced the largest chemical shift of $\Delta\delta = 0.55$ (*meta*) and 1.19 (*ortho*) ppm compared to $\Delta\delta = 0.38$ and 0.80 ppm for those on the more conjugated C20. The resonances at $\delta = 7.07$ and 7.24 ppm were assigned as the *meta* and *ortho/para* phenyl protons on C5 (pink). The resonances at 3.81 and 3.89 ppm were assigned to the methoxy group on C5 and C20 respectively. This signal resonated at $\delta = 4.13$ ppm in the parent porphyrin. Again, the OCH_3 protons on C5 experienced the greatest chemical shift ($\Delta\delta = 0.32$).

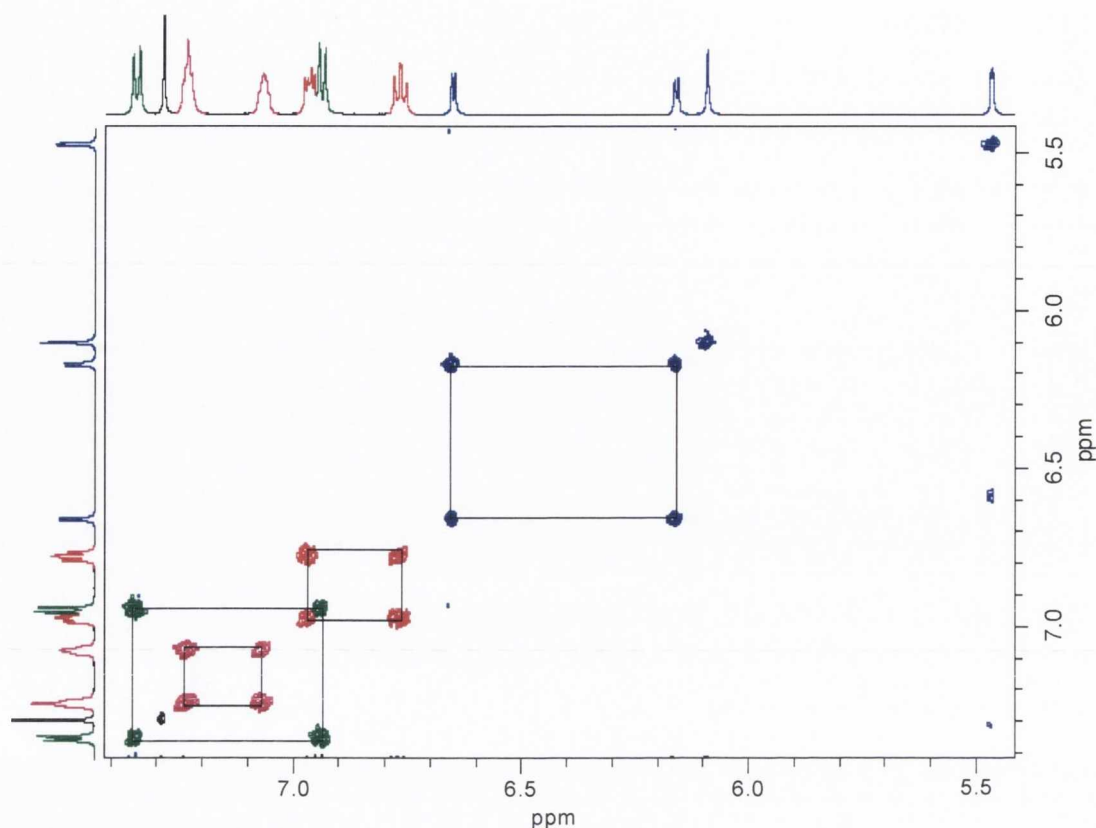


Figure 2.14. H-H COSY spectrum of 5,10-porphodimethene **87** recorded in CDCl_3 .

HSQC and HMBC experiments were performed to fully assign the ^{13}C spectra. A similar trend to the ^1H NMR spectra was seen. However, using HMBC, a correlation between $\beta\text{-H}^7$ and N-H^{22} was observed. The two N-protons could therefore be differentiated. N-H^{22} was assigned as $\delta = 10.59$ ppm and N-H^{24} as $\delta = 12.58$ (Fig. 2.15).

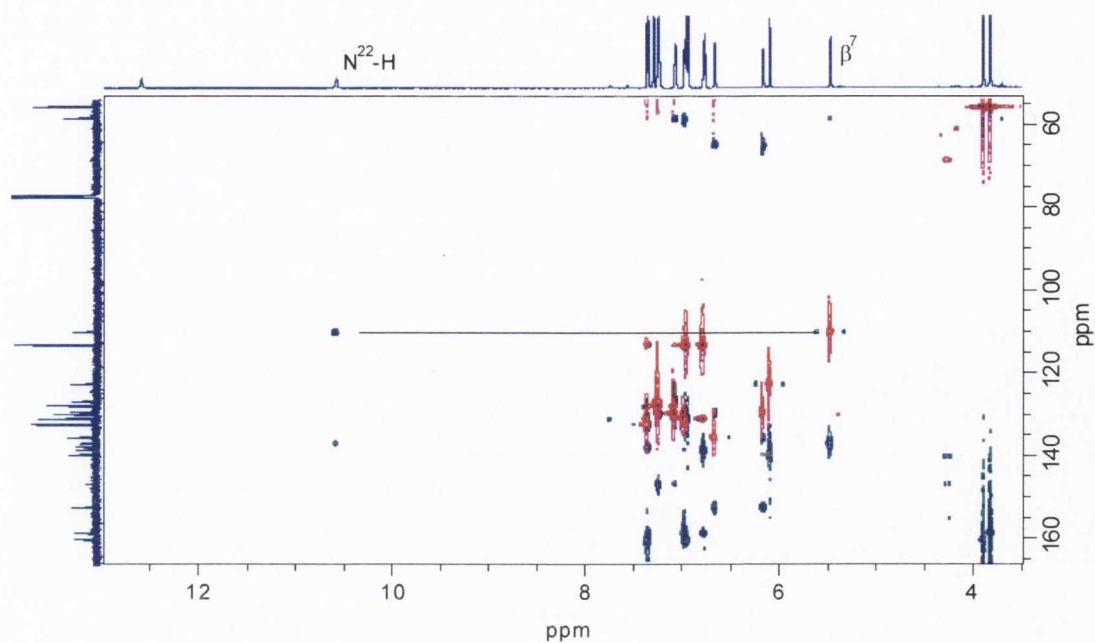
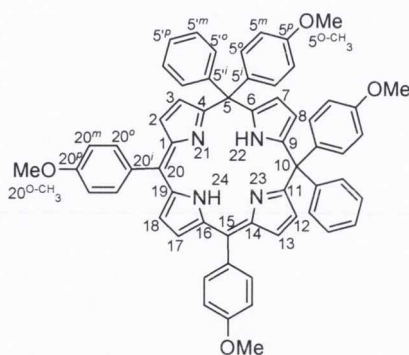


Figure 2.15. HSQC/HMBC spectra of **87** indicating the correlation between N-H²² and β -H⁷.

Table 2.1. ^1H and ^{13}C NMR assignment for **87** recorded in CDCl_3 .

^1H					^{13}C
Position	δ (ppm)	Mult. J (Hz) (Int)	COSY	Sel ROESY	δ (ppm)
2/13	6.65	d (4.6) (2 H)	3/12	20 ^o	134.7
3/12	6.16	d (4.4) (2 H)	2/13	5 ^o , 5 ^{o/p}	129.0
7/8	5.47	d (2.3) (2 H)	-	5 ^o , 5 ^{o/p}	109.7
17/18	6.09	s (2 H)	-	20 ^o	122.3
5 ^o	6.96	m (4 H)	5 ^m	-	130.7
5 ^m	6.77	m (4 H)	5 ^o	-	112.92
5 ^p			-	-	158.1
5-OCH ₃	3.81	s (6 H)	-	5 ^m	55.6
5 ^o	7.24	m (6 H)*	5 ^m	3/12, 7/8	127.6/126.4
5 ^m	7.07	m (4 H)	5 ^{o/p}	3/12, 7/8	129.6
5 ^p	7.24	m (6 H)*	5 ^m	3/12, 7/8	127.6/126.4
20 ^o	7.35	d (8.4) (4 H)	20 ^m	2/13, 17/18	132.1
20 ^m	6.94	d (8.6) (4 H)	20 ^o	2/13, 17/18	112.86
20 ^p			-	-	159.8
20-OCH ₃	3.89	s (6 H)	-	20 ^m	55.3
N-H ²²	10.58	s (1 H)	-	-	-
N-H ²⁴	12.58	s (1 H)	-	-	-

2.4.3 Structural features of 5,10-PDMs

In the addition reaction to form **87**, the product was expected to contain a mixture of diastereomers. Both 5,10-PDMs were compared with previous data reported for 5,15-PDMs of H_2OEP ($\text{OEP} = 2,3,7,8,12,13,17,18$ -octaethylporphyrin). According to the results published by Buchler *et al.* in 1987,¹⁹² 5,15-PDMs exist in two different

conformations: syn-axial “aa” as the major conformation (5–58%) and diagonal “dd”(2–8%) as the minor conformer. The term syn-axial “aa” configuration for 5,15-porphodimethenes describes conformations with large substituents at *meso* sp^3 -carbon atoms positioned axial to the folding axis of the porphyrin core and parallel to each other. The term “dd” refers to the diagonal conformation of two groups if the porphodimethene core is planar (Figure 2.16). The two substituents at the 5- and 15-positions can no longer be termed axial or equatorial, due to their intermediate positions.

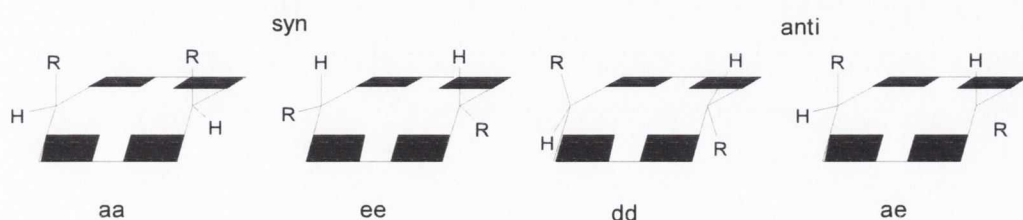


Figure 2.16. Schematic representation of 5,15-porphodimethene configurations.

Spectroscopic studies for the series (syn-axial “aa”) showed that the 5,15-PDM skeleton was far from planar and displayed a folding at the *meso* sp^3 -hybridised carbon atoms. Studies of the syn-5,15-PDM complexes confirmed a high symmetry in the system. In the ^1H NMR spectra only two sets of signals appeared for the corresponding $\beta\text{-CH}_2$ and $\beta\text{-CH}_3$ of the ethyl groups. Also, one set of signals was observed for the enantiotopic protons *meso* $\text{CH}^{5,15}$ at the sp^3 -carbon atoms. The atoms at *meso* $\text{CH}^{10,20}$ are enantiotopic in all the configurations too. A strong tautomeric effect of the NH protons resulted in the appearance of one broad signal. The corresponding “dd” isomer of the 5,15-PDM with two *meso tert*-butyl groups derived from OEP, showed two sets of signals for the enantiotopic protons *meso* $\text{CH}^{5,15}$ (at sp^3 -carbon) and *meso* $\text{CH}^{10,20}$ (at sp^2 -carbon), additionally, $\beta\text{-CH}_2$ (2.56 ppm) and $\beta\text{-CH}_3$ (1.17 ppm) appeared as multiplets.¹⁹²

Figure 2.17 displays an expanded view of the β -protons at positions 7/8 and 17/18 of compounds **86** and **87**. Singlet resonances were expected in both porphodimethenes, however, the resonances were unexpectedly split. In light of the research carried out by Buchler *et al.* the splitting was ascribed to the presence of different configurations in solution.

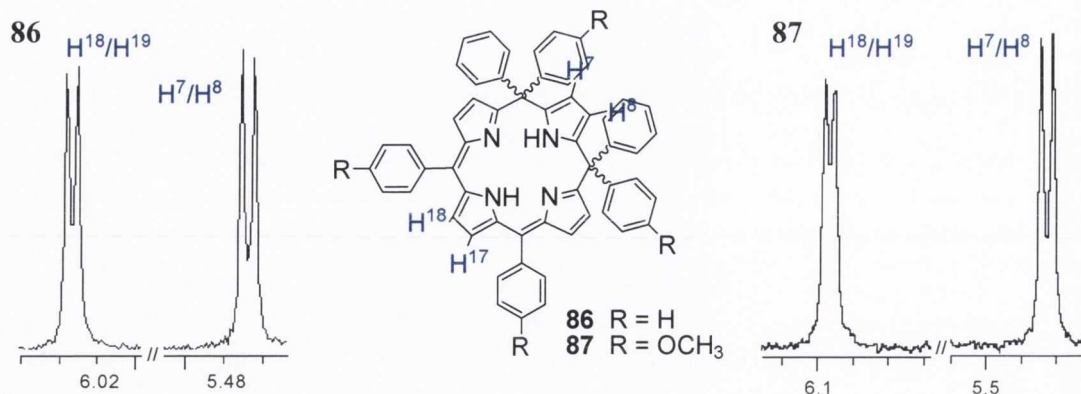


Figure 2.17. ^1H NMR spectra of the β -7 and β -18 protons of 5,10-PDMs **86** and **87**.

In compound **86**, residues at the syn and axial positions are the same (phenyl), thus “aa”, “ee”, and “ae” give rise to the same conformations. This suggested that along with “dd,” only two conformations were possible. The splitting could either be attributed to a mixture of both conformations, or, as Buchler outlined, the “dd” conformation alone could give rise to this observed splitting.

Compound **87**, with different residues at the axial and equatorial positions (phenyl and 4-methoxyphenyl), could potentially display both syn and anti configurations resulting in a mixture of all four conformations. However, as the signal is split into two resonances and not into four, it was believed that only the syn or anti configuration formed in the reaction. X-ray structures of each conformation will need to be elucidated before the syn and/or anti configurations can be unambiguously assigned.

2.5. Functionalised 5,10-porphodimethenes

Nitro and amino substituted amphiphilic porphyrins are useful precursors to biologically active molecules and they can be easily conjugated with bioactive molecules such as polymer backbones and cyclodextrins.¹⁹³ In addition, nitro and amino groups can be easily functionalised.¹⁶⁵ Given the development of a new synthetic pathway, that selectively provided access to 5,10-disubstituted PDMs, several synthetic targets were set, which would yield PDMs bearing functional groups.

Firstly, a series of *meso* tetrasubstituted nitro- and aminophenylporphyrins were prepared as synthetic precursors for the functionalised hydroporphyrins. These will then undergo nucleophilic addition reactions to yield the sought after 5,10-porphodimethenes.

A series of A₄- **92** and **93**, and A₂B₂-type porphyrins **94-99** were prepared for reaction with organic nucleophiles. These porphyrins would ensure the formation of a single isomeric product. Synthetic routes for the formation of **92-103** included: 1) the Adler-Longo (mixed) aldehyde condenstation reaction **92** and **100**; 2) Suzuki cross coupling with boronic acids **94**, **96**, **99**, **102** and **103**; 3) Electrophilic addition to the *para* phenyl position of H₂TPP **97** and 3) reduction using stannous chloride or palladium on carbon and sodium borohydride **93**, **95**, **98**, and **101**.

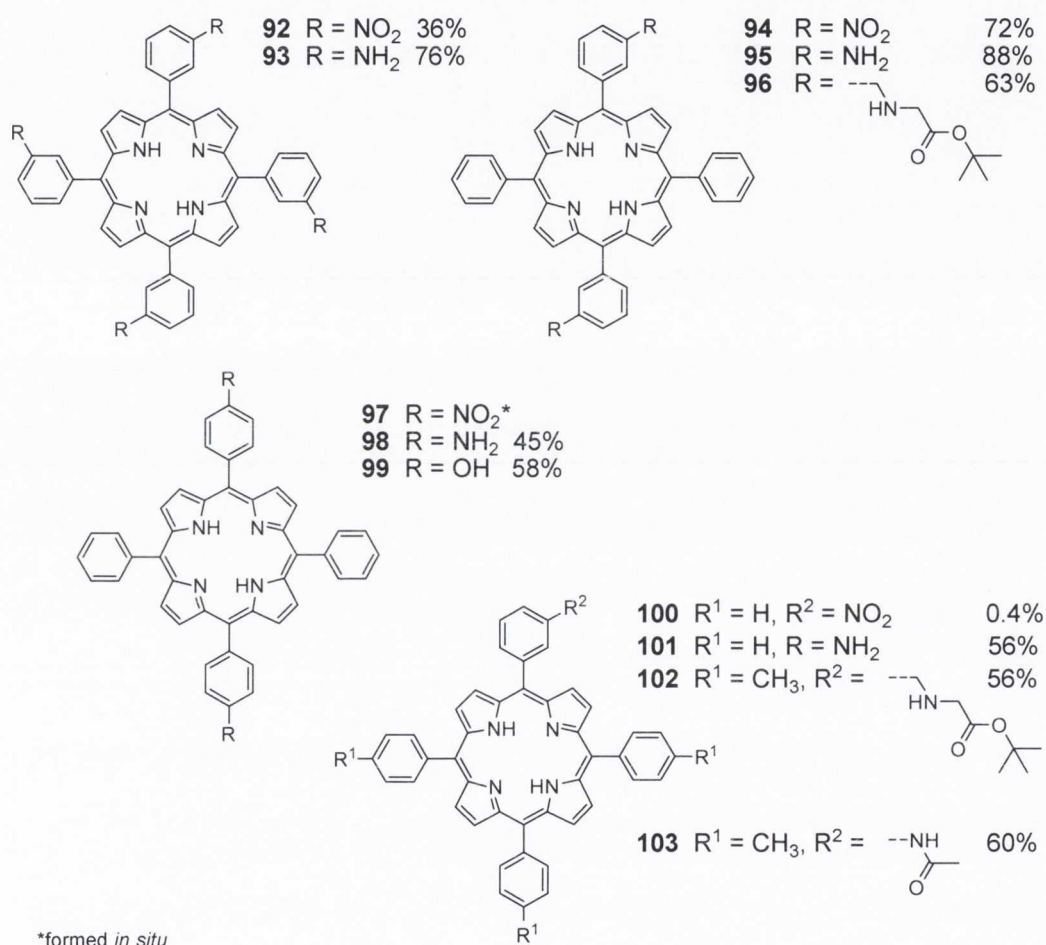
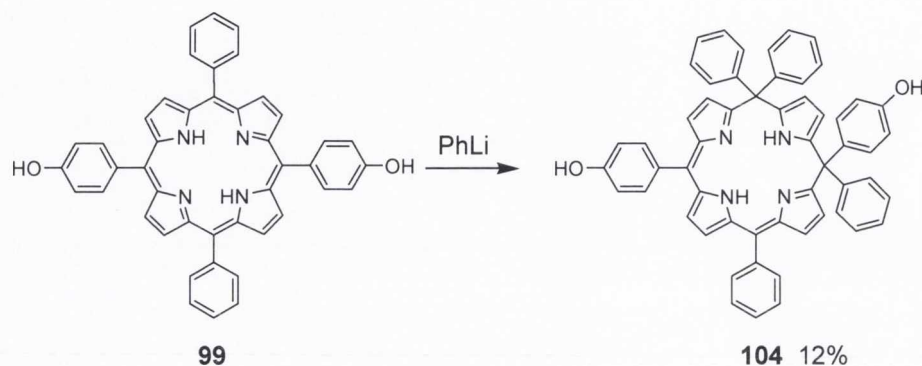


Figure 2.18. *meso* Tetraarylporphyrin precursors prepared for the synthesis of functionalised 5,10-porphodimethenes.

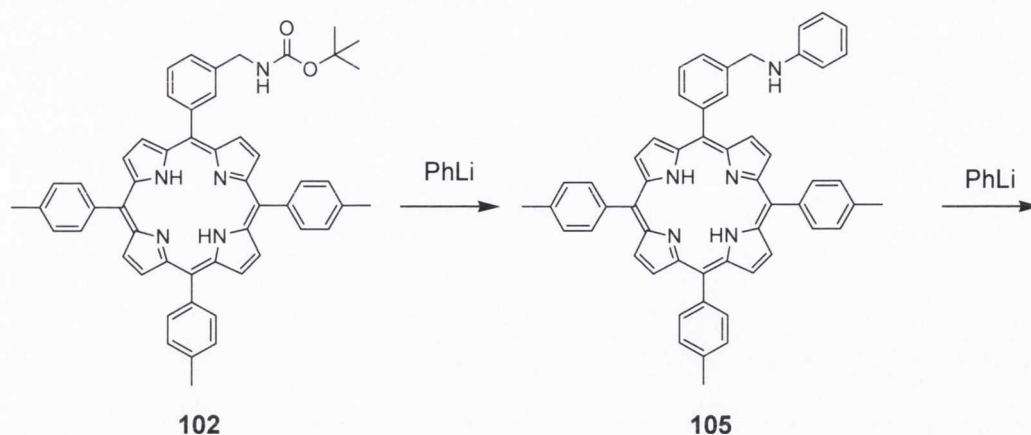
Unfortunately unfavourable results were obtained for the reaction of the above precursors with phenyllithium, in the absence of a catalyst. Reaction of **92** and **93** with either phenyllithium or *tert*-butyllithium did not proceed. When the number of functional groups was reduced to two **94-99**, reactions proceeded however, mostly with the production of multiple side products. The reaction of **99** with phenyllithium

proceeded smoothly with three fractions observed by TLC (starting material and two additional fractions). Attempts at purification afforded only starting material (21%) and one of the other two observed fractions (14.9 mg, 12%). This was identified as porphodimethene **104** using ^1H NMR and UV-vis spectroscopy, however further ^1H NMR investigations were not possible, due to the instability of the porphodimethene.



Scheme 2.4. Nucleophilic addition for the synthesis of functionalised 5,10-PDMs.

In a final attempt, the reaction was attempted with *meso* tetraarylporphyrins that bore just one functional group **100-103**. Unsatisfactory results were obtained for the reaction of nitro and amino derivatives **100** and **101** with phenyllithium. Multiple side products were formed. The reactions of **103** with PhLi did not proceed however reaction with **102** yielded the substitution product **105** (Scheme 2.6).



Scheme 2.5. Nucleophilic substitution reaction occurring at the *meso* phenyl position.

Compound **105**, was further reacted with the organic nucleophile, however, the reaction was unsuccessful, with no reaction occurring.

2.6 Conclusions

The use of palladium-based catalysts in the organolithium reaction of porphyrins resulted in formation of both *meso* and β -substituted hydroporphyrins. The mechanism of the reaction is a type of nucleophilic addition reaction, however, the precise pathway involving the Pd/organo/Cu complex could not be proven. The regiochemistry of the hydroporphyrins depended on the type of the catalyst. Predominantly, chlorins were formed in reactions with aliphatic organolithium reagents and PDMs in reactions with phenyllithium. Particular success was achieved in the reactions of H₂TPP **58**. When reacting alkylolithium reagents with **58**, selective formation of the 2-mono- or 2,3-disubstituted chlorin was achieved. Whereas, using phenyllithium and no catalyst, 5,10-PDMs were isolated as the sole product in yields up to twelve times higher than those previously reported in the literature. The role of copper(I) iodide was uncertain. However additional experiments were performed without the copper(I) reagent. It was found that the number of side products increased and no hydroporphyrin derivatives could be isolated.

Both UV-vis and ¹H NMR spectroscopies were employed to classify the hydroporphyrin products. UV-vis techniques proved a crucial indicating tool to determine the outcome of certain reactions. ¹H NMR spectroscopy revealed the drastic effect of the loss of conjugation on the ring current of the tetrapyrrole.

Attempts at synthesising functionalised porphodimethenes were largely unsuccessful. Reactions with functionalised *meso* tetraaryl and phenyllithium did not proceed, however, a mixture of products was obtained from the reaction of di- and monofunctionalised porphyrins. This indicated the extra steric bulk around the reaction site hampered the progress of the reaction. Reaction with 5,15-dihydroxyphenyl-10,20-diphenylporphyrin were promising, however, the instability of the products precluded full characterisation.

Chapter 3

Nonplanar porphyrins

3.1. Nonplanar porphyrins: Porphyrin dications

The conformation of porphyrins is widely studied with regard to the connection between macrocycle distortion and physicochemical properties. In 1971 Hoard revealed the flexibility that porphyrin macrocycles were capable of,¹⁹⁴ and since then many factors that influence conformational distortion have been investigated. The degree of distortion of the macrocycle can depend on environmental, metal, packing and axial ligand effects.¹⁴⁵ Conformational flexibility has wide implications for the study of chromophore-protein interactions *in vivo*¹⁹⁵ and nonplanar tetrapyrrole conformations have been observed in the bacterial photosynthetic reaction centre,^{135,196} a photosynthetic antenna complex,^{137,197} haem proteins, methyl reductase and vitamin B₁₂-dependent enzymes.¹⁹⁸

The photophysical properties of nonplanar porphyrins differ significantly from those of their planar analogues (bathochromic shifts, larger Stokes shifts, etc.).^{199,150} The nonplanar distortions of the macrocycle were initially induced by the introduction of steric bulk at all available peripheral positions, for example, dodecasubstituted porphyrins such as 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin **106**, ($\lambda_{\text{max}} = 446$ nm in dichloromethane)^{113,195,200} which combined the substitution pattern of both the well known β -octaethylporphyrin ($\lambda_{\text{max}} = 398$ nm)²⁰¹ and *meso* tetraphenylporphyrin ($\lambda_{\text{max}} = 417$ nm) (Fig. 3.1). In most cases, these porphyrins exhibited severely distorted *saddle* conformations (Section 1.6),^{113,195,200,202,203} with the exception of sterically hindered porphyrins bearing *meso* alkyl groups. These compounds tend to crystallise in *ruffled* conformations.²⁰⁴ Ema *et al.* reported that 5,10,15,20-tetrakis(*tert*-butyl)porphyrin **107** ($\lambda_{\text{max}} = 446$ nm) underwent a nucleophilic addition reaction at the *meso* position to yield 5,15-porphodimethenes.¹⁸³ Senge *et al.* later reported that this was caused by a severely *ruffled* distortion.²⁰⁵

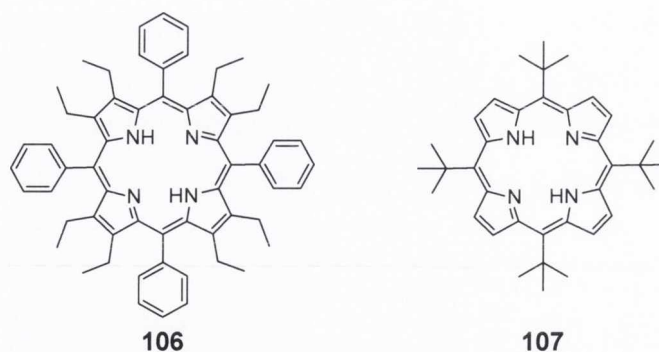


Figure 3.1. Highly distorted porphyrin compounds.

However, core substitutions, either by protonation of the two pyrrolidine nitrogen atoms^{147,206} or by the preparation of *N*-alkyl or *N*-aryl porphyrins²⁰⁷ have been shown to lead to significantly distorted macrocycles. This is caused by a) the steric hindrance that results when all four inner hydrogen atoms are coplanar and by b) the electrostatic repulsion of the inner nitrogen atoms assuming that each of them has a charge of $+1/2$. There is a vast conformational difference between the diprotonated porphyrin and that of the analogous free base macrocycle.¹⁴⁷ In fact, the dication of 5,10,15,20-tetraphenylporphyrin, $[H_4TPP]^{2+}$ **58** ($\lambda_{\max} = 438$ nm), displays a similar *saddle*-type distortion to that observed for dodecasubstituted porphyrins **108** ($\lambda_{\max} = 466$)²⁰⁸ (Fig. 3.2).²⁰⁹

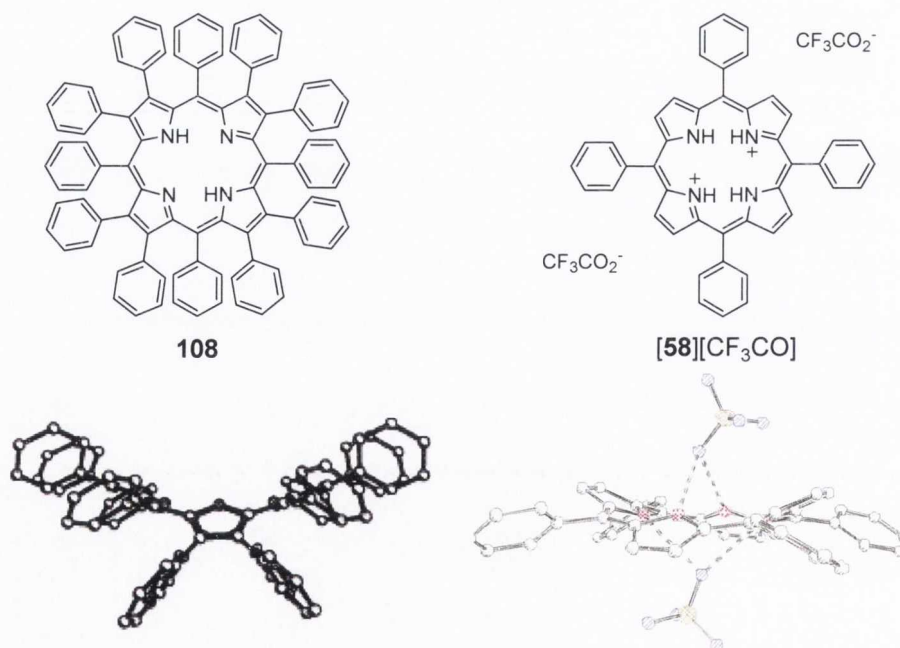


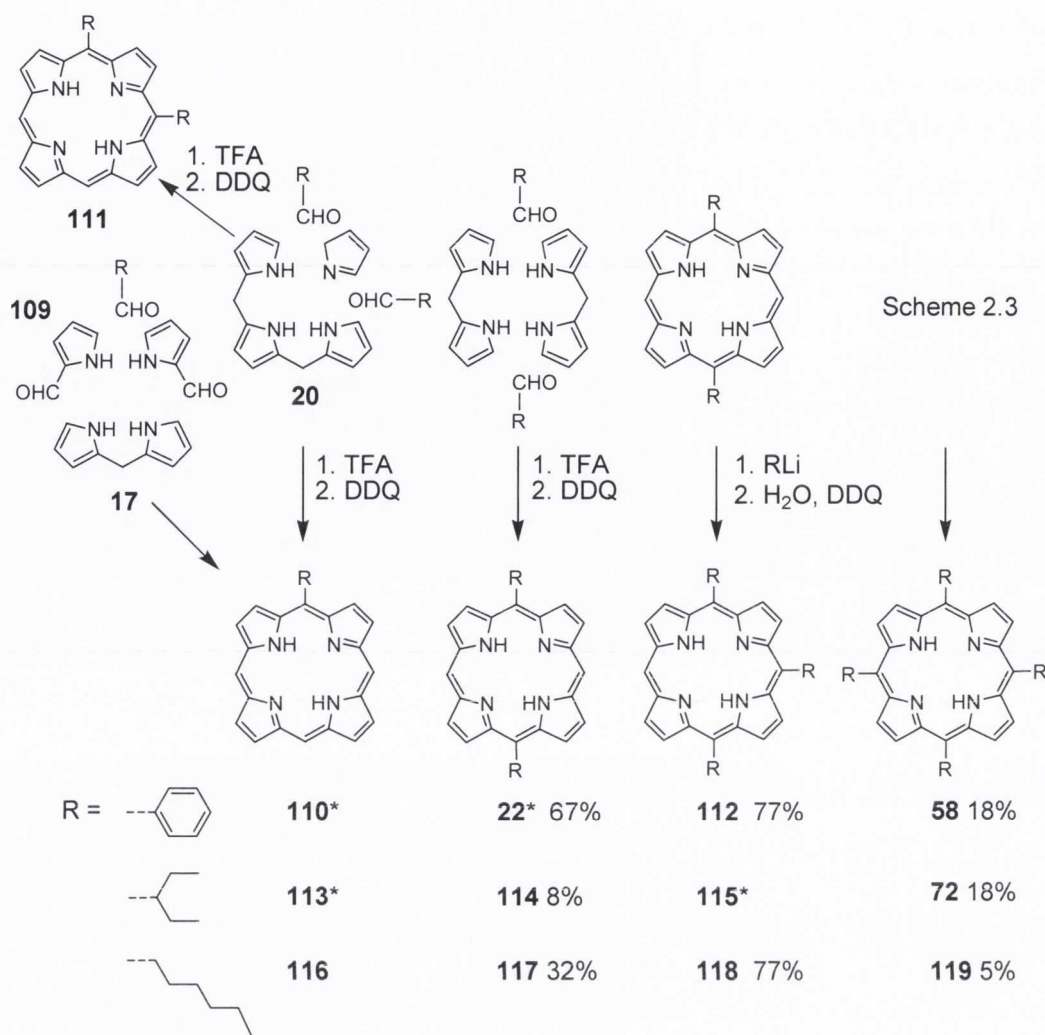
Figure 3.2. Crystal structure of highly substituted, (left)²⁰⁴ and diprotonated,²⁰⁹ nonplanar porphyrins.

Three series of porphyrin dications, with different degrees of *meso* substitution, were prepared. Using UV-vis spectroscopy and X-ray crystallography the effect of peripheral substitution on porphyrin macrocycles could be determined.

3.2 Results and discussion

3.2.1 Synthesis

Monosubstituted A-type porphyrins can be obtained by condensation of pyrrole-2-carbaldehyde **109** (2 equiv.) with dipyrromethane **17** (1 equiv.) in yields of up to 7% (Scheme 3.2).⁴⁶ However, they have also been observed as by-products in the synthesis of 5,10-disubstituted porphyrins from tripyrrane **20** and pyrrole.⁴⁶ 5,15-Disubstituted porphyrins were synthesised using dipyrromethane and the appropriate aldehyde to yield **22**, **114** and **117** in 67%, 67%, and 32% yields respectively. A₃-Type 5,10,15-trisubstituted porphyrins were prepared by reaction of the above 5,15-derivative with the desired organolithium reagent. A₄-Type 5,10,15,20-tetrasubstituted porphyrins were prepared according to standard Lindsey methods,²⁵ as outlined in the previous chapter.



Scheme 3.1. Synthetic approaches for the syntheses of A-, A₂-, A₃- and A₄-type porphyrins from pyrrolic precursors.*

Porphyrin dications were prepared by stirring free base porphyrins in a solution of dichloromethane containing 5% trifluoroacetic acid.

3.2.2 UV-vis spectroscopy

The UV-vis spectrum of a free base porphyrin comprises an intense Soret band at ca. 420 nm accompanied by four less intense Q bands at longer wavelengths.²¹⁰ The UV-vis spectra of aromatic porphyrins have extinction values in the order of $10^6 \text{ M}^{-1}\text{cm}^{-1}$.

* Provided by Prof. Mathias O. Senge.

A. Phenylporphyrin series

Ryppa *et al.* investigated the absorption spectra of a complete series of *meso* phenylporphyrins (Table 3.1) after reporting methods for the syntheses of the elusive 5-mono- **110** and 5,10-disubstituted **111** porphyrins.⁴⁶ Both the Soret and Q bands gradually shifted bathochromically with increasing number of phenyl residues (Table 3.1). As the UV-vis spectra of **22** and **111** displayed similar shifts in both the Soret and Q band regions, the sequential bathochromic shifts with increasing number of phenyl residues was attributed to mainly electronic effects.^{195,211-213}

Table 3.1. UV-vis absorption spectra for free base *meso* phenylporphyrin (fb) recorded in dichloromethane and trifluoroacetate dications (dc) recorded in dichloromethane + 5% trifluoroacetic acid.

	Soret band (fb)	Q bands (fb)	Soret band (dc)	Q bands (dc)
110	403 ⁴⁶	595, 526, 568, 622	-	-
111	406 ⁴⁶	504, 534, 579, 630	-	-
22	406 ²¹⁴	502, 536, 574, 630	420	569, 614
112	412 ¹⁷⁴	508, 543, 582, 638	429	581, 633
58	417 ²⁵	514, 549, 589, 644	437	594, 653

Upon the addition of trifluoroacetic acid to *meso* substituted porphyrins, the Soret band in UV-vis spectrum was shifted to longer wavelengths and the four Q bands were replaced by two more intense bands (Table 3.1). The spectral simplification for porphyrin dications was attributed to the higher symmetry of porphyrin dications compared to that of their free base forms.¹ A bathochromic shift of 14, 17 and 20 nm was observed upon the formation of the 5,15-di- **22**, 5,10,15-tri- **112** and 5,10,15,20-tetraphenylporphyrin **58** dications respectively.

B. 1-Ethylpropylporphyrin series

The solutions of compounds **113-115** and **72** in free base form ranged in colour from blue (for the mono derivative) to purple (tetrasubstituted derivative), whereas the dications ranged in colour from pink to green (mono to tetra). A comparison of the UV-vis spectra of the free base forms clearly showed bathochromic shifts correlated with the presence of extra *meso* substituents (Fig. 3.3) and like in the *meso* phenyl series, was attributed to electronic effects.

Bathochromic shifts of 5, 8, 9 and 8 nm were observed upon formation of the mono-, bis-, tris- and tetrakis(1-ethylpropyl)porphyrin dications (**113-115** and **72**) respectively (Table 3.2). This was correlated with a lower degree of distortion from planarity than what was observed for the series of *meso* phenyl substituted porphyrin dications (14-20 nm).

Table 3.2. UV-vis absorption spectra for *meso* 1-ethylpropylporphyrins free base (fb) in dichloromethane and dications (dc) in dichloromethane + 5% trifluoroacetic acid.

	Soret band (fb)	Q bands (fb)	Soret band (dc)	Q bands (dc)
113	399 ⁴⁶	497, 526, 568, 621	404	551, 643
114	403 ⁴⁶	504, 535, 575, 630	411	562, 608
115	412	512, 546, 587, 642	421	574, 623
72	420 ¹⁸⁴	522, 539, 601, 669	428	593, 643

C. Hexylporphyrin series

UV-vis analysis of a second series of *meso* alkylporphyrins **117-119** revealed similar bathochromic shifts upon formation of the dications (5-9 nm) to those observed above (Table 3.3). Of note was the 5 nm shift observed upon addition of two protons to the tetrasubstituted derivative **119**. This compared with an 8 nm shift upon dication formation in **72**, and could possibly be attributed to extra steric bulk surrounding the *meso* positions in **72**, thus forcing the macrocycle display a higher distortion from planarity.

Table 3.3. UV-vis absorption spectra for *meso* hexylporphyrins free base (fb) in dichloromethane and dications (dc) in dichloromethane + 5% trifluoroacetic acid.

	Soret band (fb)	Q bands (fb)	Soret band (dc)	Q bands (dc)
116	401 ⁴⁶	496, 525, 570, 622	-	-
117	404 ²¹⁵	504, 535, 578, 639	411	564, 615
118	412 ²¹⁶	512, 545, 582, 647	421	567, 615
119	418 ²¹⁵	520, 555, 601, 660	423	586, 633

3.2.3 ^1H NMR Spectroscopy

Upon addition of two hydrogen atoms to the core of the porphyrin, there was a downfield shift of the N-H resonances (~ 1.2 -2 ppm) and an upfield shift of the β -resonances. Many investigations have revealed that the chemical shifts in porphyrins are strongly influenced by hydrogen bonding, particularly those of the N-protons.^{191,217} In addition, the concentration of trifluoroacetic acid influences the chemical shifts.^{218,219} Thus, the N-H resonance is not a good indication of ring distortion and will not be discussed further in this thesis.

3.2.4 X-ray Crystallography

In order to address the question of the extent that dication formation and different substituents in A_x porphyrins (with $x < 4$) affect the conformation a number of simple porphyrin derivatives were used for an initial crystallographic study.

An impression to what extent multiple conformations and crystal modifications are possible comes from an analysis of 5,15-diphenylporphyrin (Fig. 3.3). Here, a monoclinic ($P2_1/c$) modification of a methylene chloride solvate structure showed small but distinct deviations from planarity. The macrocycle was planar with a mean deviation of the 24 macrocycle atoms from their least-squares-plane ($\Delta 24$) of 0.083 Å, and the largest deviations from this plane were observed for the two substituted *meso* positions (0.16 and 0.18 Å, respectively). Upon closer inspection, differences between the *meso* H and *meso* phenyl quadrants of the molecule were detected. The C_α - C_{meso} bond lengths were elongated (1.406 vs. 1.386 Å) whereas the N - C_α - C_{meso} (124.4 vs. 126.9°) and C_α - C_{meso} - C_α (123.8 vs. 127.5°) bond angles were narrowed in the *meso* phenyl quadrants. The phenyl rings were twisted with respect to the least squares plane, which reduced steric repulsion between the phenyl rings and the hydrogens at the β -positions of neighbouring pyrrole rings.¹⁴⁵

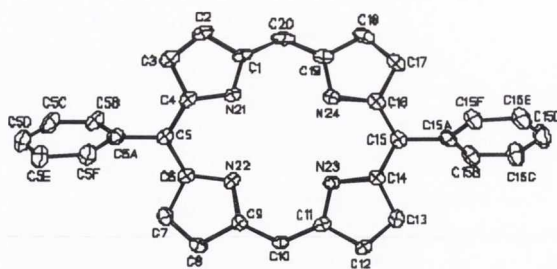


Figure 3.3. View of the molecular structure of **22** in the crystal. Hydrogen atoms have been omitted for clarity, thermal ellipsoids are drawn for 50 % occupancy.

A small but significant degree of *ruf* distortion was present as well. Another modification (unsolvated, space group P-1) of 5,15-diphenylporphyrin showed minor deviations from planarity with a Δ_{24} of 0.06 Å. Here, a degree of pyramidalisation was observed for the nitrogen atoms ($\Delta = 0.14$ and 0.02 Å, respectively).

The free base form of compound **114** crystallised in trigonal space group R-3 and contained a disordered cyclohexane molecule of salvation. As shown in Figure. 3.4, the asymmetric unit contained half of the porphyrin molecule. The Δ_{24} value was 0.007 Å. Again, the C_{α} - C_{meso} bond lengths were elongated (1.41 vs. 1.39 Å), whereas the N- C_{α} - C_{meso} (124.4 vs. 126.8°) and C_{α} - C_{meso} - C_{α} (122.9 vs. 129.3°) bond angles were narrowed in the *meso* substituted quadrants.

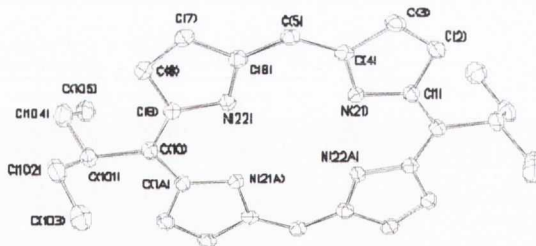


Figure 3.4. View of the molecular structure of **114** in the crystal. Hydrogen atoms have been omitted for clarity, thermal ellipsoids are drawn for 50 % occupancy.

The impact of the formation of a dication, i.e. the steric overload of the core of the porphyrin with four NH groups was clearly seen in the structure of the bis(trifluoroacetate) salt of 5,15-bis(1-ethylpropyl)porphyrin. The compound crystallised with half the tetrapyrrole and one trifluoroacetate residue in the independent unit. A side view of the dication structure formed is shown in Figure 3.5.

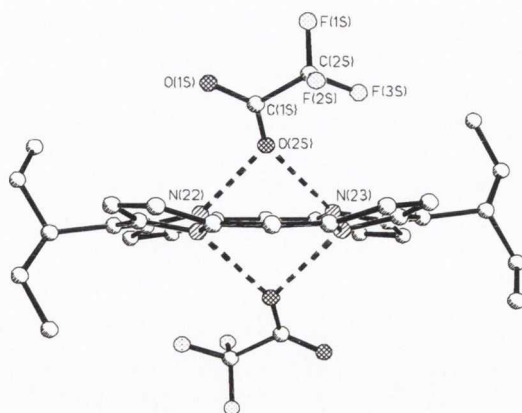


Figure 3.5. View of the molecular structure of the dication salt of **114** formed in the crystal. Hydrogen atoms have been omitted for clarity.

Hydrogen bonds and the weak interactions formed are shown below in Table 3.4.

Table 3.4. Hydrogen bonding interactions.

Unit	Translation	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
N(22)-H(22A)···N(23)	intramolecular	0.88	2.32	2.825(4)	117
N(22)-H(22A)···O(2S)	-x,1-y,-z	0.88	1.93	2.711(4)	147
C(10)-H(10A)···O(1S)	x,1/2-y,1/2+z	0.95	1.93	3.284(5)	151
C(13)-H(13A)···O(1S)		0.95	2.31	3.199(4)	155

In the bulk crystal the molecules formed a close spaced lattice structure in which neighbouring dication units were related by a contact between a *meso* C-H and the oxygen atom of the anion not involved in N-H binding [C10A···O1SA 2.426 Å] (not shown).

The tetrapyrrole macrocycle exhibited a rather unusual conformation, where two neighbouring N-H units pointed towards the same face of the molecule. The NSD (normal coordinate structural decomposition) analysis clearly showed this to be the result of a wave distortion (Section 1.6). The in-plane distortions were very large with major contributions from *meso*-stretch, N-stretch and macrocycle breathing distortion modes (Fig. 3.7). The average Δ_{24} was 0.18 Å (compared to 0.007 for the free base form).

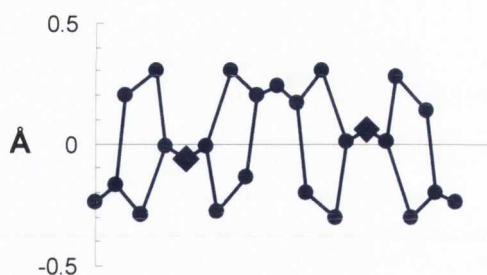


Figure 3.6. View of the skeletal deviations from the Δ_{24} plane of $[\text{H}_4\mathbf{114}]^{2+}$. The sequence of *meso* carbon atoms is C20, C5, C10, C15, C20 from left to right. Substituted *meso* positions are indicated.

A crystal structure of the dication of the trisubstituted derivative **118** was also obtained, however, as the sample could not be refined satisfactorily, only an overview of some key observations will be reported in this thesis.

The impact of further *meso* substituents was indicated by preliminary data from a crystal structure of **118** bistrifluoroacetic acid solvate. The structure showed high vibrational movement of the *meso* alkyl substituents and preliminary data indicated that the Δ_{24} was significantly larger with a value of 0.44 Å.

3.3 Conclusions

The porphyrin dications obtained *via* protonation of the respective free base porphyrins exhibited nonplanar conformations, as could be evidenced by UV-vis spectroscopy. A preliminary crystallographic study revealed the occurrence of in-plane distortions in the macrocycle of the free base forms of both aryl and alkyl disubstituted porphyrins. The dication of the alkyl derivative displayed a significant out-of-plane *wave* distortion which was due to overcrowding in the core of the porphyrin. In addition, evidence for significant conformational flexibility of 5,15-diphenylporphyrin was observed. Until further crystallographic analysis can be performed, the precise influence of overcrowding in the porphyrin core on the conformation cannot be determined.

Chapter 4

**Structural, spectroscopic and anion binding properties of 5,10-
porphodimethenes**

4.1 Porphodimethenes

Tetrapyrroles include both the fully conjugated porphyrins and the unconjugated calixpyrroles. Calixpyrroles have been established as excellent anionic and neutral receptor systems.^{24,119,121,220-227} Anions are essential to life as many biological processes depend on their recognition, transport or transformation.²²⁸⁻²³⁰ They function in the majority of enzyme-substrate and enzyme-cofactor complexes as well as in the interaction between proteins and RNA or DNA.²²⁸⁻²³¹ Conversely, anions have detrimental effects on the environment. Anionic pollutants such as phosphate and nitrate are the cause of eutrophication of lakes and inland waterways.^{232,233} There is a discernible demand for the production of selective anion receptors and sensors. Calix[4]pyrroles have been identified as neutral, non-aromatic polypyrrolic macrocycles that selectively bind anions.^{119,220,224,226} Likewise, sapphyrins, pentapyrrolic aromatic macrocycles, have been proven as excellent receptor systems when diprotonated.^{159,160}

Until now, there have been no investigations into the coordination and ligand binding properties of these compounds, how they compare to porphyrins and their value as receptors. Due to their appearance in the porphyrin biosynthetic pathway, 5,15-disubstituted PDMs have been thoroughly researched.^{234,235} The isomeric class, 5,10-disubstituted PDMs, however, has not received the same attention since it was first isolated in 1996 by Callot *et al.*^{162,180,236} Thus, we have carried out in-depth research into 5,10-PDMs in order to more fully understand the properties and functionalities of this intriguing class of receptors.

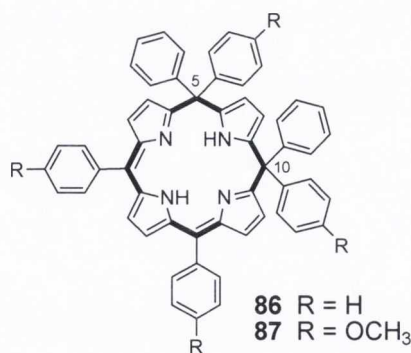


Figure 4.1. sp^2 and sp^3 -carbon centres present in 5,10-disubstituted porphodimethenes.

Due to the presence of sp^3 -hybridised centres the macrocycles must adopt nonplanar conformations.^{61,114,127,174,236-241} As shown in chapter 2, this leads to changes in their

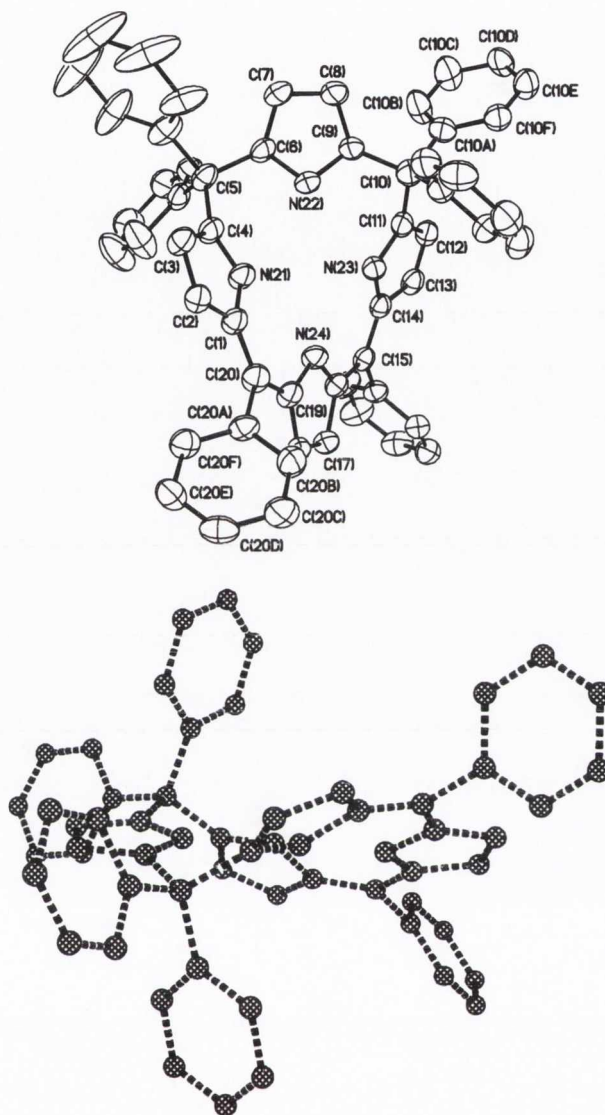
photophysical properties. There is a large catalogue of research papers dedicated to the chemistry, properties and applications of these nonplanar molecules.^{142,143,148,242-245} Due to the significance of protons in essential biological processes and the effect of protonation on the porphyrin chemical and biological functions, a number of research groups have studied the porphyrin protonation process in the past decades. In *meso* arylporphyrins, the dication is formed in one step, without the isolation of an intermediate monocation. The differences in physical and chemical properties between the free base and the diprotonated species have been observed by using different acids such as trifluoroacetic acid, glacial acetic acid and perchloric acid.^{142,143,148,242-248} To date, only limited research has been carried out on the effect of protonation and the properties of calixphyrin chemistry. This was an ideal starting point to investigate more closely the properties of PDM diacids and how they differ from their PDM and porphyrin analogues.

We were able to obtain and characterise the diacid form $[H_4(PDM)][X]_2$ upon the addition of several acids to PDM's **86** and **87**, where X denotes the anions of acids; HCl, HBr, MeSO₃H, CF₃CO₂H and HClO₄.

4.2 Results

4.2.1 Crystallography

In order to establish the conformation and structural properties of the 5,10-PDM we grew crystals suitable for single crystal X-ray crystallographic analysis of the 5,5',10,10',15,20-hexaphenylporphyrin **86** (Fig. 4.2). The structure clearly shows the two sp^3 centres at the 5- and 10-position. As expected, the macrocycle is extremely nonplanar as indicated by the Δ_{24} value of 0.40 Å for the 24 macrocycle atoms. Δ_{24} is the average deviation of the 24 macrocycle atoms from their least squares plane.¹⁹⁹ The displacement of the *meso* carbon atoms is highly unsymmetrical. Displacement for the C5, C10, C15 and C20 atoms from the 24 macrocycle atom least-squares-plane are 1.23, 1.22, 0.59 and 0.58 Å, respectively. The related values for deviation from the 4N plane are 0.85, 1.0, 0.95 and 0.83 Å, respectively. The conformation can roughly be described as an unsymmetrical roof-type conformation (as found for 5,15-PDM)¹⁶⁶ with significant contributions from other distortion modes.²⁰⁹ The two N-H vectors point towards each other in the central core of the macrocycle. Thus, they are still somewhat



We were able to obtain crystals of the dication of **86**, [H₄**86**][ClO₄]₂. The compound crystallised with four independent molecules in the unit cell and included several solvent molecules. Together with low high angle reflection this resulted in a structure of only marginal quality (not shown). Thus only an overall conformational analysis will be given here. As expected, the structure is more distorted than the free base **86**, and the four independent molecules exhibited Δ_{24} values of 0.62 to 0.66 Å. The displacement of the *meso* carbon was unsymmetric. For example, for one molecule the C5, C10, C15,

and C20 displacements from the least-squares plane of the 24 macrocycle atoms were 0.46, -0.08, 0.24 and -0.2 Å, respectively. In the other molecules these values varied between 0 and 0.42 Å while β -displacements reached up to 1.4–1.5 Å. Thus, the asymmetry in the macrocycle distortion of the free base is retained in the dication.

4.2.2 UV-Vis Analysis

Upon the addition of each acid to H₂TPP and H₂T(4-MeOP)P the solutions changed colour from purple to green. The Soret band in the porphyrin UV-vis spectrum was shifted to longer wavelengths upon protonation and the four Q bands were replaced by one more intense band (Fig. 4.3). The porphyrin dications formed with acid halides Cl⁻ and Br⁻ gave absorbances that were more red shifted than those formed from the oxygen donor anions CF₃CO₂⁻ and MeSO₃⁻. The Soret band of the dication was of lower intensity than that of the respective free base *meso* arylporphyrin.

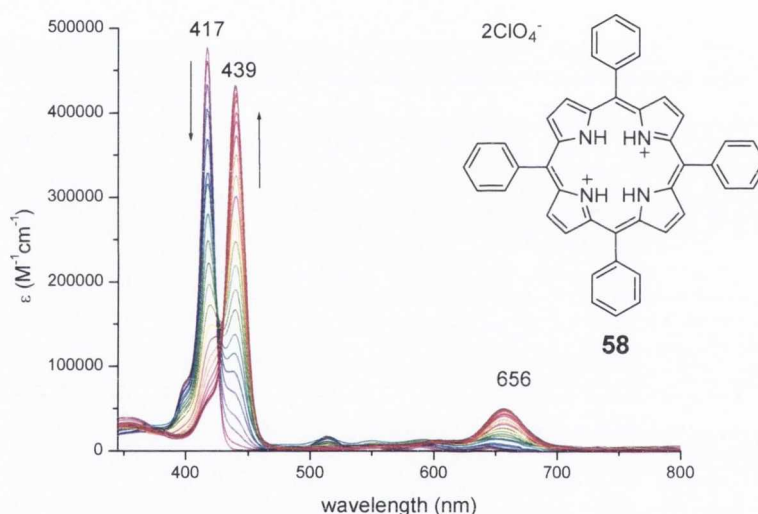


Figure 4.3. UV-vis titration of H₂TPP **58** (1×10^{-6} M) with HClO₄ recorded in dichloromethane.

A series of UV-vis investigations were carried out on compounds **86** and **87** with several acids to determine the effect of protonation on the PDM macrocycle, to observe any anion effects that might occur and to compare the spectra to the analogous porphyrin. No fluorescence is observed for PDMs **86** and **87** due to their lack of aromaticity.

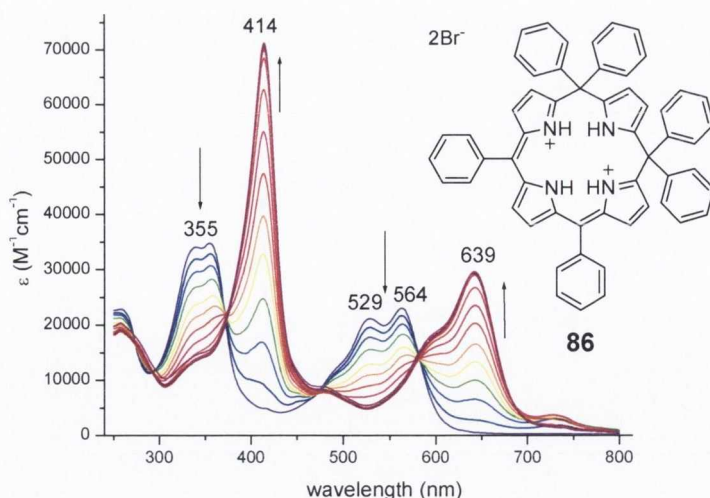


Figure 4.4. UV-vis titration of PDM **86** (1×10^{-5}) with HBr recorded in dichloromethane.

The UV-vis spectrum of 5,10-PDMs comprises two absorption bands of similar intensity, one at ~ 350 nm and the other at ~ 550 nm (Fig. 4.4).^{162,180,190} The UV-vis spectra of PDM dications displayed an intense absorption band at ca. 412 nm (**86**) or at ca. 425 nm (**87**) and a less intense band at ca. 635 nm (Fig. 4.4). In both PDMs the MeSO_3H dication was most blue shifted, followed by the dication formed from the addition of TFA to the porphyrin. The HBr dication was the most red shifted.

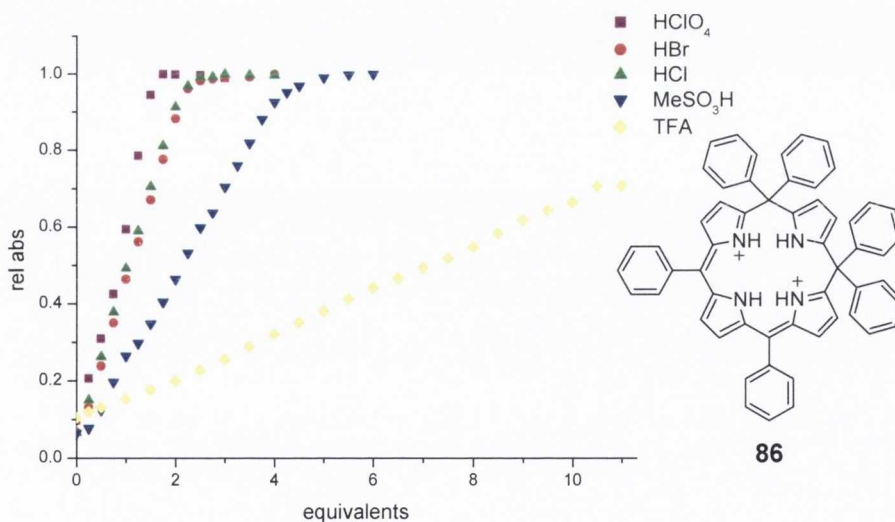


Figure 4.5. Relative absorption of PDM **86** (1×10^{-5} M) versus equivalents of acid recorded in dichloromethane.

Upon addition of 2 equiv. of HCl, HBr and HClO_4 , complete protonation of both PDMs was observed. Full protonation of PDMs **86** and **87** was achieved with 4.5 and 2.5 equiv.

of MeSO_3H respectively, whereas 70 (**86**) and 5 (**87**) equiv. of TFA were needed (Fig. 4.5). This trend was in agreement with the pK_a values of the acids.²⁴⁹ The titration of TFA with both H_2TPP and **86** required over 40 equiv. of acid to form the dication, whereas with $\text{H}_2\text{T(4-MeOP)P}$ and **87**, less than 10 equiv. of acid were required. We have attributed this to a higher basicity of the pyrroline nitrogen atoms in the phenyl derivatives.

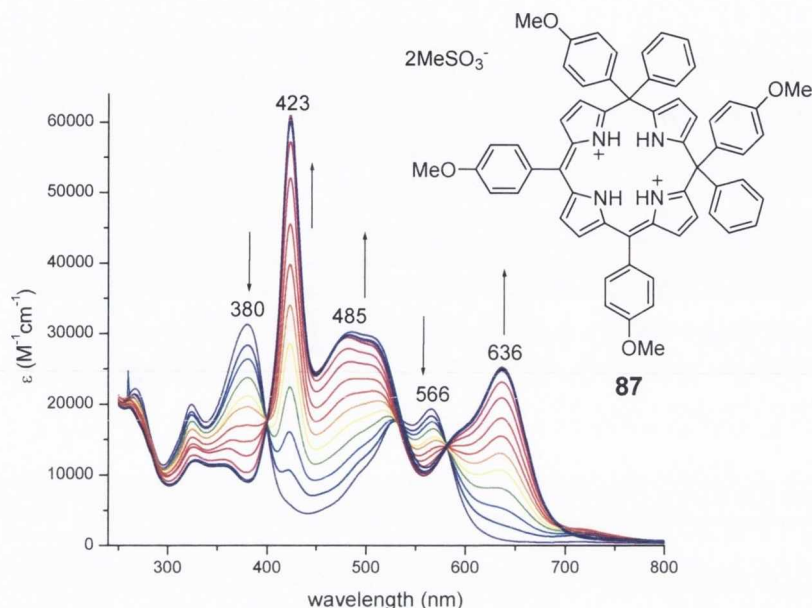


Figure 4.6. UV-vis titration of PDM **87** ($1 \times 10^{-5}\text{M}$) with MeSO_3H recorded in dichloromethane.

The UV-vis absorption spectra of the dications of compound **87** displayed an additional absorption band which was not present in the hexaphenyl derivative **86** (Fig. 4.6). In the area of 460–520 nm there was one broad absorption band that so far, we have been unable to account for. As similar equivalents of acid were required to fully protonate both PDMs, it is likely that the methoxy groups on the periphery influenced the behaviour of the PDM in solution.

4.2.3 NMR Analysis

In order to elucidate the protonation in more detail, ^1H NMR titrations were carried out with H_2TPP and PDMs **86** and **87**. ^1H NMR titrations were not performed with $\text{H}_2\text{T(4-MeOP)P}$ due to its low solubility in chloroform and dichloromethane.

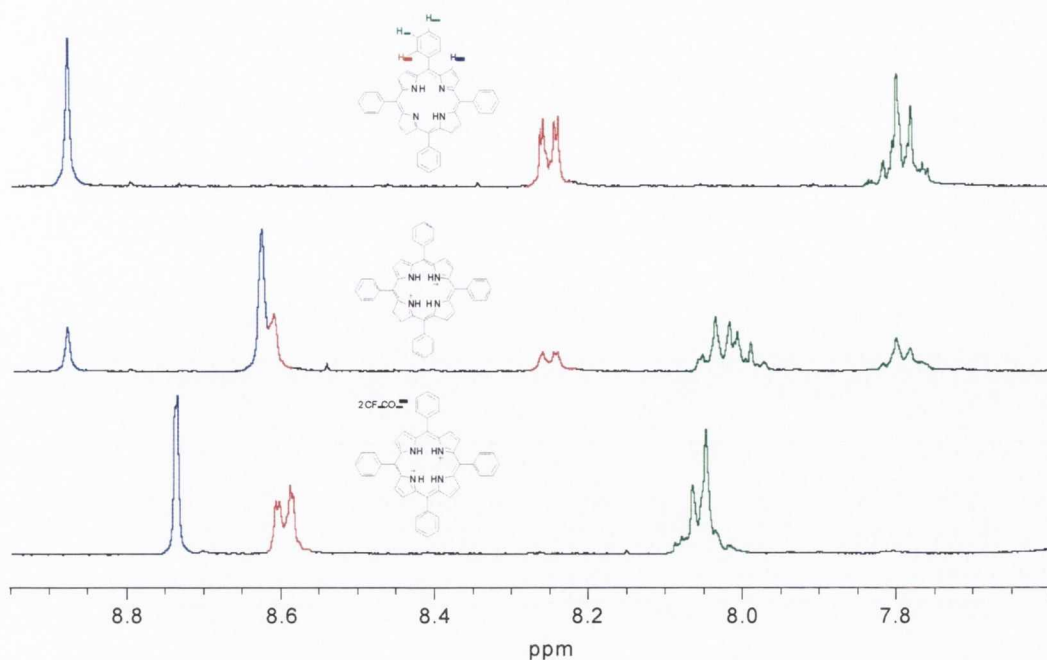


Figure 4.7. ^1H NMR of H_2TPP **58** (top), intermediate spectrum (middle) and dication (bottom) formed upon addition of TFA recorded in CDCl_3 .

Upon protonation of H_2TPP with TFA, the β -proton resonance at 8.87 ppm shifted to higher field to 8.62 ppm and the phenyl protons shifted to lower field ($\Delta\delta = 0.37 \pm 0.01$ ppm for the ortho protons and $\Delta\delta = 0.24$ ppm for the *meta* and *para* protons) (Fig. 4.7). The nitrogen protons were more sensitive to acid than the peripheral protons. The NH resonance shifted downfield by $\Delta\delta = 3.2$ ppm (Fig. 4.8). The higher field shift of the β -protons and the downfield shift of the nitrogen protons relate to a decrease in the aromatic ring current with protonation.²⁵⁰ When the concentration of acid was increased beyond the minimum amount required for dication formation, the direction of the shift changed. Aromatic and β -signals generally shifted to lower field and all signals continuously shifted with increasing acid concentration. The NH resonance shifted to higher field by $\Delta\delta = 0.98$ ppm with 10 equiv. and $\Delta\delta = 1.44$ ppm with 100 equiv. (Fig. 4.8). This continuous shift was in agreement with previous literature data where it was reported that the resonances shifted continuously to limiting values in TFA solvent.²¹⁹

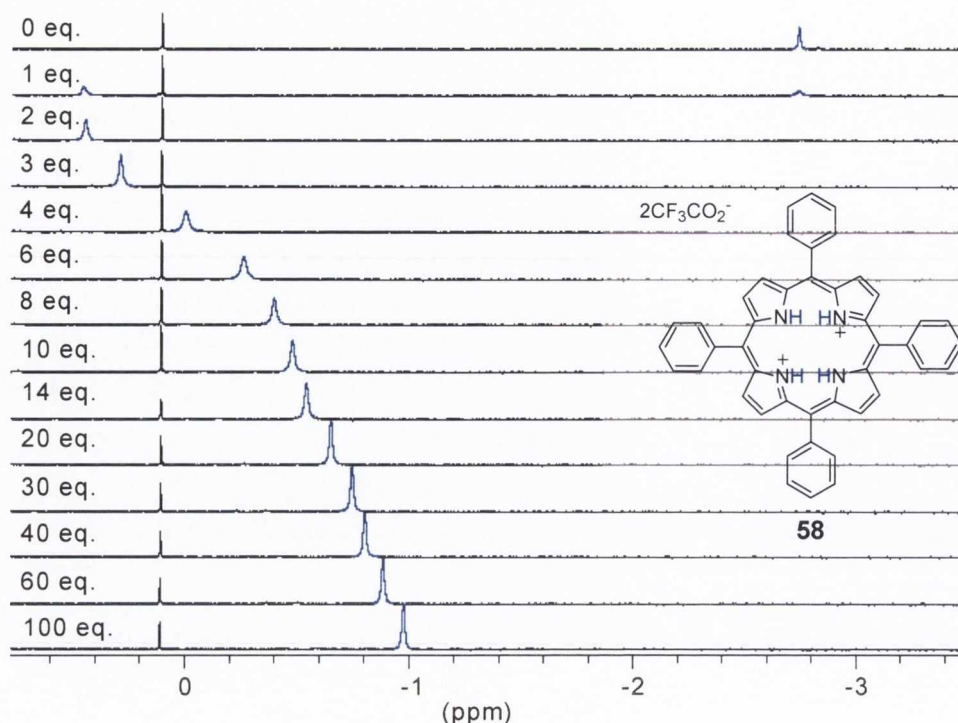


Figure 4.8. Spectral changes in the ^1H NMR of nitrogen protons of H_2TPP **58** upon addition of TFA recorded in CDCl_3 .

A similar trend was observed for the other acids. In $[\text{H}_4\text{TPP}][\text{Cl}]_2$ the nitrogen protons shifted downfield by $\Delta\delta = 3.39$ ppm. With the addition of up to 10 equiv. of acid, an upfield shift was observed ($\Delta\delta = 0.64$ ppm). In $[\text{H}_4\text{TPP}][\text{ClO}_4]_2$ an overall shift of $\Delta\delta = 3.59$ ppm was observed and in $[\text{H}_4\text{TPP}][\text{MeSO}_3]_2$, $\Delta\delta = 3.72$ ppm.

In the ^1H NMR of the PDM dications of **86** and **87**, different behaviour was observed. In contrast to the conjugated porphyrin dications, the β -protons of the PDM dications shifted downfield upon protonation and the proton at N22 moved upfield (Fig. 4.9). Similar to the nitrogen protons in the porphyrin, the proton at N24 shifted to lower field which was attributed to the proton being located at the more conjugated part of the PDM. This behaviour suggested that the aromatic ring current was increasing with diprotonation, more noticeably at the unconjugated component of the macrocycle. In the PDM dications, the resonance at 6.09 ppm (β -18 proton) displayed the largest downfield shift (up to $\Delta\delta = 0.87$ ppm) followed by the resonance at 6.15 ppm (β -3 proton). The resonances due to β -7 and β -2 generally displayed similar downfield shifts upon protonation.

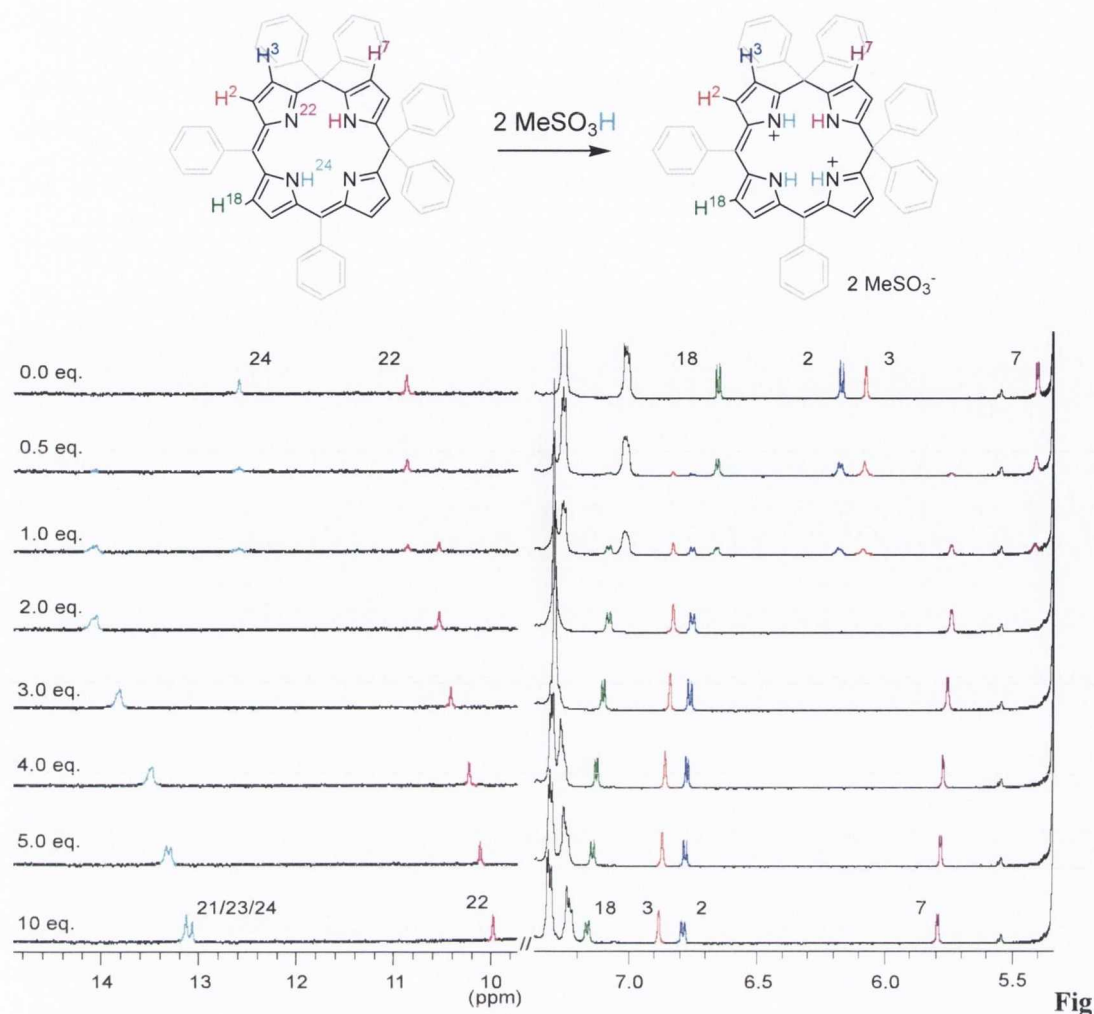


Figure 4.9. ^1H NMR spectral changes for the central protons N24/N21/23 (cyan) and N22 (magenta) and β -18 (green), β -2 (blue), β -3 (red) and β -7 (purple) observed upon addition of MeSO_3H to PDM **86** in CD_2Cl_2 .

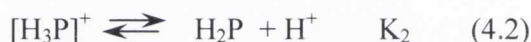
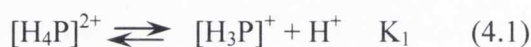
Using HClO_4 as the proton source, the β -protons shifted to lower field by $\Delta\delta = 0.63$ ppm compared to $\Delta\delta = 0.53 \pm 0.01$ ppm, 0.52 ± 0.01 ppm and 0.50 ± 0.05 ppm, when the dication was formed with HCl , MeSO_3H and TFA respectively. Consequently, the proton at N22 in $[\text{H}_4\text{PDM}][\text{ClO}_4]_2$ displayed the largest upfield shift from $\delta = 10.52$ to 8.94 ppm in $[\text{H}_4\text{86}][\text{ClO}_4]_2$ and 10.56 to 8.65 ppm in $[\text{H}_4\text{87}][\text{ClO}_4]_2$. When further aliquots of HClO_4 were added, a downfield shift was observed. Using MeSO_3H to form the PDM dication, the proton at N22 shifted upfield and then shifted further upfield upon addition of further amounts of acid ($\Delta\delta = 0.81 \pm 0.10$ ppm). Generally, the ^1H NMR resonances of the free base PDMs disappeared as those for the protonated species appeared. However, when the PDM dication of **86** was formed by protonation with TFA , the original resonances for the free base were only seen to shift. This is indicative of

binding. This also contrasted to the trend observed in the porphyrin. HCl displayed different behaviour entirely, as the signal for the proton at N22 appeared at low field at ca. 11.38 ppm (**86**) and 11.09 ppm (**87**) and then proceeded to shift to high field after further aliquots of acid were added ($\Delta\delta = 0.38 \pm 0.05$ ppm with 10 equiv.). This initial downfield shift, followed by an upfield shift, was seen in the porphyrin dications and indicated a decrease in ring current upon protonation.

4.2.4 Monocation Intermediate

Upon protonation of PDMs **86** and **87** with HClO₄, transient UV-vis and ¹H NMR spectra were observed which have been attributed to the presence of a monocation species. The observation of a monoprotonated porphyrin has rarely been reported before and proof of their existence has been the subject of considerable effort.^{147,248,251,252}

Free base porphyrins with two unprotonated nitrogen atoms are capable of exhibiting the following acid-base equilibria:



There have been many investigations into the above equilibria for various porphyrins and chlorins using both potentiometric and spectrophotometric techniques.^{247,248,253-256}

By more fully understanding the acid-base properties of tetrapyrroles, more information can be obtained on metal-macrocycle reactivity, π -electron delocalisation, resonance energy N,N'-tautomerism, substitution pattern and stereochemistry.²⁵⁷

Both $[\text{H}_4\text{P}]^{2+}$ and H_2P are very stable molecules, with the former possessing a four-fold axis of symmetry and the latter a two-fold. The difficulty in observing the monocation species of *meso*-arylporphyrins was attributed to loss of symmetry which decreased resonance stabilisation and distorted the macrocycle. The monoprotonated derivative could therefore only exist over a very narrow pH range, i.e. $K_1 \ll K_2$.^{147-149,209,242,248,258-264}

In the UV-vis and ¹H NMR studies we carried out on the porphyrin, we found that the ring current decreased upon protonation. In the UV-vis studies this was shown by a less intense Soret band in the dication compared to the free base. Whereas in the ¹H NMR titrations, a lower field shift of the nitrogen protons and a higher field shift of the β -protons were consistent with a decrease in aromatic character and consequently, a decrease in stability. In contrast, in the PDM dications the major band was more intense

and the chemical shifts in the NMR moved in the opposite directions, suggesting a more stable dication than free base form and conceivably, a more stable monocation.

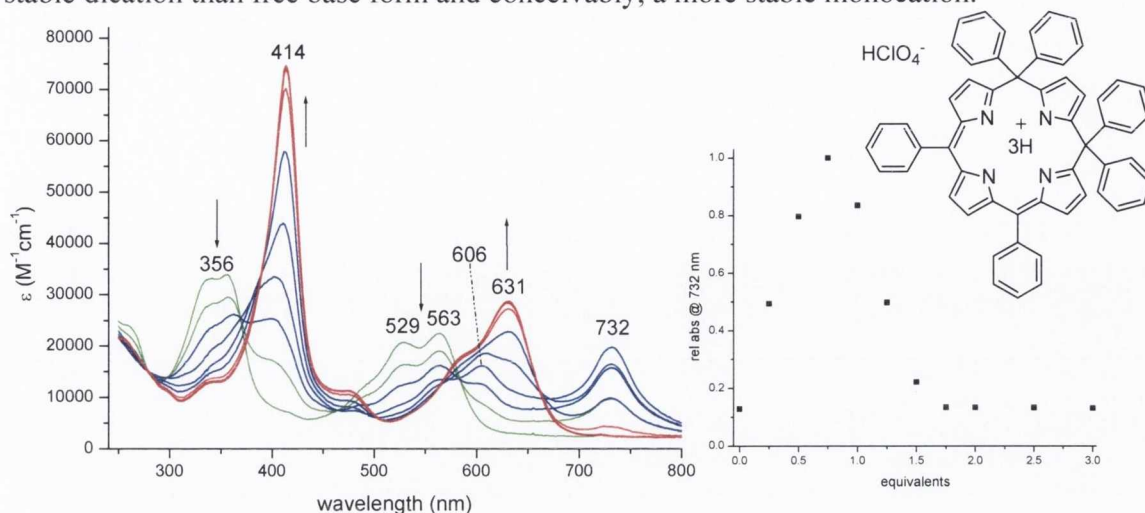


Figure 4.10. UV-vis titration of PDM **86** (1×10^{-5} M) with HClO_4 with free base (green) monocation (blue) and dication (red) spectra indicated, and relative absorption at 732 nm (inset) recorded in dichloromethane.

Complex changes in the absorption profile of $\text{H}_2(\text{PDM}) \rightarrow [\text{H}_4\text{PDM}][\text{ClO}_4]_2$ pointed towards the occurrence of multiple equilibria in solution. This was attributed to the conversion of the free base species to its diacid form via the formation of a PDM monoprotonated at the core $[\text{H}_3\text{PDM}][\text{ClO}_4]$. In PDM **86**, there was a shift in isosbestic points from 371 nm to 387 nm, from 466 nm to 493 nm and also a red shift from 606 nm in the monocation to 631 nm in the dication. A new maximum was observed at 732 nm. With the addition of 0.75 equiv. of acid to the PDM solution the absorbance at 732 nm reached a maximum, then weakened as further aliquots of acid were added (Fig. 4.10). These features pointed towards the presence of a chemically distinguishable monocation. In **87** there was only a slight change in isosbestic points. Here the new absorption appeared at 719 nm after the addition of 0.75 equiv. of HClO_4 and disappeared after the addition of 1.50 equiv.

With less than the 2 equiv. per mole of H_2TPP required to convert the porphyrin completely to $[\text{H}_4\text{TPP}]^{2+}$, the ^1H NMR spectra contained a set of signals for each of the species at their expected chemical shift values. There were no signals at intermediate positions which could be attributed to a monoprotonated intermediate. In the ^1H NMR titration of PDM **86** and **87** with HClO_4 , intermediate spectra were observed (Fig. 4.11). The monocation was clearly detected by four sets of signals that were present between

0.25 and 1.75 equiv. For **87**, the C-20 methoxy resonance also showed an intermediate resonance. The free base resonated at 3.89 ppm, the monocation at 3.93 ppm and the dication at 3.97 ppm. Many resonances in the aromatic region overlapped so it was not possible to isolate a full set of signals for this intermediate species.

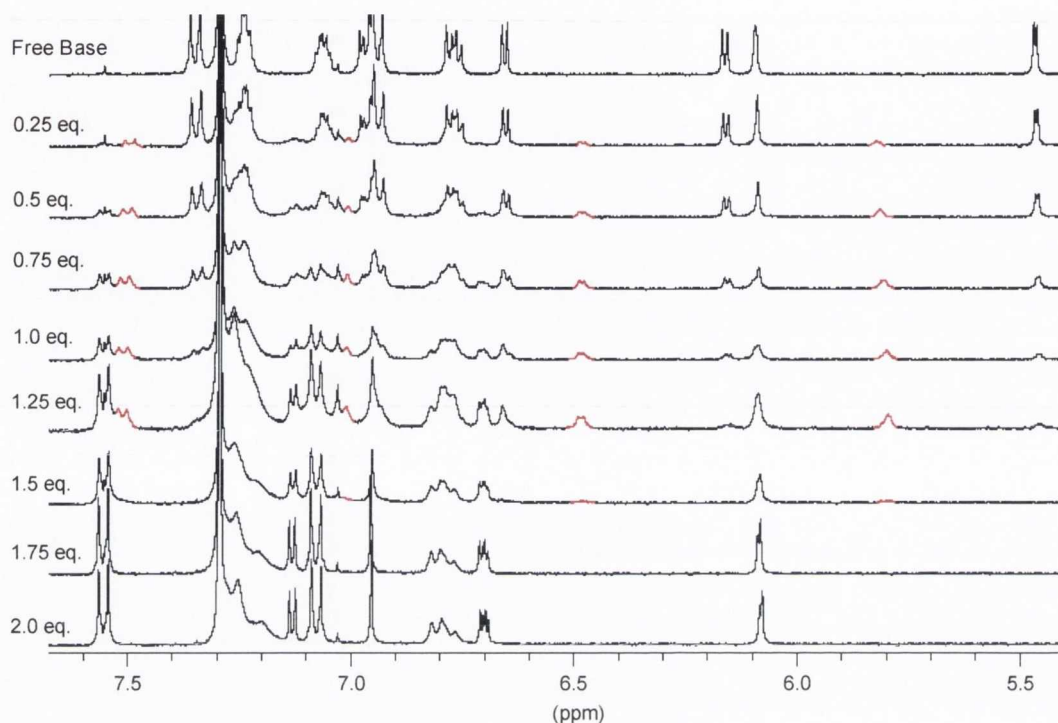


Figure 4.11. ^1H NMR titration of **87** (1×10^{-3} M) with HClO_4 (MeOD) in CD_2Cl_2 . Highlighted in red are the resonances due to a monocation species.

4.3 Conclusions

5,10-PDMs were found to exhibit highly nonplanar conformations. The effects of core protonation on 5,10-PDMs was investigated by UV-vis absorption and ^1H NMR spectroscopies and compared to porphyrin dications. It was found that PDM dications exhibited opposite behaviour to their porphyrin analogues. PDM dications were more conjugated and therefore more stable than their free base counterparts. Porphyrin dications, on the other hand were less conjugated than their free base forms. Different outcomes were observed depending on the acid used. The PDM dications formed from acid halides gave absorbances that were more red shifted than those formed with the oxygen donor anions whereas the most dramatic changes in the ^1H NMR spectra occurred when the dication was formed with HClO_4 . We achieved a clear and distinct set of spectra which support the assignment of the monoprotonated PDM. This

occurrence has not been reported or proven previously. We expect this may provide insight into the role of monoprotonated species in the coordination of metal ions into the hydroporphyrin macrocycle. In the ^1H NMR investigations, similar to porphyrins, PDMs were found to coordinate the acid anions. Thus, given the anion recognition features of sapphyrin dications, it is likely that the closely related PDMs could be used as receptors for small molecules and anions.

Chapter 5

Triptycene-linked porphyrin arrays

5.1 Rigid porphyrin linkers

Synthetic multiporphyrin arrays can mimic naturally occurring tetrapyrrolic aggregates that are involved in photosynthesis, light harvesting and electron transfer. In nature, the rates of these processes are optimised by organising the active components at ideal distances and orientations, which is achieved by the use of multiple, non-covalent interactions.²⁶⁵⁻²⁶⁸ Synthetically this can be achieved using multiple covalent and/or coordination bonds which serve to dramatically increase the association constants between components and ensure a well-defined geometry for the resulting complex.²⁶⁹⁻²⁷¹

Triptycene and its derivatives possess rigid three-dimensional frameworks²⁷²⁻²⁷⁸ and thus have potential applications in host-guest complexes, molecular inclusion compounds and coordination compounds with unusual geometries.^{61,77,130,131,279-281} The 120° orientation provided by this framework constitutes a useful linker group for multichromophore assemblies.²⁸² Consequently, we became interested in using a triptycene unit as a scaffold for the construction of porphyrin arrays with applications in host-guest chemistry. Triptycene was earlier used by us for the preparation of triptycene-quinones for electron transfer studies.^{64,71}

Triptycene was first linked to a porphyrin by Wasielewski *et al.* to investigate photoinduced electron transfer reactions (Figure 5.1).^{267,277,278,283,284} The porphyrin quinones were prepared *via* mixed condensation reactions of pyrrole, 2-anthraldehyde and benzaldehyde. Further modifications with anthroquinone **120**, naphthoquinone **121** and benzoquinone **122** yielded the desired porphyrins in up to 40% yield. Introduction of a quinone moiety to the rigid triptycene linker yielded molecules with well defined donor-acceptor distances and geometries. These properties are required to promote efficient charge separation and to hinder charge recombination.^{196,274,275,285,286}

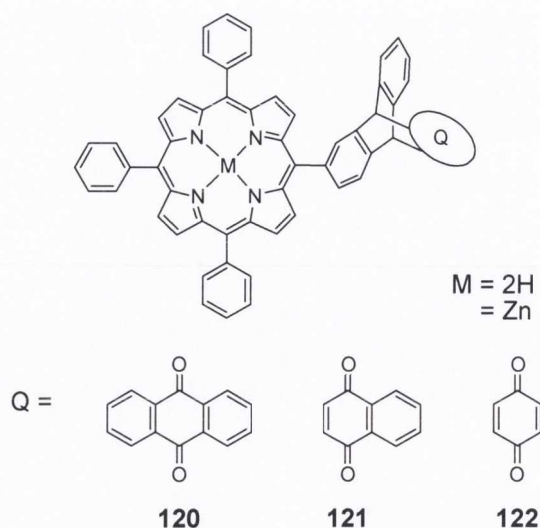


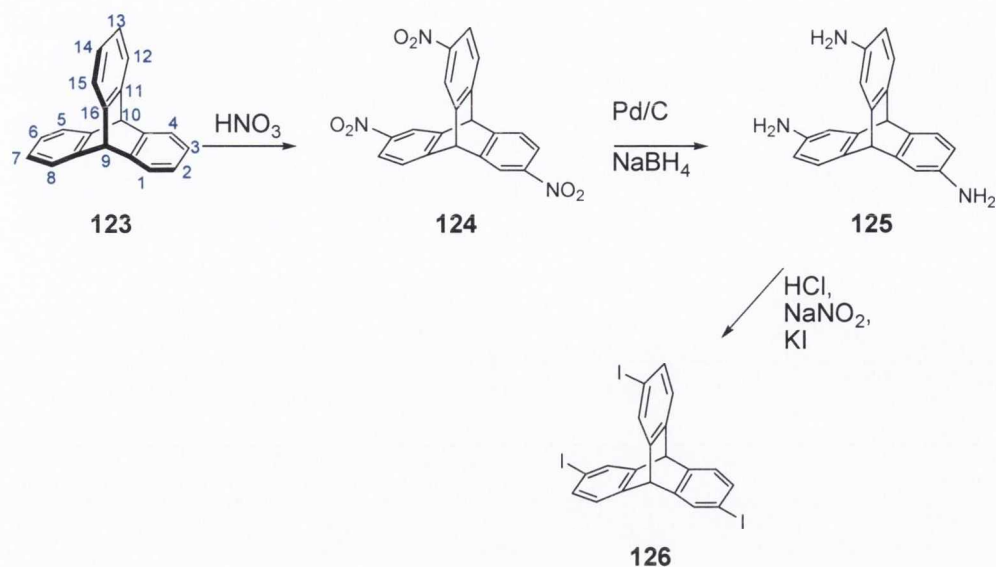
Figure 5.1. 5,10,15-Triphenylporphyrin covalently linked to quinone systems.

Three types of *meso* linked triptycenylporphyrin arrays were prepared with varying cavity sizes and were easily metalated with zinc(II). Zinc(II) porphyrins have a simple coordination chemistry and typically form 1:1 complexes with N-donor ligands.^{287,288} Thus, we also performed initial investigations into the host-guest chemistry of the zinc(II) triptycenylporphyrin arrays.

5.2 Synthetic methods

Triptycene-linked porphyrin trimers, previously synthesised within the group,²⁷² were chosen as suitable candidates for multidentate host-guest chemistry. By varying the porphyrin centre-to-centre distances, the coordination properties of the rigid trimers could be investigated.

Commercially available triptycene **123** was reacted with nitric acid under reflux according to a procedure by Zhang *et al.*²⁶⁵ A mixture of 2,6,14- **124** and 2,7,14-trinitrotriptycene was obtained, from which the former was isolated in 85% yield using column chromatography on silica gel with dichlormethane/*n*-hexane (1:1) as eluent. (Scheme 5.1). Reduction of the nitro residues to amino residues yielded 2,6,14-triaminotriptycene **125** in quantitative yield. 2,6,14-Triiodotriptycene **126** was obtained from a Sandmeyer reaction using hydrochloric acid, sodium nitrite and potassium iodide.^{280,289}

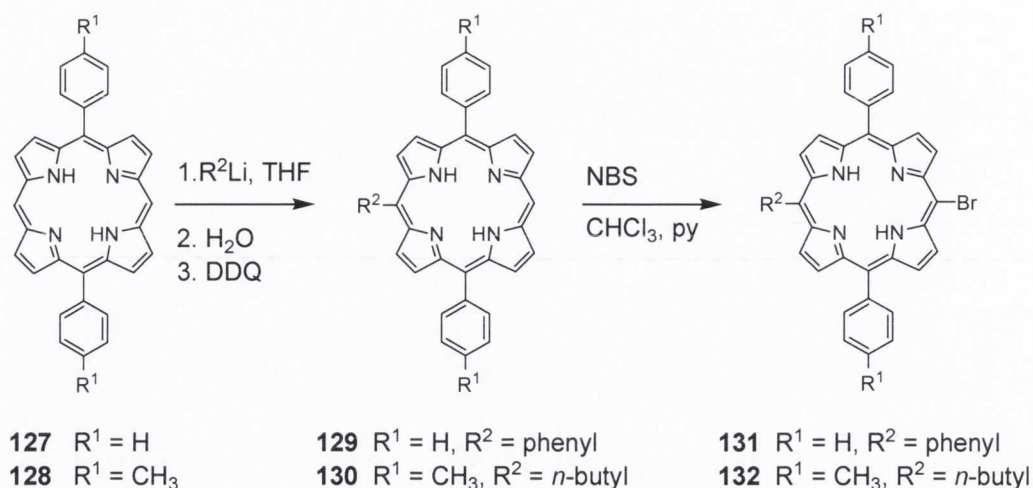


Scheme 5.1. Synthesis of 2,6,14-triodotriptycene **126** from triptycene **123**.

Introduction of a boronate or ethyne functionality onto the *meso* position of a porphyrin, allows subsequent Suzuki-Miyaura and Sonogashira coupling reactions of these derivatives. The halogen-bearing moiety **126** was thus coupled to the respective porphyrins to yield triptycene-linked porphyrin trimers. Three different porphyrin monomers were synthesised bearing a boronic ester, an ethyne and a phenylethyne functionality, respectively.

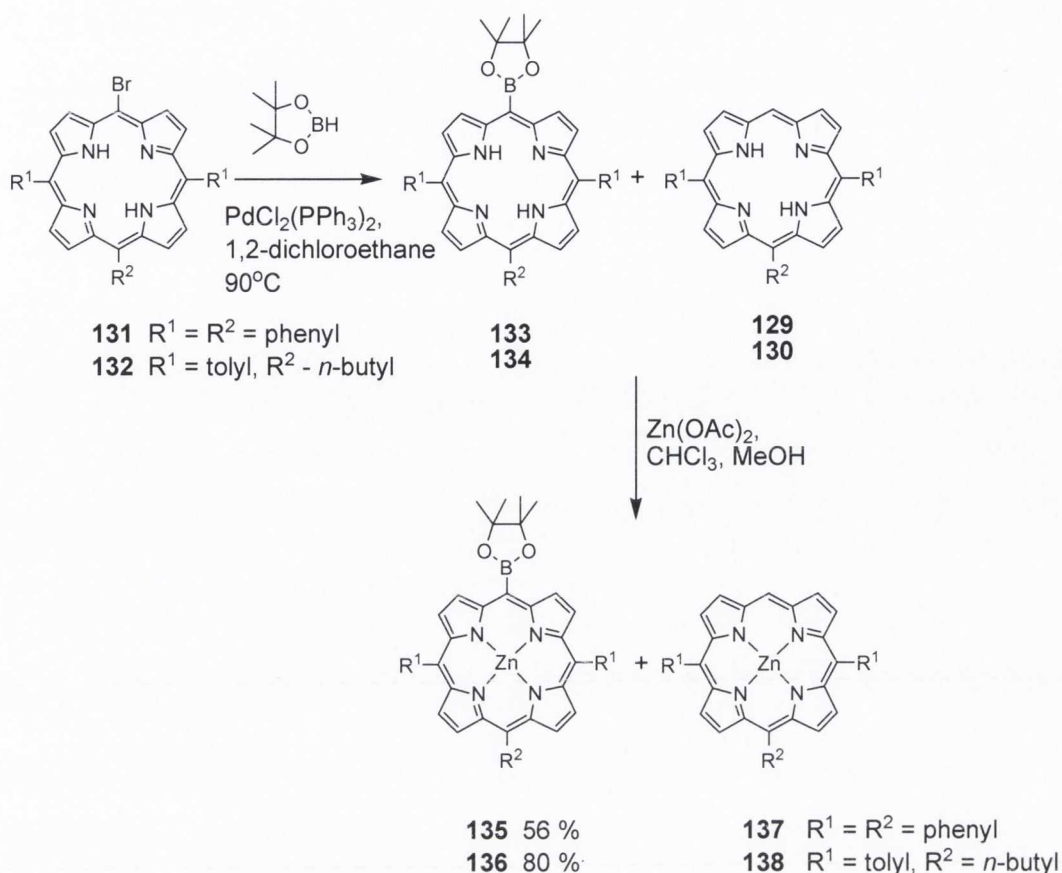
5.2.1 Suzuki-Miyaura coupling reaction

Porphyrins modified at the *meso* positions were obtained *via* condensation of pyrrole or a pyrrolic derivative with various aldehydes. A_2 -type porphyrins, **127** and **128**, with two unsubstituted *meso* positions available for further functionalisation, were synthesised from the dipyrromethane precursor following a procedure developed by Lee and Lindsey.²⁷⁹ A nucleophilic substitution reaction yielded trisubstituted porphyrins in good yields. The organic nucleophile reacted with one of the free *meso* carbons in A_2 -type porphyrins **127** and **128**. Hydrolysis with water, followed by oxidation with DDQ yielded the desired A_2B -type porphyrins **129** (77%) and **130** (77%) (Scheme 5.2). Bromination with *N*-bromosuccinimide (NBS) yielded the porphyrin precursors **131** and **132**.



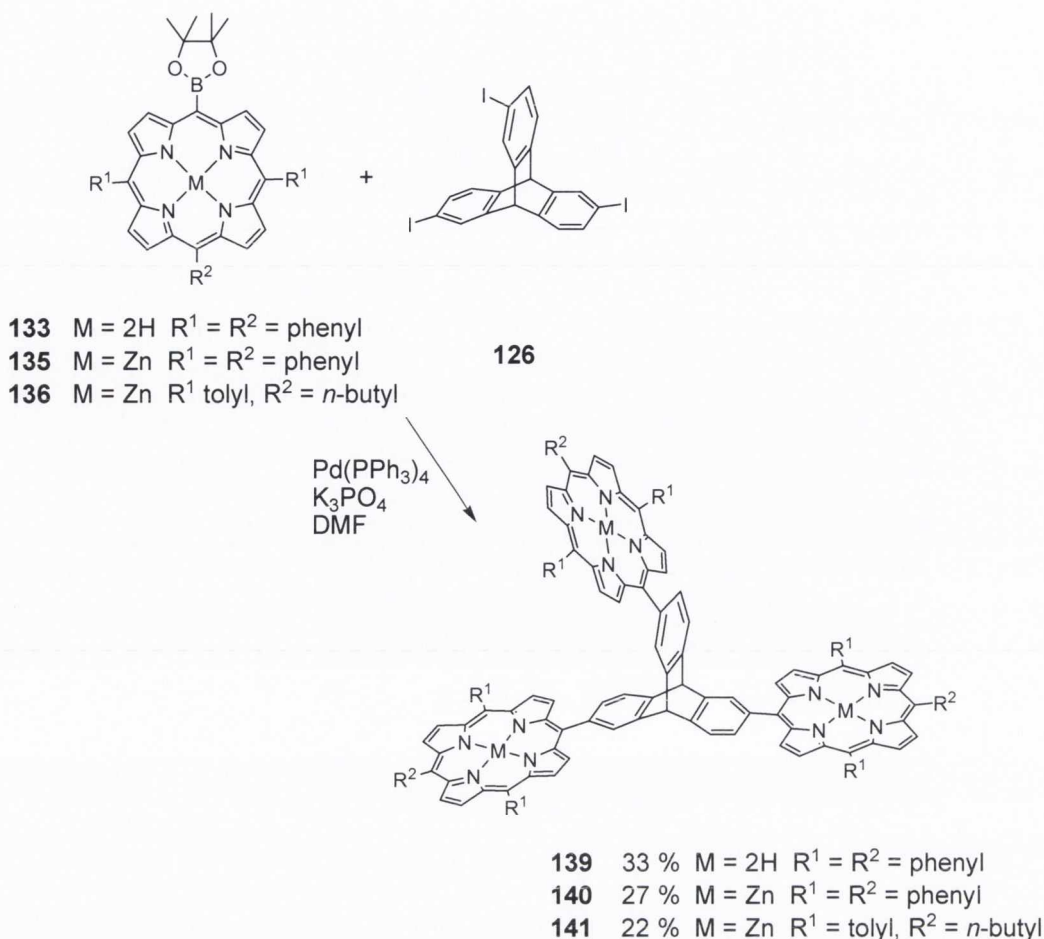
Scheme 5.2. Modification and functionalisation of A_2 -type porphyrins using organolithium reagents and NBS.

meso-Boronylation of bromoporphyrins **131** and **132** was performed according to a procedure by Therien and coworkers (Scheme 5.3).⁷⁷ The reaction of **131** and **132** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane proceeded as expected in 12 hours. Debromination of the starting material was a competing reaction, thus a 10-fold excess of pinacolborane was used to ensure a high yield of the boronate porphyrins **133** and **134** (Scheme 5.3). Metallation with zinc(II) acetate yielded **135** (56%) and **136** (80%). The boronate porphyrins, required for the Suzuki-Miyaura coupling reaction, were isolated at this point. The large difference in the retention factors of the metallated tetrapyrroles allowed the porphyrins to be separated easily by silica gel filtration.



Scheme 5.3. Boronylation and metallation of bromoporphyrins. Yields are isolated yields over two steps.

In the following step boronate porphyrins **135** and **136** were reacted with 2,6,14-triiodotriptycene **126** using conditions described by Chng *et al.* for the preparation of a dibenzofuran-linked porphyrin dimer.²⁸² The Suzuki cross-coupling reaction yielded **140** in 27% yield (Scheme 5.4). Due to the difficulty in purifying the zinc(II) trimer by column chromatography, the cross-coupling reaction was attempted with the free base monomer **133**. The yield for this reaction increased to 33% and was due to the improved separation of the free base trimer over the zinc(II) trimer, thus leading to minimal loss of product. Metallation of **139** with zinc(II) acetate yielded the desired zinc(II) trimer **140** in quantitative yield.

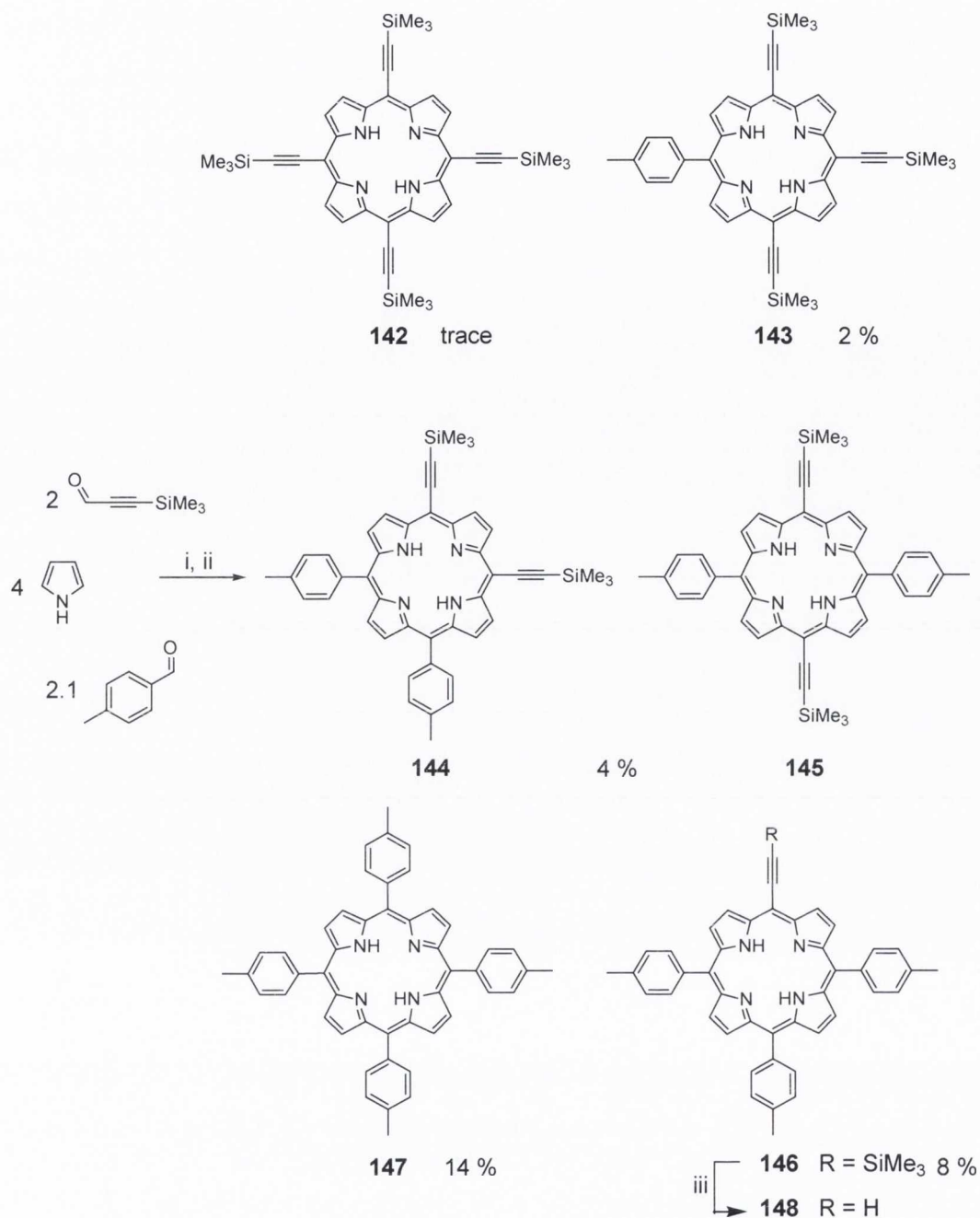


Scheme 5.4. Synthesis of triptycene-linked porphyrin trimers *via* Suzuki-Miyaura cross-coupling reactions with 2,6,14-triodotriptycene.

5.2.2 Sonogashira coupling reaction

Precursors of the Sonogashira coupling reaction^{65,290} required an ethyne moiety to react with the triiodotriptycene. The porphyrin monomer was synthesised from a mixed condensation reaction of pyrrole with two different aldehydes.

A mixed condensation reaction can be employed to synthesise differently *meso* substituted porphyrins.^{38,39,43,248} Depending on the desired substitution pattern required, different ratios of aldehyde are used. The reaction of pyrrole with two aldehydes affords a set of six porphyrins (Scheme 5.5). Mixed condensation reactions are sometimes advantageous as they replace the elaborate, multi-step syntheses seen in Scheme 5.2. However, this is replaced by an elaborate purification step. The ease of separation of the mixture depends on the differences in polarity of the two types of *meso* substituents.



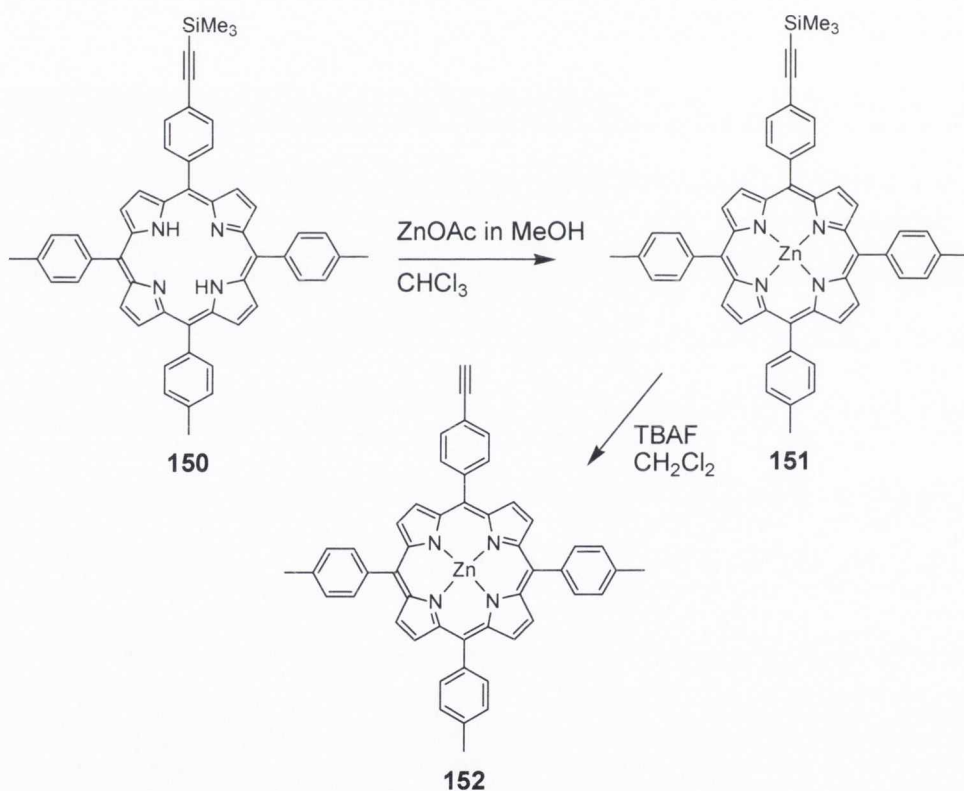
Reagents and conditions: (i) BF₃·OEt₂, CHCl₃, rt, 6 h; (ii) DDQ, rt, 1 h;
 (iii) TBAF, CH₂Cl₂, 30 min.

Scheme 5.5. Synthesis of A₃B-type porphyrin **146** via a mixed condensation reaction.

3-Trimethylsilylpro-2-pynal served as the reactive aldehyde, whereas, *p*-tolualdehyde was chosen because of its availability and enhanced solubility of the porphyrin over the phenyl derivative, thus aiding chromatography. Different ratios of pyrrole, *p*-tolualdehyde and 3-trimethylsilylpro-2-pynal were used including 4:3:1,^{23,38,39,41} 6:6:1 and 4:2.1:2.⁴² The latter gave the highest yield of the desired product. Deprotection of

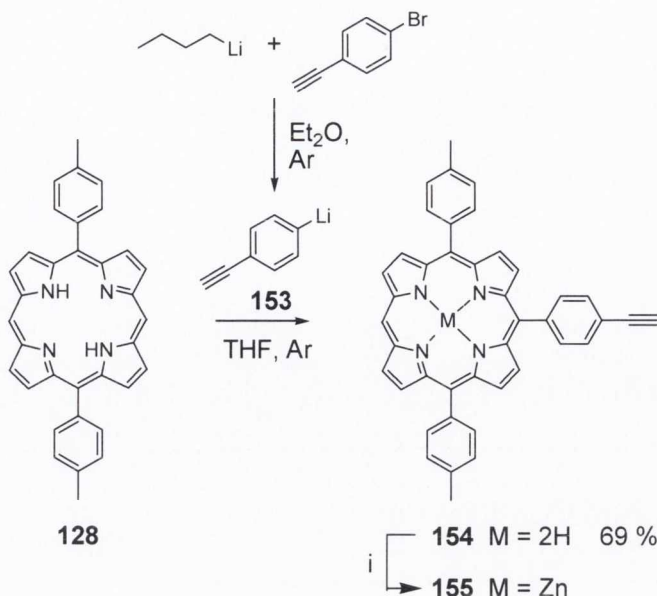
the ethyne group in **146** with tetrabutylammonium fluoride (TBAF) yielded the ethynyl-substituted porphyrin **148** in a quantitative yield (Scheme 5.5).

A mixed condensation reaction was also attempted for the synthesis of porphyrin **150** according to a procedure previously reported by Fazio *et al.*²⁹¹ Several attempts were made to isolate the desired product from the reaction mixture but were unsuccessful. The mixture was then submitted to metallation in order to obtain **151**, but purification was difficult at this stage, too (Scheme 5.6). The mixture was then subjected to a procedure to deprotect the ethynyl group in the hope of being able to isolate the desired product **152** from the reaction mixture. This was not possible either. The expected products were observable in the ^1H NMR spectra of the mixtures and the difficulties in purifying these mixtures could be due to the similar polarities of the components of the mixtures.



Scheme 5.6. Attempted isolation of **152**.

The 4-ethynylphenyl residue was introduced into **128** by a nucleophilic substitution reaction (Scheme 5.7). 1-Bromo-4-ethynylbenzene was reacted with *n*-butyllithium under inert conditions, to yield the desired organolithium reagent **153**. Addition of **128**

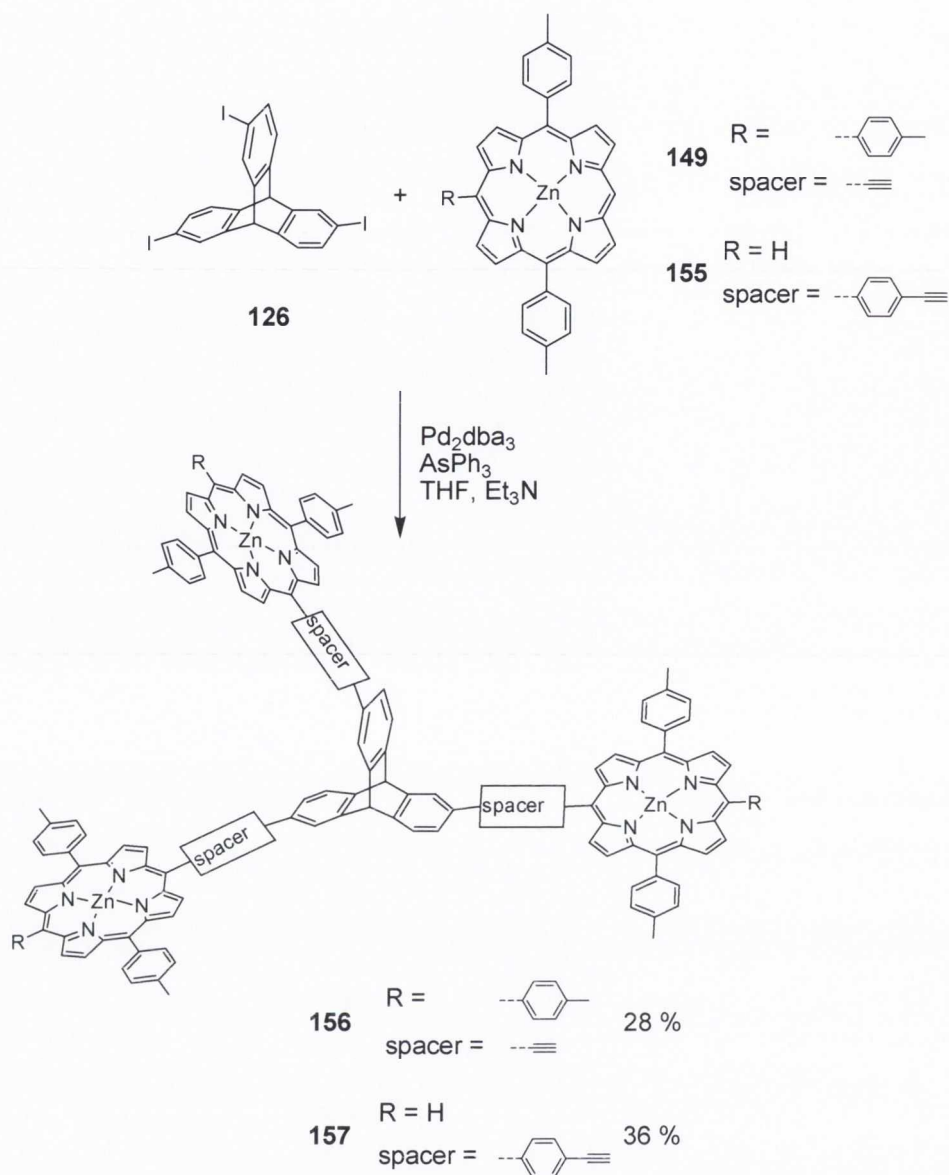


Reagents and conditions: (i) CHCl_3 , ZnOAc , py

Scheme 5.7. Synthesis of A_2B -type porphyrins *via* a nucleophilic substitution reaction.

in THF yielded **154** in 69% yield. Subsequent treatment with zinc(II) acetate yielded the desired porphyrin precursor **156**.

Sonogashira coupling reactions have commonly been used for the synthesis of multicomponent systems.²⁹² The palladium coupling conditions are reasonably attractive as they are performed in neutral to basic conditions, where demetallation does not occur. However, using copper as a co-catalyst, and under specific conditions, transmetallation can occur with the zinc(II)porphyrin. In agreement with Farina *et al.* who reported an improved rate of the Stille reaction upon addition of triphenylarsine,²⁹³ Lindsey *et al.* successfully outlined the conditions for a copper-free Sonogashira reaction involving triphenylarsine and tris(dibenzylideneacetone)di-palladium(0).²⁹⁴ Thus, under mild, nonacidic, nonmetallating conditions, zinc(II) porphyrins **149** and **155** were coupled with 2,6,14-triiodotriptycene **126** to yield the desired ethynyl- and phenylethynyl-linked porphyrin trimers **156** and **157** (Scheme 5.8).



Scheme 5.8. Sonogashira coupling reaction of 2,6,14-triodotriptycene with an ethynyl functionalised porphyrin.

5.3 Host-guest properties

In order to understand the behaviour of the trimer complexes **140**, **156** and **157**, upon ligand coordination, investigations were first carried out to determine how the bidentate ligand, 4,4'-bipyridine (bipy) coordinated to a monomeric metalloporphyrin (5,10,15,20-tetramesitylporphyrinato)zinc(II) **158**. UV-vis spectroscopy has been used to elucidate the stoichiometry of binding, binding constants and a limited amount of structural information. Previous studies showed that upon coordination of an N-donor ligand to a zinc(II) porphyrin, a bathochromic shift of about 10 nm occurred in the Soret

region indicating a 1:1 binding stoichiometry.^{295,296} In addition, ^1H NMR spectroscopy had shown that at millimolar concentrations a 2:1 porphyrin/ligand sandwich complex (Fig. 5.2b) was formed upon addition of 0.5 equiv. of a bidentate ligand.²⁹⁷ The 2:1 complex then opens up to give the 1:1 open complex (Fig. 5.2c) in the presence of excess ligand.

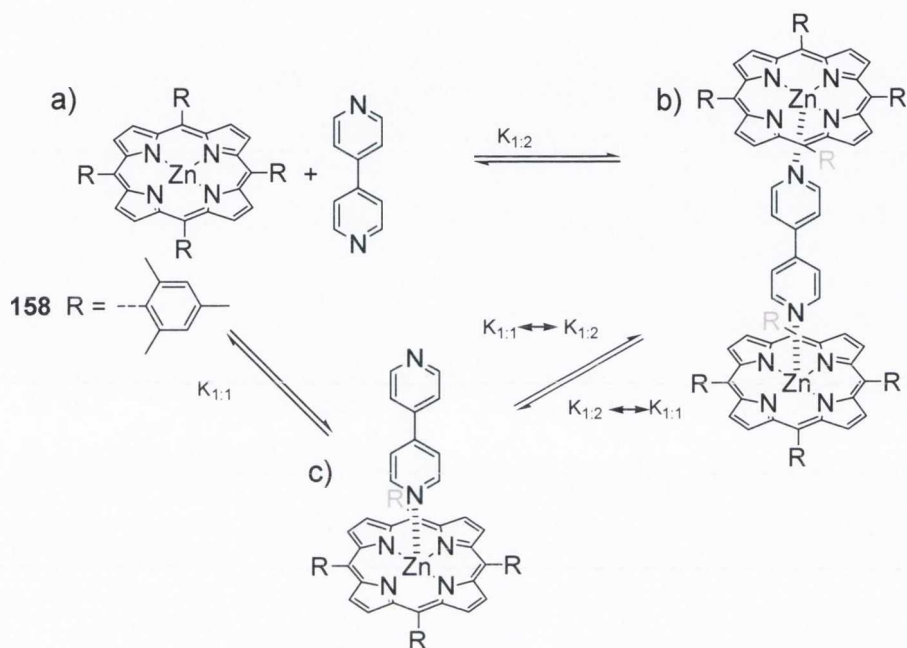


Figure 5.2. Schematic representation of the species involved in the binding equilibria of bipy to zinc(II) porphyrin.

The addition of incremental amounts of bipy to **158** ($\epsilon = 756,600 \text{ M}^{-1}\text{cm}^{-1}$) in dichloromethane resulted in a Soret band shift from 420 to 428 nm ($\Delta\lambda = 8 \text{ nm}$) with one definite isosbestic point at 424 nm, clearly indicating an equilibrium between two defined species (Fig. 5.3).²⁹⁸ The titration data were analysed using the nonlinear regression analysis program SpecfitTM which analyses the entire series of spectra simultaneously.^{299,300} The data was best fit for a 1:1 binding model and resulted in a binding constant of $\log K_{1:1} = 4.4 \pm (0.004)$, which was expected for the formation of the open complex.^{295,296} Methods for the determination of binding constants are described in the experimental chapter, Section 6.8.

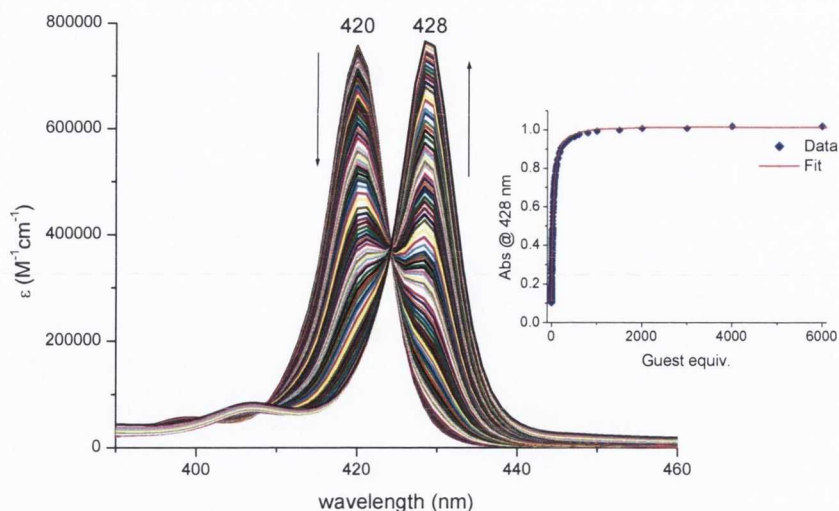


Figure 5.3. Changes in the absorption spectra (Soret band spectral region) of **158** (1.34×10^{-6} M) recorded in dichloromethane, upon addition of bipy. Insert: The changes at 428 nm with a 1:1 fit (0 to 6,000 equiv.).

UV-vis experiments were carried out on trimers **140**, **156** and **157** with mono- and bidentate ligands to determine the coordination properties of these rigid porphyrin arrays. Bidentate ligands are capable of displaying multiple binding interactions with these porphyrin trimers (Fig. 5.5). Previous UV-vis and ^1H NMR investigations on porphyrin systems have revealed that dimeric bridging ligand complexes preferentially adopt the bridged structure at low concentrations of ligand, in spite of the fact that the *exo* side is considerably more accessible than the *endo* side.^{296,301-304} In ^1H NMR spectroscopy, this phenomenon resulted in a high-field resonance at $\delta = -5$ ppm for the CH_2 protons of a 1,4-diazabicyclo[2.2.2]octane ligand (DABCO) tightly bound to two zinc(II) porphyrins, which was completely absent when monodentate ligands were used.^{295,296,305} Monomeric and dimeric binding have also been differentiated using UV-vis spectroscopy. Formation of a 1:1 dimer/ligand sandwich complex (Fig. 5.4a) was accompanied by a 5 nm red-shift, compared to a 10 nm red-shift in the 1:2 open system (Fig. 5.4b) which was observed with the addition of excess ligand.²⁹⁵

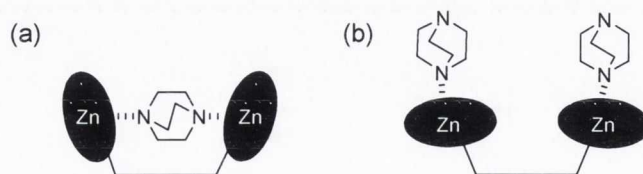


Figure 5.4. Schematic representation of a 1:1 bidentate ligand sandwich complex (a) and 2:1 open complex (b).

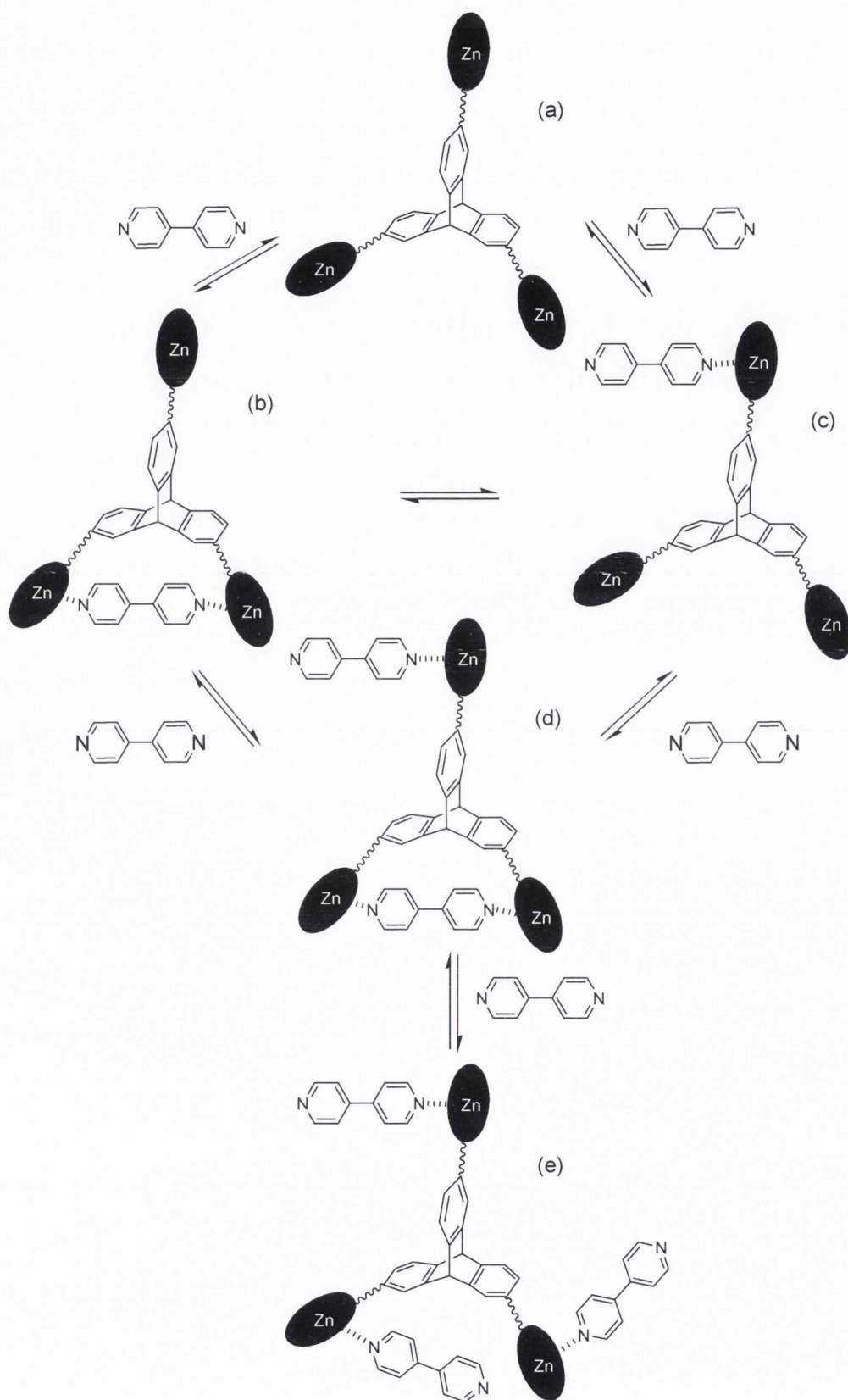


Figure 5.5. Schematic representation of the species in the equilibria of binding bipy to a triporphyrin.

Also, association constants determined from UV-vis titrations for the formation of dimeric sandwich complexes are much greater than those for the corresponding monodentate binding motifs.³⁰⁶ Unfortunately, due to time constraints, ¹H NMR titrations could not be performed, however, in-depth studies were carried out using UV-vis spectroscopy. UV-vis titrations were performed on directly-linked **140**, ethynyl-linked **156** and phenylethynyl-linked **157** porphyrin trimers.

5.3.1. Absorption titration of directly linked trimer **140** with bipy

The absorption spectrum of the directly linked trimer **140** ($\epsilon = 816,000 \text{ M}^{-1}\text{cm}^{-1}$) exhibited a λ_{max} at 424 nm with a shoulder at 417 nm. This was indicative of slight electronic interaction between the porphyrin components.³⁰⁷ Upon titration of **140** with bipy in dichloromethane, two new transitions formed at 430 ($\Delta\lambda = 6 \text{ nm}$) and 433 nm ($\Delta\lambda = 9 \text{ nm}$), with isosbestic points at 427 and 428 nm respectively (Fig. 5.6). Titration with the monomeric ligand, pyridine, resulted in a 9 nm bathochromic shift (Table 5.1), thus confirming that the final species in the **140**/bipy solution was the 1:3 open complex.

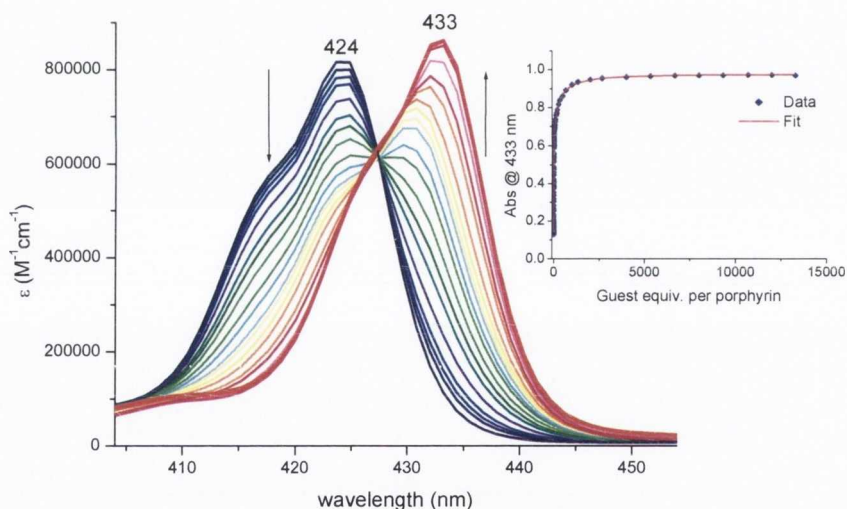


Figure 5.6. The changes in the absorption spectra (Soret region) of **140** ($8 \times 10^{-7} \text{ M}$) upon addition of bipy, recorded in dichloromethane. Insert: The changes at 433 nm fit to a five-component system.

Table 5.1. The absorption maxima and binding constants for the complexation between **140** and mono- and bidentate ligands.

	λ_{max}	$\text{Log}K_{1:1}$	$\text{Log}K_{1:2}$	$\text{Log}K_{1:3}$
140	424, 548, 587			
140 + bipy	433, 563, 602	5.3 ± 0.03	5.4 ± 0.03	3.3 ± 0.02
140 + pyr	433, 563, 602	4.8 ± 0.18	4.1 ± 0.22	3.4 ± 0.23

The changes in the spectra were best fit to a five-component system (host, guest, and 1:1, 1:2 and 1:3 host/guest) using SpecfitTM and are shown as an insert in Figure 5.6. In the case of the current trimer **140**, it seemed unlikely that the zinc(II) metal would remain four-coordinate in the presence of excess bipy so we proposed that the 6 nm red shift was due to the formation of a 1:2 trimer/ligand complex where one bidentate ligand formed a sandwich, and the other, an open complex (i.e. monodenate binding) as shown in Figure 5.5d. The overall shift of 10 nm was assigned to the 1:3 trimer/ligand open complex (Fig 5.6e). The binding constants for this fit were $\log K_{1:1} = 5.28 (\pm 0.03)$, $\log K_{1:2} = 5.45 (\pm 0.03)$ and $\log K_{1:3} = 3.25 (\pm 0.02)$. The binding constants for the 1:1 and 1:2 species were of similar magnitude and indicated the formation of the more stable sandwich complexes.

The species distribution plot for the five-component system (Fig. 5.7) showed the simultaneous formation of the 1:1 and 1:2 trimer/ligand species at low concentrations of bipy. We were unable to unambiguously classify the two species. However, given the close proximity of the metal coordination sites in **140** compared to those in **156** and **157**, we assumed that the higher binding constant for the formation of the 1:2 trimer/ligand species was as a result of a structural influence.

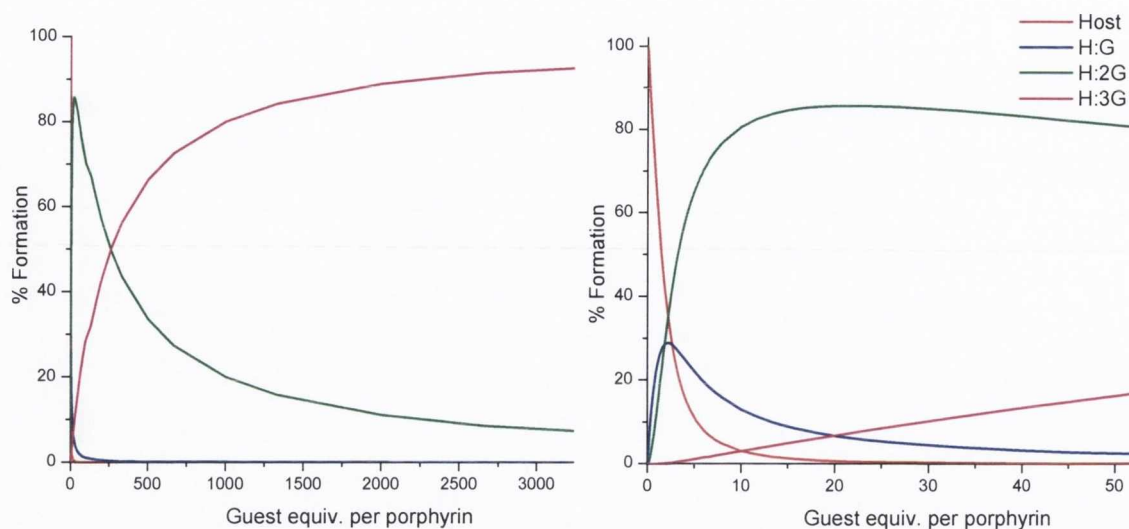


Figure 5.7. The species distribution plot of **140** (8×10^{-7} M) upon the addition of bipy recorded in dichloromethane 0 to 3,000 equiv. (left) and 0 to 50 equiv. (right).

5.3.2. Absorption titration of ethyne-linked porphyrin trimer **156** with bipy

The spectra for compound **156** ($\epsilon = 996,400 \text{ M}^{-1}\text{cm}^{-1}$) exhibited a λ_{max} at 443 nm. Upon titration with bipy, a new transition at 449 nm ($\Delta\lambda = 6 \text{ nm}$) developed and an isosbestic point at 444 nm (Fig. 5.8) could be identified. The changes in the spectra with increasing concentrations of bipy were best described by a five-component system (host, guest, 1:1 host/guest and 1:2 host/guest) after fitting using SpecfitTM, the fit of which is shown as an insert in Figure 5.8.

Upon the formation of a 1:1 complex monomer **158** exhibited an 8 nm red shift (Section 5.3). In the case of dimeric ligands, the formation of a 1:1 open complex was accompanied by a 10 nm red shift, whereas the formation of a sandwich complex resulted in a 5 nm red shift.^{296,297,301,302,304} However, titration with pyridine also resulted in an overall bathochromic shift of 6 nm (Table 5.2).

Table 5.2. The absorption maxima and binding constants for the complexation between **156** and mono- and bidentate ligands.

	λ_{max}	$\text{Log}K_{1:1}$	$\text{Log}K_{1:2}$	$\text{Log}K_{1:3}$
156	443, 567, 614			
156 + bipy	449, 582, 635	6.18 ± 0.01	5.14 ± 0.09	3.79 ± 0.09
156 + pyr	449, 581, 636	4.62 ± 0.18	3.95 ± 0.17	3.43 ± 0.14

The changes in the spectra were therefore attributed to a five component system (Host, guest and 1:1, 1:2 and 1:3 host/guest complexes). The binding isotherm is shown as an insert in Figure 5.8. Again, the binding constants for the formation of the 1:1 and 1:2 **156**/bipy complexes were considerably higher than for the formation of the **156**/pyr complexes, and indicated the formation of sandwich-type complexes with the bidentate ligand.

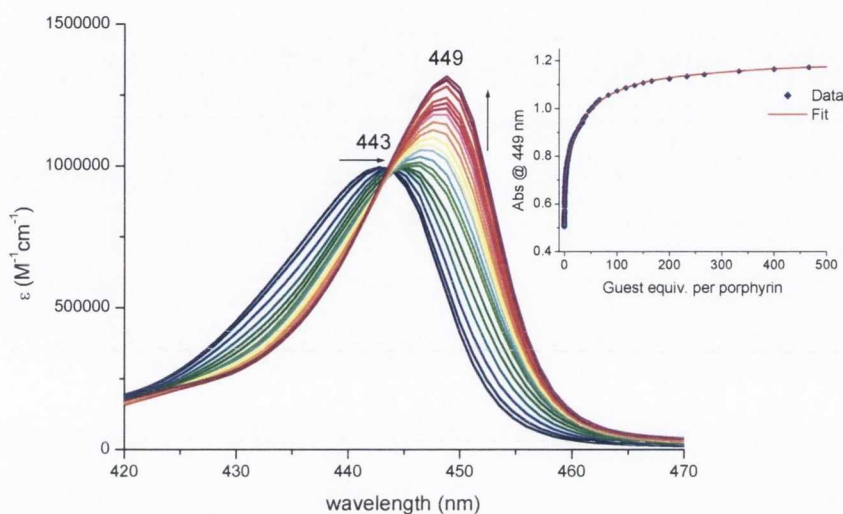


Figure 5.8. UV-vis titration (Soret region) of **156** ($9.2 \times 10^{-7}\text{M}$) with bipy recorded in dichloromethane (0 to 70,000 equiv.). Insert: The changes at 449 nm with a 1:2 trimer/ligand fit (0 to 500 equiv.).

The species distribution diagram in Figure 5.9 obtained from the fit showed that the 1:1 complex reached 62% formation at only 1 equivalent of ligand per porphyrin. The 1:2 complex became the main species in solution after the addition of 3 equiv. of ligand, whereas the 1:3 species was predominant in solution after the addition of almost 60 equiv. of bidentate ligand.

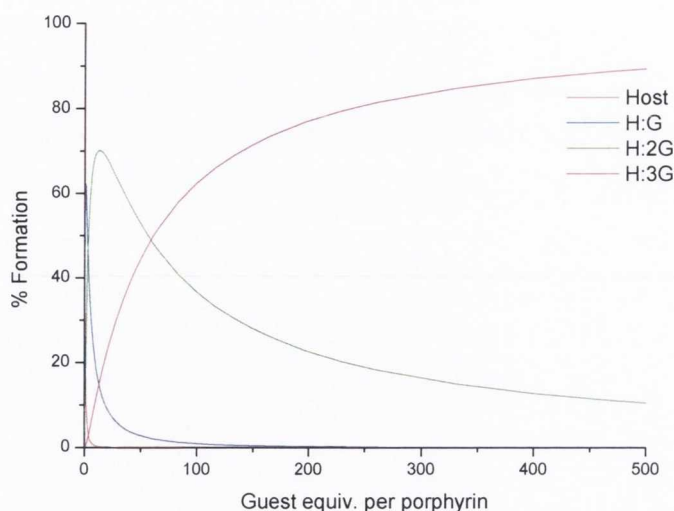


Figure 5.9. The species distribution diagram of **156** ($9.22 \times 10^{-7} \text{M}$) upon the addition of bipy (0 to 500 equiv.) recorded in dichloromethane.

5.3.3. Absorption titration of phenylethynyl-linked trimer **157** with bipy

In the case of the phenyl acetylene linked porphyrin trimer **157** ($\epsilon = 958,100 \text{ M}^{-1}\text{cm}^{-1}$), the addition of bipy resulted in a decrease in the absorption at 415 nm while a new band appeared at 422 nm ($\Delta\lambda = 6 \text{ nm}$), with an isosbestic point at 419 nm (Fig. 5.10). With the addition of further equivalents of bipy, a second isosbestic point could be identified at 421 nm, and a final absorption with a λ_{max} at 425 ($\Delta\lambda = 10 \text{ nm}$) resulted. This was comparable to UV-vis investigations carried out with pyridine, where a new absorption at 425 nm ($\Delta\lambda = 10 \text{ nm}$) was observed with a single isosbestic point at 420 nm. This confirmed the final species in the trimer/bipy solution to be the 1:3 open complex. Using SpecfitTM the changes in the absorption spectra upon titration with bipy were assigned to a five-component system (host; guest; and 1:1; 1:2 and 1:3 trimer/ligand complexes). The binding isotherm is shown as an insert in Figure 5.10.

The binding constants obtained for this fit were $\log K_{1:1} = 5.11 (\pm 0.01)$, $\log K_{1:2} = 3.69 (\pm 0.07)$ and $\log K_{1:3} = 3.88 (\pm 0.07)$. The 6 nm red shift, also seen in trimer **140**, was attributed to the formation of a 1:2 trimer/ligand complex (Fig. 5.5d), whereas the overall red shift of 10 nm relative to the original trimer absorption was consistent with the formation of the 1:3 open complex (Fig. 5.5e).

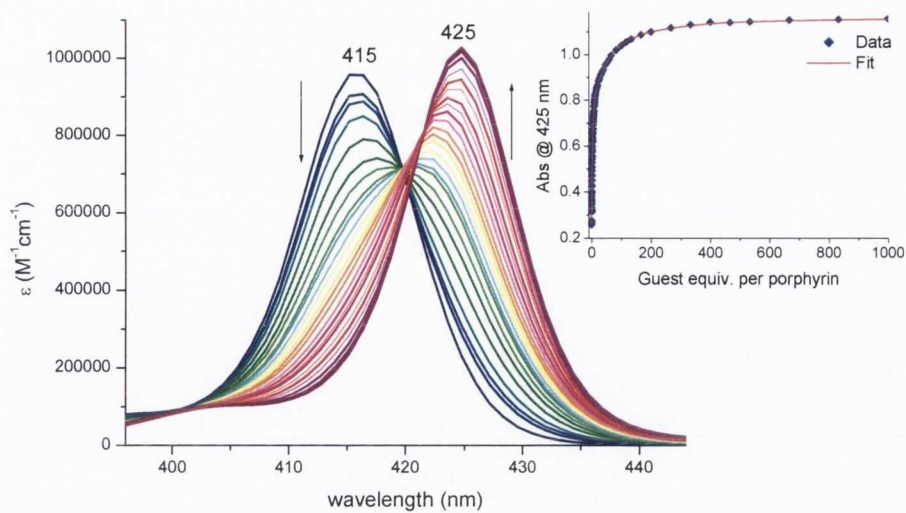


Figure 5.10. UV-vis titration spectra (Soret region) of **157** (1.13×10^{-6} M) with bipy recorded in dichloromethane (from 0 to 5,000 equiv.). Insert: The binding isotherm with 1:3 trimer/ligand fit, which was determined using Specfit™, at 425 nm (0 to 1,000 equiv.).

The binding constants obtained for this fit are shown in Table 5.3. The binding constant for the formation of the 1:1 complex was greater than the latter two, indicating the formation of the more stable sandwich complex. The lower 1:2 and 1:3 constants, indicated the formation of open complexes.

Table 5.3. The absorption maxima and binding constants for the complexation between **157** and mono- and bidentate ligands.

	λ_{max}	$\text{Log}K_{1:1}$	$\text{Log}K_{1:2}$	$\text{Log}K_{1:3}$
157	415, 542, 578			
157 + bipy	425, 557, 595	5.1 ± 0.01	3.7 ± 0.07	3.9 ± 0.07
157 + pyr	425, 556, 596	3.5 ± 0.08	3.3 ± 0.17	3.5 ± 0.09

The speciation diagram in Figure. 5.11 depicted 69% formation of the 1:1 ligand/trimer complex at 11 equivalents of bipy per porphyrin. The 1:2 and 1:3 trimer/ligand species formed simultaneously, with the former reaching its maximum concentration at 53 equiv. of guest. Both species had similar binding constants and were consistent with external complexation.³⁰⁶

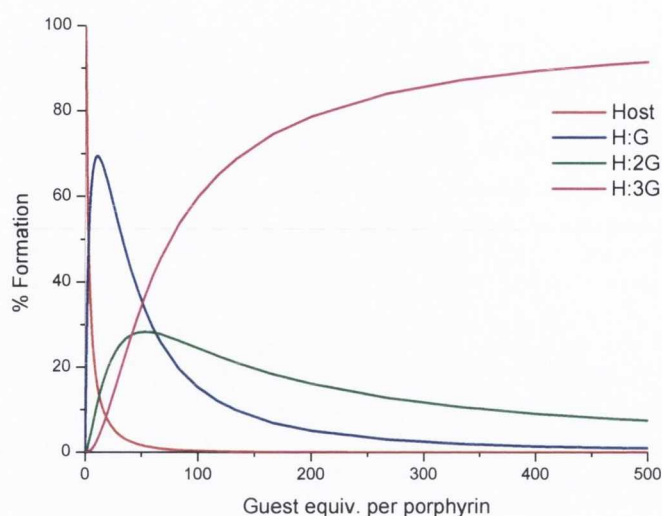


Figure 5.11. The species distribution plot of **157** (1.13×10^{-6} M) upon addition of bipy recorded in dichloromethane.

5.3.4 Comparison

Plotting the variation of the absorbance versus the number of added equiv. of bipy per porphyrin revealed that complexation occurred at lower concentrations of bipy for the trimers than for the reference monomer **158** (Figure 5.12).

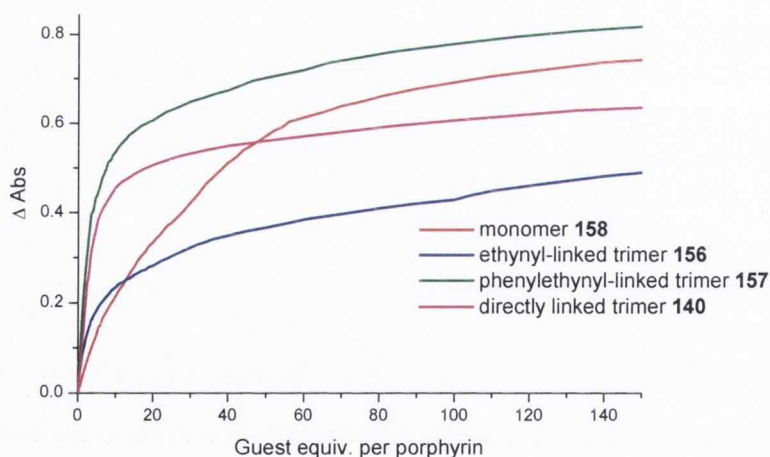


Figure 5.12. Plot of the variation of absorption versus the equiv. of bipy added per porphyrin.

5.4 Conclusions

2,6,14-Trisubstituted triptycenylporphyrins were synthesised in yields up to 36% *via* both Suzuki and Sonogashira coupling reactions. The porphyrin precursors were

prepared by nucleophilic addition reactions of A₂-type porphyrins or mixed condensation reactions. The best ratio for the formation A₃B-type porphyrins from the mixed condensation reaction was 4:2.1:2 pyrrole/reactive aldehyde/aldehyde. The systems investigated provide a proof of concept for the construction of larger porphyrin arrays based on a rigid triptycene core.

Preliminary studies were performed to investigate the host/guest properties of the triptycene-linked porphyrin trimers. Complexation experiments with the trimers and bidentate 4,4'-bipyridine were performed and binding constants were determined using SpecfitTM. Pyridine, a monodentate ligand, was used for a comparative study. In each array, the binding constants for the formation of the 1:1 complex were greater by an order of magnitude with 4,4'-bipyridine compared with pyridine. This was consistent with intramolecular sandwich-type complexation. Larger binding constants were also obtained for the formation of the 1:2 trimer/ligand complexes of **140** and **156** with bipy, whereas **157**, displayed a comparable value for both bipy and pyr.

An intermediate species was detected for compounds **140** and **157** and was 6 nm red shifted from the uncoordinated porphyrin array. This was assigned to the 1:2 trimer/ligand complex which displayed both sandwich and open binding interactions. At higher concentration of bipy, overall red-shifts of 9/10 nm were observed. These shifts were comparable to results obtained with pyridine and were consistent with the formation of a 1:3 trimer/ligand open complex. Compound **156** displayed different behaviour: An intermediate species, with a clear set of isosbestic points could not be detected and a red-shift of 6 nm was observed in the presence of excess ligand. A comparison with pyridine confirmed that the final species was in fact the 1:3 open complex.

These types of trimers have not been investigated previously. They are not fully symmetric with the result that both sandwich and open complexation was observed simultaneously in titrations with bipy. Previous investigations into the coordination chemistry of multiporphyrin arrays focused either on fully symmetric systems, whereby sandwich and/or open complexes were observed sequentially,^{296,297,301,308} or on dendrimer-type systems whereby the intermediate complexes could not be decisively classified.³⁰⁹

Chapter 6

Experimental

6.1 Instrumentation and General Considerations

All chemicals were of analytical grade and were purchased from Aldrich Co. unless otherwise stated. Dichloromethane was dried over phosphorus pentoxide followed by distillation and tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon. All condensation reactions were performed under an argon atmosphere with the reaction flask shielded from ambient light. Reactions with organolithium reagents were carried out using standard Schlenk techniques and glassware under an atmosphere of argon. NMR spectra were recorded on Bruker DPX 400 (400.13 MHz for ^1H NMR, 100.61 MHz for ^{13}C NMR) and/or Bruker AV 600 (600.13 MHz for ^1H NMR, 150.90 MHz for ^{13}C NMR). Chemical shifts recorded in ppm refer to tetramethylsilane (TMS) set at 0.00 ppm. Data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: double doublet, t: triplet, q: quartet, br: broad, m: multiplet), coupling constants (J in Hz), integration and assignment. High resolution mass spectrometry was carried out on a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with electrospray source. UV-vis measurements were performed on Shimadzu multiSpec-1505 using dichloromethane as solvent. Melting points were acquired on Stuart SMP10 melting point apparatus and were uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60F₂₅₄ (Merck) precoated aluminum sheets. Chromatography on silica gel was carried out using a forced flow of the indicated solvent system on Fluka Silica Gel 60 (230-400 mesh).

Crystal structure determination: Growth and handling of crystals followed the concept developed by Hope.³¹⁰ Intensity data were collected at 108 K with a Saturn724 system complete with 3-circle goniometer and CCD detector utilizing Mo-K α radiation ($\lambda = 0.71073$ Å). The intensities were corrected for Lorentz, polarization and extinction effects. The structure was solved with Direct Methods using the SHELXTL PLUS program system³¹¹ and refined against $|F_2|$ with the program XL from SHELX-97 using all data.³¹² Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally placed into geometrically calculated positions and refined using a riding model. The N-H hydrogen atoms were located in difference maps and refined using the standard riding model. Some of the phenyl groups showed high thermal librational movement. Refinement with split positions did not improve the refinement model.

6.2 Starting materials

Dipyrromethane,^{313,314} 5,15-bis(1-ethylpropyl)porphyrin,⁴⁶ 5,15-dihexylporphyrin,⁴⁶ 5,15-diphenylporphyrin,³¹⁵ 5,15-ditolylporphyrin,³¹⁵ 5,10,15-trihexylporphyrin²¹⁶ and 15,10,15-triphenylporphyrin^{172,174} were prepared, metallated²¹ and brominated⁵⁷ according to literature procedures.

General procedure for the synthesis of 5,10,15,20-tetra-substituted porphyrins

5,10,15,20-tetrakis(1-ethylpropyl)-porphyrin **72**, 5,10,15,20-tetra(isobutyl)porphyrin **73**, 5,10,15,20-tetraphenylporphyrin **58**, 5,10,15,20-tetrakis(3-methoxy)phenylporphyrin **74** and 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin **75** were prepared according to a procedure by Lindsey *et al.*²⁵ Pyrrole (10.5 mL, 0.15 mol) and the appropriate aldehyde (0.15 mol) were dissolved in dry dichloromethane (1.8 mL) in a three-neck 2 L round bottom flask equipped with a gas inlet (argon). The flask was shielded from ambient light before trifluoroacetic acid (1.7 mL, 15 mmol) was added. The reaction mixture was stirred for 12 h at rt, after which, DDQ (38.2 g, 0.165 mol in dichloromethane) was added. The reaction mixture was stirred for a further hour before the addition of triethylamine (3 mL). The crude porphyrin mixture was filtered through a layer of silica gel using dichloromethane as eluent. Recrystallisation from dichloromethane/methanol yielded the desired porphyrins.

72: Prepared according to the above procedure using 2-ethylbutyraldehyde (18.5 mL, 0.15 mol) to yield **72**; 4.04 g, 18.2%; $R_f = 0.54$ (SiO₂ ethyl acetate/*n*-hexane 1:6, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta = -2.25$ (s, 2H, NH), 1.00 (t, ³*J* = 7.4 Hz, 24H, CHCH₂CH₃), 2.73-2.97 (m, 16H, CHCH₂CH₃), 4.89 (m, 4H, CHCH₂CH₃), 9.54 (s, 8H, β H) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 420 (5.27), 522 (4.14), 655 (4.17) nm. The analytical data were in agreement with the literature.¹⁸⁴

73: Prepared according to the above procedure using 3-methylbutyraldehyde (16.1 mL, 0.15 mol) to yield **73**; 3.2 g, 11.9%; $R_f = 0.57$ (SiO₂ dichloromethane/*n*-hexane 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta = -2.65$ (s, 2H, NH), 1.21 (d, ³*J* = 6.4 Hz, 24H, CH₃), 2.78 (sept, ³*J* = 7.0 Hz, 4H, CH), 4.87 (d, ³*J* = 7.6 Hz, 8H, CH₂), 9.50 (s, 8H, β H) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 418 (5.56), 521 (4.42), 555 (4.35), 655 (4.47) nm. The analytical data were in agreement with the literature.¹⁸⁴

58: Prepared according to the above procedure using benzaldehyde (15.2 mL, 0.15 mol to yield **58**; 8.06 g, 35%; $R_f = 0.71$ (SiO₂ ethyl acetate/*n*-hexane 1:6, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta = -2.70$ (s, 2H, NH), 7.81 (d, ³ $J = 7.0$ Hz, 12H, Ar-H), 8.28 (d, ³ $J = 7.4$ Hz, 8H, Ar-H), 8.92 (s, 8H, β H) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 417 (5.7), 515 (4.3), 550 (4.0), 593 (3.8), 646 (3.7) nm. The analytical data were in agreement with the literature.²⁵

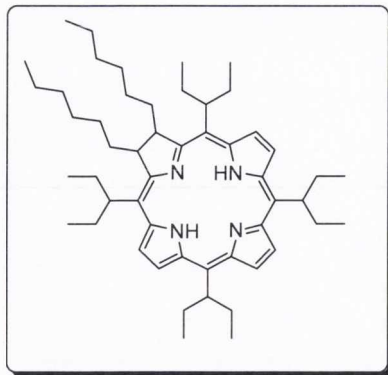
74: Prepared according to the above procedure using *m*-anisaldehyde (18.3 mL, 0.15 mol to yield **74**; $R_f = 0.53$ (SiO₂ ethyl acetate/*n*-hexane 1:4, v/v); 5.84 g, 21%; ¹H NMR (400 MHz, CDCl₃): $\delta = -2.78$ (s, 2H, NH), 4.01 (s, 12H, OCH₃), 7.36 (d, ³ $J = 8.0$ Hz, 4H, Ar-H), 7.67 (t, ³ $J = 7.6$ Hz, 4H, Ar-H), 7.83 (m, 8H, Ar-H), 8.91 (s, 8H, β H) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 419 (5.06), 515 (3.98) nm. The analytical data were in agreement with the literature.²⁵

75: Prepared according to the above procedure using *p*-anisaldehyde (18.3 mL, 0.15 mol to yield **75**; 2.98 g, 11%; $R_f = 0.53$ (SiO₂ ethyl acetate/*n*-hexane 1:4, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta = -2.79$ (s, 2H, NH), 4.13 (s, 12H, OCH₃), 7.35 (d, ³ $J = 8.6$ Hz, Ar-H), 8.17 (d, ³ $J = 8.4$ Hz, Ar-H), 8.92 (s, 8H, β H) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 421 (5.6), 518 (4.1), 556 (3.9), 591 (3.5), 650 (3.6) nm. The analytical data were in agreement with the literature.²⁵

6.3 Hydroporphyrins

General procedure for the reaction of *meso* tetrasubstituted porphyrins with organolithium reagents.

A 100 mL Schlenk flask was charged with porphyrin (1 equiv.), a palladium-based catalyst (0.1 equiv.), and copper iodide (0.15 equiv.) in dry THF (40 mL) under an argon atmosphere. The reaction mixture was cooled to -80 °C for the addition of *n*-hexyl-, *tert*-butyl- and *sec*-butyllithium, or 0 °C for the addition of phenyllithium. Organolithium reagents were added dropwise *via* syringe over 10 min upon which, a colour change to green was observed. After removal of the cold bath, the solution was allowed to stir for 4 h (TLC control). A colour change to green/brown was observed. Aqueous NH₄Cl (1 mL) was added to quench the reaction. After stirring for 10 min, the reaction mixture was filtered through silica gel. The crude porphyrin mixture was dried *in vacuo* and subjected to either column chromatography or preparative TLC.

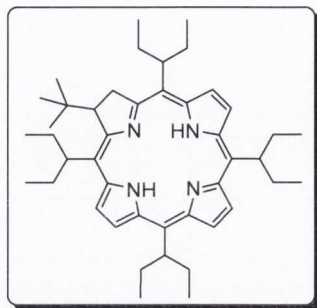
5,10,15,20-tetrakis(1-ethylpropyl)-2,3-di(hexyl)chlorin 77

Following the above procedure, H_2TEPP **72** (100 mg, 0.17 mmol), tetrakis(triphenylphosphine)palladium(0) (19.6 mg, 0.017 mmol), copper iodide (4.8 mg, 0.025 mmol) and hexyllithium (0.74 mL of a 2.3 M solution in hexane, 1.7 mmol) were reacted and subjected to column chromatography on silica gel using ethyl acetate/*n*-hexane (1:20, v/v) as eluent. The second fraction gave the title compound as a purple solid (18.1 mg, 14%); mp 190 °C; R_f = 0.34 (SiO_2 , ethyl acetate/*n*-hexane 1:20, v/v); ^1H NMR (400 MHz, CDCl_3): δ = -0.21 (s, 2H, NH), 0.57 (t, 3J = 7.32 Hz, 6H, CHCH_2CH_3), 1.33 (m, 6H, Hex- CH_3), 1.55 (t, 6H, J = 7.4 Hz, CHCH_2CH_3), 1.71 (m, 10 H, Hex- CH_2), 2.05-2.35 (m, 8 H, CHCH_2CH_3), 2.37-2.78 (m, 10H, Hex- CH_2), 2.83-3.07 (m, 8H, CHCH_2CH_3), 3.69 (quin, 3J = 7.4 Hz, 2H, CHCH_2CH_3), 4.51, (d, 3J = 10.2 Hz, 2H, βH), 4.56 (b, 2H, CHCH_2CH_3), 8.93 (d, 3J = 4.9 Hz, 2H, βH), 9.13 (s, 2H, βH), 9.19 (b, 2H, βH) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): δ = 13.3 (Hex- CH_3), 22.2 (CH_2), 27.5 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.3 (CH_2), 30.9 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 32.2 (CH_2), 32.5 (CH_2), 47.3 (CH), 49.7 (CH), 51.4 (βH), 111.5 (qC), 121.4 ($\beta\text{-CH}$), 125.0 ($\beta\text{-CH}$), 129.1 ($\beta\text{-CH}$), 166.2 (qC) ppm; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ) = 422 (4.08), 536 (3.08), 564 (3.11), 660 (3.20) nm; HRMS (ES^+) [$\text{C}_{52}\text{H}_{80}\text{N}_4+\text{H}$] calcd. 761.6461, found 761.6432.

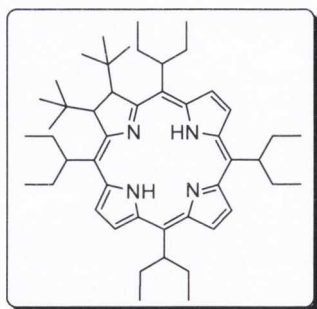
2-*tert*-Butyl-5,10,15,20-tetrakis(1-ethylpropyl)porphyrin 78 and 2,3-di(*tert*-butyl)-5,10,15,20-tetrakis(1-ethylpropyl)porphyrin 79

Following the above procedure, H_2TEPP **72** (100 mg, 0.17 mmol), tris(dibenzylideneacetone)dipalladium(0) (17.5 mg, 0.017 mmol), copper iodide (4.8 mg, 0.025 mmol) and *t*-butyllithium (1.0 mL of a 1.7 M solution in pentane, 1.7 mmol) were reacted and subjected to column chromatography on silica gel using methanol/*n*-hexane (1:40, v/v) as eluent. The second fraction gave **79** as a purple solid (24.7 mg, 21%). The

final fraction contained a mixture of two compounds which were further purified by preparative TLC on silica gel using dichloromethane/*n*-hexane (1:1, v/v). Fraction one contained unreacted starting material **72** (30 mg, 30%), fraction two contained **78** (11.1 mg, 10%).



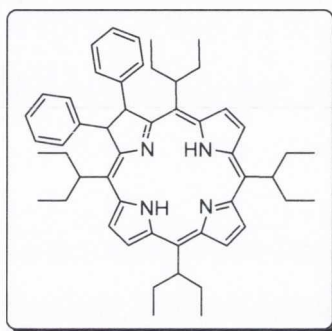
78: mp 199 °C; R_f = 0.22 (SiO₂, *n*-hexane/methanol 80:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = -0.09 (br, 2H, NH), 0.39 (s, 9H, *t*BuCH₃), 1.21 (t, ³*J* = 7.3 Hz, 6H, CHCH₂CH₃), 1.28 (m, 14H, CHCH₂CH₃, CHCH₂CH₃), 1.43 (t, ³*J* = 7.4 Hz, 6H, CHCH₂CH₃), 1.91 (m, 2H, CHCH₂CH₃), 2.75 (m, 12H, CHCH₂CH₃), 3.67 (s, 1H, CHCH₂CH₃), 3.89 (s, 1H, CHCH₂CH₃), 4.37 (d, ³*J* = 7.7 Hz, 1H, β H), 4.53 (m, 3H, CHCH₂CH₃, β H), 4.68 (d, ³*J* = 7.4 Hz, 1H, β H), 8.80 (m, 2H, β H), 9.08 (m, 4H, β H) ppm ¹³C NMR (150.9 MHz, CDCl₃): δ = 13.1 (CH₃), 13.5 (CH₃), 13.8 (CH₃), 14.1 (CH₃), 26.8 (CH₃), 29.3 (CH₂), 30.1 (CH₂), 30.4 (CH₂), 32.5 (CH₂), 33.1 (CH₂), 35.3 (qC), 40.9 (β -C), 47.5 (CH), 48.4 (CH), 49.4 (CH), 49.8 (CH), 54.0 (β -C), 108.9 (qC), 114.5 (qC), 120.4 (β -C), 122.2 (β -C), 123.6 (β -C), 125.9 (β -C), 128.6 (β -C), 133.2 (qC), 138.5 (qC), 162.8 (qC) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) 424 (4.0), 538 (3.0), 662 (3.1) nm; HRMS (ES⁺) [C₄₄H₆₄N₄+H] calcd. 649.5209, found 649.5217.



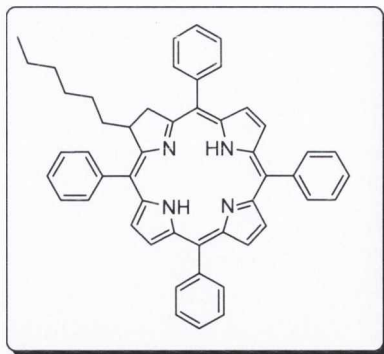
79: mp 248 °C; R_f = 0.45 (SiO₂, *n*-hexane/methanol 80:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 0.21 (s, 2H, NH), 0.85 (s, 18H, *t*Bu-CH₃), 1.10 (t, ³*J* = 7.3 Hz, 15H,

CHCH₂CH₃), 1.47 (b, 4H, CHCH₂CH₃), 1.74 (t, ³J = 4.9 Hz, 9H, CHCH₂CH₃), 2.37 (m, 4H, CHCH₂CH₃), 2.90 (m, 4H, CHCH₂CH₃), 3.28 (m, 2H, CHCH₂CH₃), 3.83 (b, 2H, CHCH₂CH₃), 4.48 (b, 2H, CHCH₂CH₃), 4.69 (s, 2H, βH), 8.77 (d, ³J = 4.9 Hz, 2H, βH), 9.07 (s, 2H, βH), 9.12 (d, ³J = 4.6 Hz, 2H, βH) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ = 13.4 (CH₃), 18.5 (CH₃), 31.8 (CH₂), 34.2 (CH₂), 34.3 (CH₂), 36.9 (CH₂), 47.9 (CH), 49.7 (CH), 60.6 (β-CH), 116.2 (qC), 123.3 (β-CH), 125.4 (β-CH), 129.0 (β-CH), 161.9 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 429 (4.1), 458 (3.8), 581 (3.1), 6.03 (3.2), 656 (3.2) nm; HRMS (ES⁺) [C₄₈H₇₂N₄+H] calcd. 705.5835, found 705.5801.

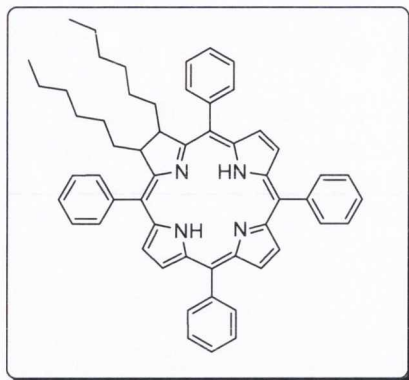
5,10,15,20-Tetra(1-ethylpropyl)-2,3-diphenylchlorin 80



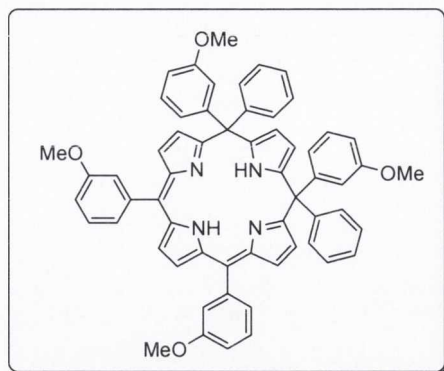
Following the above procedure, H₂TEPP **72** (100 mg, 0.17 mmol), tetrakis(triphenylphosphine)palladium(0) (19.6 mg, 0.017 mmol), copper iodide (4.8 mg, 0.025 mmol) and phenyllithium (0.94 mL of a 1.8 M solution in dibutyl ether, 1.7 mmol) were reacted. After warming the solution to rt, no reaction had occurred and the solution remained green. The reaction mixture was warmed to 60 °C upon which, a colour change to dark green/brown was observed. The crude porphyrin mixture was subjected to column chromatography on silica gel using ethyl acetate/*n*-hexane (3:7 v/v) as eluent. The first fraction contained traces of metallated porphyrin. The second fraction contained unreacted starting material **72** (13 mg, 13%). The product was obtained as the third fraction (6.6 mg, 5.5%) R_f = 0.56 (SiO₂, ethyl acetate/*n*-hexane 30:70, v/v); ¹H NMR (400 MHz, CDCl₃): δ = -0.53 (s, 2H, NH), 0.86 (m, CHCH₂CH₃), 0.92 (m, CHCH₂CH₃), 2.47-3.08 (m 16H, CHCH₂CH₃), 3.36 (b, 1H CHCH₂CH₃), 3.82 (b, 1H, CHCH₂CH₃), 4.56 (m, 3H, CHCH₂CH₃, βH), 5.14 (m, 1H, CHCH₂CH₃), 7.56 (m, 6H, Ar-H), 7.74 (m, 4H Ar-H), 8.96 (m, 2H, βH), 9.16 (m, 2H, βH), 9.25 (m, 2H, βH) ppm; UV-vis (CHCl₂): λ_{max} (lg ε) 376 (3.5), 423 (4.0), 533 (3.0), 659 (3.1) nm.

2-Hexyl-5,10,15,20-tetraphenylporphyrin **83**

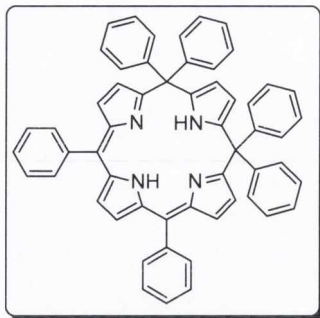
Following the above procedure, H₂TPP **58** (100 mg, 0.16 mmol), tetrakis(triphenylphosphine)palladium(0) (18.8 mg, 0.016 mmol), copper iodide (4.8 mg, 0.025 mmol) and *n*-hexyllithium (1.42 mL of a 1.7 M solution in pentane, 3.27 mmol) were reacted and subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:3 v/v) as eluent. The second fraction gave the title compound **83** as a brown solid (31.9 mg, 25%); mp 241 °C; *R_f* = 0.45 (SiO₂, dichloromethane/*n*-hexane 1:3, v/v); ¹H NMR (400 MHz, CDCl₃): δ = -1.47 (br, 2H, NH), 0.77 (t, ³*J* = 7.46 Hz, 3H, CH₃), 0.94 (m, 4H, CH₂), 1.09 (m, 2H, CH₂), 1.43 (m, 2H, CH₂), 1.62 (m, 2H, CH₂), 3.94 (d, ³*J* = 16.96 Hz, 1H, β-CH₂), 4.49 (dd, ³*J* = 9.36 Hz, 1H, ²*J* = 16.96 Hz, β-CH₂), 4.70 (m, 1H, βH), 7.72 (m, 14H, Ar-H), 8.06 (m, 2H, Ar-H), 8.16 (m, 2H, Ar-H), 8.24 (m, 2H, βH), 8.27 (m, 2H, Ar-H), 8.47 (s, 2H, βH), 8.62 (m, 2H, βH) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ = 13.5 (CH₃), 22.0 (CH₂), 25.3 (CH₂), 28.2 (CH₂), 30.9 (CH₂), 34.7 (CH₂), 42.3 (β-CH₂), 44.5 (β-C [*n*Hex]), 111.85 (qC), 112.4 (qC), 121.9 (qC), 122.2 (qC), 123.16 (β-C), 123.18 (β-C), 126.3 (br. Ar-C), 126.7 (Ar-C), 127.0 (Ar-C), 127.1 (Ar-C), 127.3 (Ar-C), 127.4 (Ar-C), 127.48 (C), 127.52 (β-C), 127.6 (Ar-C), 131.4 (Ar-C), 131.6 (Ar-C), 131.7 (Ar-C), 132.05 (β-C), 132.1 (β-C), 133.3 (Ar-C), 133.4 (Ar-C), 133.5 (Ar-C), 133.6 (Ar-C), 134.2 (Ar-C), 134.7 (qC), 134.8 (qC), 140.2 (qC), 140.8 (qC), 141.6 (qC), 141.7 (qC), 141.8 (qC), 142.8 (qC), 151.9 (qC), 152.1 (qC), 165.0 (qC), 170.0 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 420 (3.9), 519 (3.0), 547 (2.9), 598 (2.8), 651 (3.2) nm; HRMS (ES⁺) [C₅₀H₄₄N₄+H]⁺: calcd. 701.3644, found 701.3635.

2,3-Dihexyl-5-10,15,20-tetraphenylporphyrin 84

Following the above procedure, H₂TPP **58** (100 mg, 0.16 mmol), tris(dibenzylideneacetone)dipalladium(0) chloroform complex (16.9 mg, 0.016 mmol), copper iodide (4.8 mg, 0.025 mmol) and *t*-butyllithium (1.42 mL of a 1.7 M solution in pentane, 3.27 mmol) were reacted and subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:3 v/v) as eluent. The second fraction gave the title compound **84** as a brown solid (31.9 mg, 25%); mp >250 °C; *R_f* = 0.50 (SiO₂, dichloromethane/*n*-hexane 1:3, v/v); ¹H NMR (400 MHz, CDCl₃): δ = -1.41 (b, 2H, NH), 0.87 (m 6H, CH₃), 0.91 (m, 4H, CH₂), 1.06 (m, 4H, CH₂), 1.18 (m, 4H, CH₂), 1.61 (m, 8H, CH₂), 4.37 (m, 2H, βH), 7.77 (m, 14H, Ar-H), 7.97 (m, 2H, Ar-H), 8.17 (m, 2H, Ar-H), 8.20 (m, 2H, βH), 8.29 (m, 2H, Ar-H), 8.45 (m, 2H, βH), 8.50 (m, 2H, βH) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ = 13.5 (CH₃), 22.0 (CH₂), 26.1 (CH₂), 28.2 (CH₂), 31.0 (CH₂), 33.6 (CH₂), 51.3 (β-CH), 112.4 (qC), 121.9 (qC), 123.2 (β-C), 126.2 (Ar-C), 126.7 (Ar-C), 126.9 (Ar-C), 127.1 (Ar-C), 127.2 (Ar-C), 127.3 (β-CH), 132.3 (Ar-C), 133.4 (m, Ar-C), 133.6 (Ar-C), 134.7 (qC), 140.7 (qC), 141.7 (qC), 141.9 (qC), 151.9 (qC), 168.7 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 420 (5.3), 519 (4.4), 548 (4.3), 598 (4.2), 652 (4.5) nm; HRMS (ES⁺) [C₅₆H₅₆N₄+H]: calcd. 785.4583, found 785.4583.

5,10,15,20-Tetrakis(3-methoxyphenyl)-5',10'-diphenylporphyrin 85

Following the above procedure, $\text{H}_2\text{T}(3\text{-MeOP})\text{P}$ **74** (100 mg, 0.14 mmol), tetrakis(triphenylphosphine)palladium(0) (23.6 mg, 0.02 mmol), copper iodide (2.5 mg, 0.01 mmol) and phenyllithium (1.50 mL of a 1.8 M solution in dibutyl ether 2.72 mmol) were reacted and subjected to purification *via* preparative TLC using ethyl acetate/*n*-hexane (1:4 v/v) as eluent. The second fraction gave the title compound **85** as a pink solid (17.1 mg, 14%); mp 232 °C; $R_f = 0.61$ (SiO_2 , ethyl acetate/*n*-hexane 3:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.71$ (m, 6H, OCH_3), 3.84 (s, 6H, OCH_3), 5.51 (m, 2H, βH), 6.08 (d, $^3J = 2.12$ Hz, 2H βH), 6.15 (m, 2H, βH), 6.66 (m, 6H, βH , Ar-H), 6.80 (d, $^3J = 8.1$ Hz, 2H, Ar-H), 7.03 (m, 10H, Ar-H), 7.16 (t, $^3J = 7.9$ Hz, 2H, Ar-H), 7.23 (m, 6H, Ar-H), 7.32 (t, $^3J = 7.9$ Hz, 2H, Ar-H), 10.57 (s, 1H, NH), 12.57 (s, 1H, NH) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): 54.7, 54.9, 109.7, 111.5, 113.6, 115.3, 115.8, 121.9, 122.9, 128.0, 129.0, 129.1, 134.7; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ) 328 (4.1), 353 (4.1), 419 (4.0), 453 (3.6), 532 (4.0), 566 (4.0). HRMS (ES^+) [$\text{C}_{60}\text{H}_{49}\text{N}_4\text{O}_4$]: calcd for $[\text{M}+\text{H}^+]$ 889.3754, found 889.3772.

5,5',10,10',15,20-Hexaphenylporphyrin 86*Catalysed approach:*

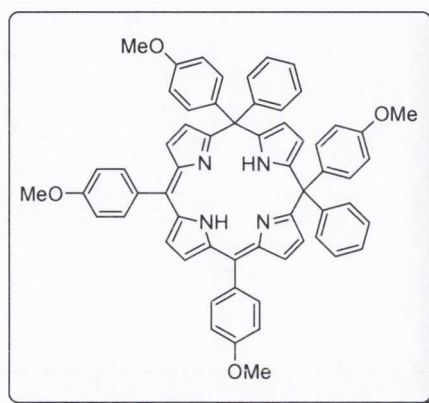
Following the above procedure, 5,10,15,20-tetraphenylporphyrin **23** (100 mg, 0.16 mmol), Pd(PPh₃)₄ (18.8 mg, 0.016 mmol), CuI (2.5 mg, 0.014 mmol) and phenyllithium (1.5 mL of a 1.8 M solution in dibutyl ether, 3.26 mmol) were reacted and subjected to purification *via* preparative TLC using ethyl acetate/*n*-hexane (1:8, v/v) as eluent. The first fraction contained unreacted starting material **23** (43.6 mg, 44%). The second contained the title compound **36** (32.5 mg, 26%) as a pink solid (24.7 mg, 21%): mp 215 °C; *R_f* = 0.59 (SiO₂, ethyl acetate/*n*-hexane 1:8, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 5.47 (d, ³*J* = 2.6 Hz, 2H, β*H*), 6.03, s, 2H, β*H*), 5.15 (d, ³*J* = 4.6 Hz, 2H, β*H*), 6.60 (d, ³*J* = 4.6 Hz, 2H, β*H*), 7.07 (m, 8H, Ar-*H*), 7.24 (m, 12H, Ar-*H*), 7.42 (m, 10H, Ar-*H*), 10.51(s, 1H, NH), 12.59 (s, 1H, NH) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ = 110.0 (β-C), 122.4, (β-C), 126.6 (Ar-C), 127.4 (Ar-C), 127.7 (Ar-C), 128.3 (Ar-C), 129.5 (β-C), 129.6 (Ar-C), 130.7 (Ar-C), 136.6 (qC), 137.5 (qC), 138.3 (qC), 139.1 (qC), 145.8 (qC), 151.8 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 341 (4.5), 356 (4.5), 529 (4.3), 563 (4.4) nm; HRMS (ES⁺) [C₅₆H₄₁N₄+H] calcd. 769.3331, found 769. 3328.

Non-catalysed approach:

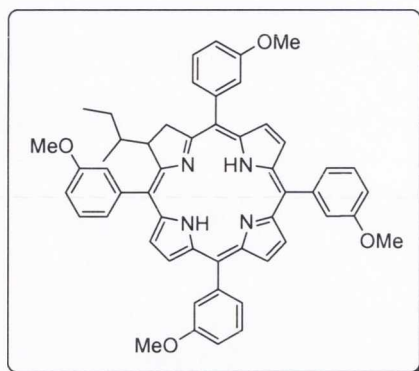
A 100 mL schlenk tube was charged with H₂TPP **58** (100 mg, 0.16 mmol) in dry THF (20 mL). The reaction mixture was cooled to 0 °C and phenyllithium (1.5 mL of a 1.8 M solution in dibutyl ether, 3.26 mmol) was added dropwise *via* syringe over a period of 10 minutes. The solution was warmed to rt and allowed to stir for 1 h (TLC control) after which no reaction had occurred. The reaction mixture was warmed to 60 °C. No colour change was observed. The reaction was quenched with saturated NH₄Cl (1 mL). After stirring for 10 min, the reaction was filtered through silica gel. The crude

porphyrin mixture was dried *in vacuo* and subjected to purification *via* preparative TLC using ethyl acetate/*n*-hexane (1:8, v/v) as eluent. The first fraction contained unreacted starting material (12 mg, 12%), the second contained the title compound **86** (77.3 mg, 62%).

5,10,15,20-Tetrakis(4-methoxyphenyl)-5'10'-diphenylporphyrin **87**

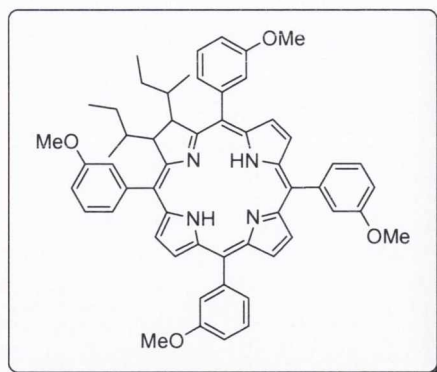


Following the procedure outlined for the non-catalysed approach, H₂T(4-MeOP)P **75** (100 mg, 0.14 mmol) and phenyllithium (0.78 mL of a 1.8 M solution in dibutyl ether, 1.4 mmol) were reacted and subjected to purification *via* preparative TLC using ethyl acetate/*n*-hexane (1:4, v/v) as eluent. The first fraction contained unreacted starting material (40 mg, 40%), the second contained the title compound **87** (56.9 mg, 47%): mp 232 °C; *R_f* = 0.61 (SiO₂, ethyl acetate/*n*-hexane 1:3, v/v); ¹H NMR (600 MHz, CDCl₃): δ = 3.81 (s, 6H, CH₃), 3.89 (s, 6H, CH₃), 5.47 (m, 2H, βH), 6.09 (s, 2H, βH), 6.16 (d, ³*J* = 4.4 Hz, 2H, βH), 6.65 (d, ³*J* = 4.6 Hz, 2H, βH), 6.77 (m, 4H, Ar-*H*), 6.94 (d, ³*J* = 8.6 Hz, 4H, Ar-*H*), 6.97 (m, 4H, Ar-*H*), 7.06 (m, 4H, Ar-*H*), 7.24 (m, 4H, Ar-*H*), 7.35 (d, ³*J* = 8.4 Hz, 4H, Ar-*H*), 10.58 (m, 1H, NH), 12.58 (s, 1H, NH) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ = 55.2 (OCH₃), 55.3 (OCH₃), 109.7 (β-C), 112.8 (Ar-C), 112.9 (Ar-C), 122.3 (β-C), 126.5 (Ar-C), 127.6 (Ar-C), 129.1 (β-C), 129.6 (Ar-C), 130.7 (Ar-C), 132.1 (Ar-C), 135.2 (Ar-C), 136.7 (qC), 137.5 (qC), 138.2 (qC), 139.4 (qC), 146.3 (qC), 152.0 (qC), 158.1 (qC), 159.8 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 325 (4.3), 380 (4.5), 531 (4.3), 566 (4.3) nm; HRMS(ES⁺) [C₆₀H₄₉N₄O₄+H] calcd. 889.3754, found 889.3772.

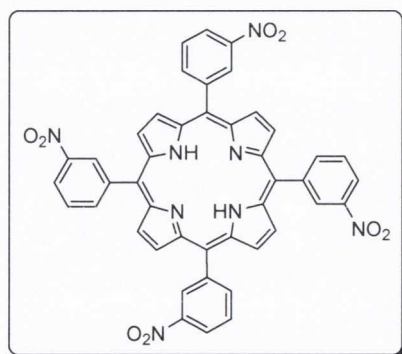
2-(*sec*-Butyl)-5,10,15,20-tetrakis(3-methoxyphenyl)chlorin **88**

Following the procedure outlined for the non-catalysed approach, $\text{H}_2\text{T}(3\text{-MeOP})\text{P}$ **74** (100 mg, 0.14 mmol) and *sec*-butyllithium (0.53 mL of a 1.4 M solution in cyclohexane, 0.75 mmol) were reacted at rt and subjected to column chromatography on silica gel using ethyl acetate/*n*-hexane (1:3, v/v) as eluent. The first fraction contained **89** (20.7 mg, 18%), the second fraction contained **88** (8.5 mg, 8%), and the final fraction contained unreacted starting material **74** (57.1 mg, 57%)

88; mp = 228 °C; R_f = 0.66 (SiO_2 , ethyl acetate/*n*-hexane 1:3, v/v); ^1H NMR (400 MHz, CDCl_3): δ = -1.48 (s, 2H, NH), 0.66 (m, 3H, CH_3), 0.88 (m, 3H, CH_3), 1.27 (m, 2H, CH_2CH_3), 1.86 (m, 1H CH), 4.00 (m, 13H, OCH_3 , $\beta\text{-CH}_2$), 4.22 (m, 1H, $\beta\text{-CH}$), 4.99 (m, 1H, $\beta\text{-CH}_2$), 7.28 (m, 4H, Ar-H), 7.62 (m, 12H, Ar-H), 8.26 (m, 2H, βH), 8.49, (s, 2H, βH), 8.64 (m, 2H, βH) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): δ = 11.4 (CH_3), 13.0 (CH), 17.3 (CH_3), 29.3 (CH_2), 36.8 ($\beta\text{-C}$), 47.2 ($\beta\text{-C}$), 55.1 (OCH_3), 113.1 ($\beta\text{-C}$), 119.2 (Ar-C), 123.2 ($\beta\text{-C}$), 126.6 (Ar-C), 127.0 (Ar-C), 127.5 (Ar-C), 128.6 (Ar-C), 131.5 (Ar-C), 134.5 (qC), 140.1 (qC), 142.9 (qC), 143.1 (qC), 151.7 (qC), 157.5 (qC), 165.7 (qC), 173.6 (qC) ppm; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ) 449 (5.2), 556 (3.6), 559 (3.9), 656 (4.4) nm; HRMS (ES^+) [$\text{C}_{52}\text{H}_{48}\text{N}_4\text{O}_4\text{+H}$] calcd. 793.3742, found 793.3732.

2,3-Di(*sec*-butyl)-5,10,15,20-tetrakis(3-methoxyphenyl)chlorin 89

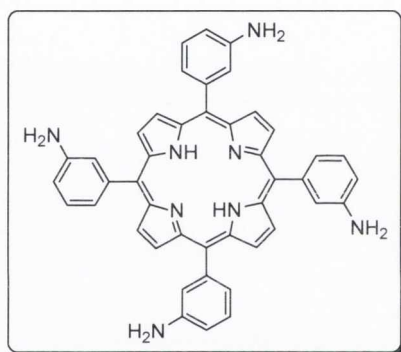
89: mp = 245 °C; R_f = 0.59 (SiO₂, ethyl acetate/*n*-hexane 1:3, v/v); ¹H NMR (400 MHz, CDCl₃): δ = -1.48 (s, 2H, NH), 0.19 (m, 6H, CH₃), 0.69 (m, 3H, CH₃), 0.95 (m, 3H, CH₃), 1.29 (m, 2H, CH₂), 1.41 (m, 2H, CH₂), 1.99 (m, 2H, CH), 3.97 (m, 12H, OCH₃), 4.55 (m, 2H, β -CH), 7.25 (m, 2H, Ar-H), 7.30 (m, 2H, Ar-H), 7.39 (m, 2H, Ar-H), 7.62 (m, 6H, Ar-H), 7.84 (m, 4H, Ar-H), 8.26 (m, 2H, β H), 8.50 (s, 2H, β H), 8.66 (b, 2H, β H) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ = 11.5 (CH₃), 17.3 (CH₃), 27.0 (CH₂), 29.3 (CH₂), 38.7 (CH), 49.8 (β -C), 53.2 (β -C), 55.0 (OCH₃), 113.0 (Ar-C), 117.2 (Ar-C), 119.2 (Ar-C), 121.4 (Ar-C), 123.4 (β -C), 124.6 (Ar-C), 126.5 (Ar-C), 127.0 (β -C), 127.3 (Ar-C), 127.4 (Ar-C), 131.5 (β -C), 134.5 (qC), 140.9 (qC), 143.0 (qC), 143.3 (qC), 151.7 (qC), 157.5 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ϵ) 446 (5.2), 552 (4.1), 595 (4.1), 656 (4.5) nm; HRMS (ES⁺) [C₅₆H₅₆N₄O₄]: calcd. 849.4301, found 849.4311.

6.4 Functionalised hydroporphyrins**5,10,15,20-Tetrakis-(3-nitrophenyl)porphyrin 92³¹⁶**

m-Nitrobenzaldehyde (13.75 g, 91 mmol) and acetic anhydride (15 mL) were added to a 1 L round bottomed flask containing propionic acid (600 mL). The solution was brought

to reflux and fresh distilled pyrrole (6.25 mL, 91 mmol) in propionic acid (25 mL) was added. After 45 min at reflux, the solution was allowed to cool and stand overnight. A dark solid (purple) was collected by filtration, washed with water (6 x 100 mL) and dried. The product was extracted into toluene (500 mL) using an insulated Soxhlet apparatus. The solvent was evaporated under reduced pressure, redissolved in dichloromethane (300 mL). Silica gel (~ 200 mL) was added and the mixture was stirred. The product was removed by filtration until the rinsings were pale. The solvent was evaporated under reduced pressure and a purple solid was obtained (2.5 g, 14%): $R_f = 0.73$ (SiO_2 , (THF/*n*-hexane 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = -2.80$ (s, 2H, NH), 8.03 (m, 4H, Ar-*H*), 8.60 (m, 4H, Ar-*H*), 8.75 (d, $^3J = 6.9$ Hz, 4H, Ar-*H*), 8.84 (s, 8H, β H). 9.12 (s, 4H, Ar-*H*) ppm. The data were in agreement with the literature.

5,10,15,20-tetrakis-(3-aminophenyl)porphyrin **93**³¹⁶



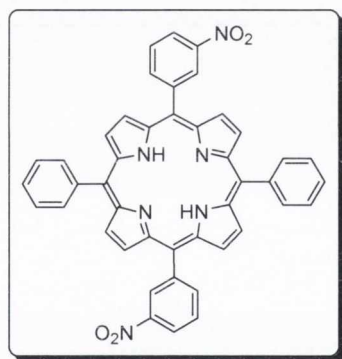
A solution of **92** (2 g, 2.5 mmol) in concentrated HCl (100 mL) was bubbled with argon for 1 h. A solution of stannous chloride dehydrate (9 g, 40 mmol) in concentrated HCl (140 mL) also bubbled with argon, was added to the porphyrin solution and the solution was stirred and heated in a water bath (75-80 °C) for 30 min. The hot water bath was replaced with a cold water bath and then with an ice bath. The reaction mixture was then neutralised under argon by slow addition of ammonia (125 mL), all the time at low temperature. The resulting solution was then filtered to yield a green solid. 5% Sodium hydroxide (200 mL) was added and the solution was stirred vigorously. The solid was filtered again, washed with water and extracted with chloroform (250 mL) using a soxhlet apparatus. The product was obtained as a purple solid (1.1 g, 52%), $R_f = 0.63$ (SiO_2 , THF/*n*-hexane 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = -2.75$ (s, 2H, NH), 5.64 (s, 8H, NH_2), 7.16 (m, 4H, Ar-*H*), 7.57 (m, (8H, Ar-*H*), 7.75 (t, $^3J = 7.6$ Hz, 4H,

Ar-*H*), 7.91 (s, 4H, Ar-*H*), 8.96 (s, 8H, β *H*) ppm. The NMR data were in agreement with the literature.

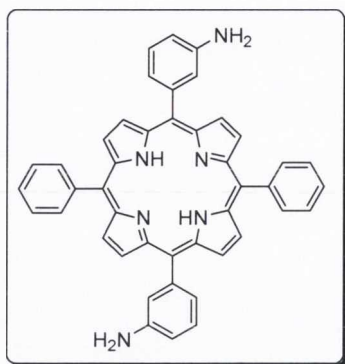
General procedure for the Suzuki-Miyaura reaction of 5,15-bromoporphyrins

5,15-Disubstituted bromoporphyrin (1 equiv.), boronic acid (10 equiv.) and potassium phosphate (20 equiv.) were added to a 100 mL Schlenk and dried under vacuum. The vacuum was released to allow the addition of anhydrous THF (60 mL). The mixture was degassed *via* three freeze-pump-thaw cycles before the vessel was purged with argon and tetrakis(triphenylphosphine)palladium(0) (0.1 equiv.) was added. The Schlenk flask was sealed and heated at reflux overnight. The solvent was removed and the residue was redissolved in dichloromethane, washed with aqueous sodium hydrogen carbonate, water, and brine before being dried over anhydrous sodium sulfate. The organic solvent was evaporated and the crude product was purified by column chromatography on silica gel.

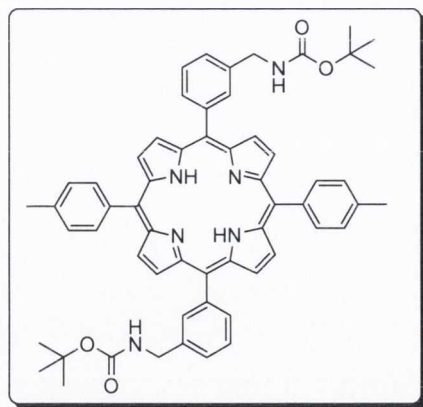
5,15-Bis(3-nitrophenyl)-10,20-diphenylporphyrin **94**³¹⁷



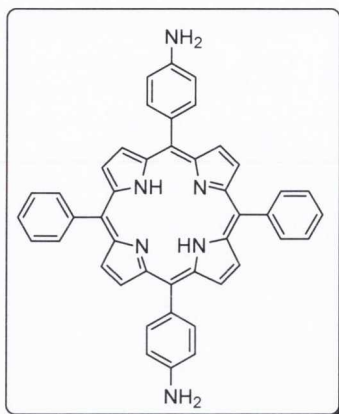
Following the above procedure 5,15-dibromo-10,20-diphenyl porphyrin (100 mg, 0.16 mmol), 3-nitrophenylboronic acid (264.83 mg, 1.59 mmol), potassium phosphate (684.0 mg, 3.22 mmol) and tetrakis(triphenylphosphine)palladium(0) (18.6 mg, 0.02 mmol) were reacted and subjected to purification *via* column chromatography on silica gel using dichloromethane/*n*-hexane (1:2, v/v) as eluent. The title compound was obtained as a purple solid (46.8 mg, 45%); R_f = 0.83 (SiO₂, dichloromethane/*n*-hexane 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = -2.78 (s, 2H, NH), 7.82 (m, 6H, Ar-*H*), 8.00 (t, ³*J* = 7.9 Hz, 2H, Ar-*H*), 8.24 (br, 4H, Ar-*H*), 8.58 (s, ³*J* = 7.6 Hz, 2H, Ar-*H*), 8.72 (d, ³*J* = 8.6 Hz, 2H, Ar-*H*), 8.77 (s, ³*J* = 4.6 Hz, 4H, β *H*), 8.94 (d, ³*J* = 4.6 Hz, 4H, β *H*), 9.11 (s, 2H, Ar-*H*) ppm. The NMR data were in agreement with the literature.

5,15-Bis(3-aminophenyl)-10,20-diphenylporphyrin 95

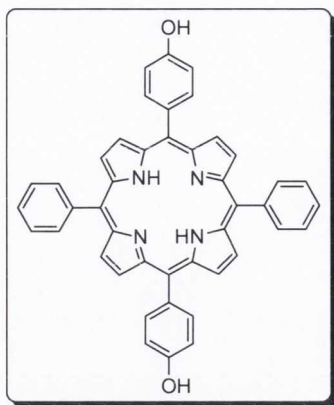
5,15-Bis-(3-nitrophenyl)-10,20-diphenylporphyrin **94** (100 mg, 0.13 mmol) was dissolved in dry dichloromethane (40 mL) and dry methanol (40 mL) and palladium on carbon (69.6 g, 10 wt.%) was added. The suspension was placed in an ice bath and sodium borohydride (123.4 mg, 3.26 mmol) was added slowly. After 30 min, the reaction mixture was filtered and washed with dichloromethane. The organic phase was washed with water (40 mL x 2) and brine (40 mL x 2). The organic solvent was removed *in vacuo* to yield a purple solid (71.4 mg, 88%). $R_f = 0.43$ (SiO₂, dichloromethane/*n*-hexane 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta = -2.78$ (s, 2H, NH), 3.97 (s, 4H, NH₂), 7.13 (d, ³ $J = 7.8$ Hz, 2H, Ar-*H*), 7.53 (t, ³ $J = 7.8$ Hz, 2H, Ar-*H*), 7.57 (s, 2H, Ar-*H*), 7.65 (m, 2H, Ar-*H*), 7.79 (m, 6H, Ar-*H*), 8.24 (d, ³ $J = 6.3$ Hz, 4H, Ar-*H*), 8.85 (s, ³ $J = 4.6$ Hz, 4H, β *H*), 8.96 (d, ³ $J = 4.6$ Hz, 4H, β *H*) ppm; ¹³C NMR (150.9 MHz, CDCl₃): $\delta = 114.2$ (Ar-C), 119.9 (qC), 120.3 (qC), 126.0 (Ar-C), 126.7 (Ar-C), 127.4 (Ar-C), 127.6 (Ar-C), 134.5 (Ar-C), 142.3 (qC), 143.2 (qC), 146.6 (qC) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) 420 (5.5), 516 (4.4), 550 (4.3), 590 (4.2), 646 (4.2) nm; HRMS (ES⁺) [C₄₄H₃₃N₄+H] calcd. 645.2767, found 645.2765.

5,15-Bis(3-*tert*-butoxycarbonylaminomethylphenyl)-10,20-ditolylporphyrin 96

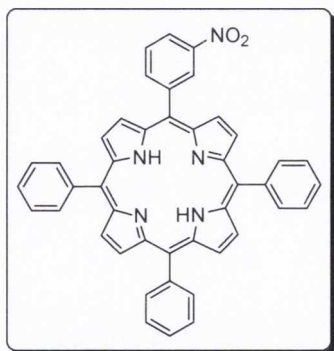
Prepared according to the procedure for a Suzuki coupling reaction using 5,15-dibromo-10,20-ditolylporphyrin (64.8 mg, 0.1 mmol), potassium phosphate (424.8 mg, 2 mmol), 3-*tert*butoxycarbonylamino phenyl)boronic acid (251.1 mg, 1 mmol) and tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.01 mmol). The crude product was purified *via* preparative TLC using dichloromethane as eluent (56.8 mg, 63%); mp 238 °C; R_f = 0.51 (SiO₂, dichloromethane) ¹H NMR (400 MHz, CDCl₃): δ = -2.77 (s, 2H, NH), 1.47 (s, 18H, CH₃), 2.74 (s, 6H, CH₃), 4.66 (br, 4H, CH₂), 5.10 (s, 2H, NH), 7.59 (d, ³*J* = 7.8 Hz, 4H, Ar-*H*), 7.73 (m, 4H, Ar-*H*), 8.12 (m, 8H, Ar-*H*), 8.86 (dd, ³*J* = 4.6, 19.4 Hz, β H) ppm; ¹³C NMR (150.9 MHz, CDCl₃) δ = 21.4 (CH₃), 28.2 (CH₃), 44.6 (CH₂), 53.2 (qC), 119.5 (qC), 120.2 (qC), 126.5 (Ar-C), 126.8 (qC), 127.3 (ar-C), 133.3 (qC), 134.4 (Ar-C), 134.8 (Ar-C), 137.2 (qC), 139.0 (qC), 142.4 (qC), 155.8 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ϵ) = 415 (5.7), 514 (4.5), 548 (4.3), 588 (4.2), 646 (4.1) nm; HRMS (ES⁺) [C₅₈H₅₇N₆O₄+H]: calcd 901.4441, found 901.4446.

5,15-Bis-(4-aminophenyl)-10,20-diphenylporphyrin **98**³¹⁸

A 50 mL round bottom flask was charged with H₂TPP **58** (200 mg, 0.33 mmol) in TFA (10 mL). Sodium nitrite (183 mg, 2.65 mmol) was added to the reaction mixture. After 90 sec, the reaction was poured into water (100 mL) and the product was extracted with dichloromethane (6 x 25 mL). The organic layers were combined and washed with saturated aqueous NaHCO₃ and water before being dried over anhydrous Na₂SO₄. The residue was then dissolved in concentrated hydrochloric acid (50 mL) and, while stirring, stannous SnCl₂ (800 mg, 3.55 mmol) was added. Mixture was heated at 65 °C under argon for 1 h before being poured into cold water (100 mL). The aqueous solution was neutralised with sodium hydroxide and extracted with dichloromethane until colourless. The organic layers were combined and the solvent, removed under reduced pressure. The two regioisomers (5,10- and 5,15-) were separated by column chromatography on aluminium oxide using dichloromethane as eluent. The 5,10-isomer eluted first (32.3 mg, 15%); *R_f* = 0.34 (Al₂O₃, dichloromethane); ¹H NMR (400 MHz, CDCl₃): δ = -2.73 (s, 2H, NH), 4.06 (s, 4H, NH₂), 7.09 (d, ³*J* = 8.2 Hz, 4H, Ar-*H*), 7.79 (m, 6H, Ar-*H*), 8.01 (d, ³*J* = 8.2 Hz, 4H, Ar-*H*), 8.23 (m, 4H, Ar-*H*), 8.84 (d, ³*J* = 4.7 Hz, 4H, β*H*), 8.95 (d, ³*J* = 4.7 Hz, 4H, β*H*) ppm. The second fraction contained the title compound **98**: (95.3 mg, 45%); *R_f* = 0.20 (Al₂O₃, dichloromethane) ¹H NMR (400 MHz, CDCl₃): δ = -2.71 (s, 2H, NH), 4.04 (s, 4H, NH₂), 7.08 (d, ³*J* = 8.2 Hz, 4H, Ar-*H*), 7.79 (m, 6H, Ar-*H*), 8.02 (s, ³*J* = 8.2 Hz, 4H, Ar-*H*), 8.25 (m, 4H, Ar-*H*), 8.85 (s, 4H, β*H*), 8.96 (s, 4H, β*H*) ppm. The data were consistent with literature data.

5,15-Bis(4-hydroxyphenyl)-10,20-diphenylporphyrin 99³¹⁹

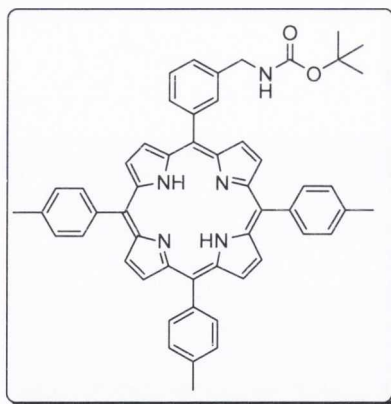
Following the procedure for the Suzuki-Miyaura coupling reaction, 5,15-dibromo-10,20-diphenylporphyrin (100 mg, 0.16 mmol), 4-hydroxyphenylboronic acid (222.3 mg, 1.61 mmol), potassium phosphate (684.0 mg, 3.2 mmol) and tetrakis(triphenylphosphine)palladium(0) (18.6 mg, 0.02 mmol) were reacted. After work-up the product was filtered through a layer of silica gel using dichloromethane as eluent, the solvent was evaporated under reduced pressure and recrystallisation from dichloromethane//methanol yield purple crystals. (81.3 mg, 78%); $R_f = 0.53$ (SiO_2 , ethyl acetate/*n*-hexane, 2:3, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = -2.75$ (s, 2H, *NH*), 6.19 (s, 2H, *OH*), 7.23 (d, $^3J = 8.3$ Hz, 4H, *Ar-H*), 7.78 (m, 4H, *Ar-H*), 8.08 (m, 6H, *Ar-H*), 8.24 (d, $^3J = 6$ Hz, 4H, *Ar-H*), 8.89 (dd, $^3J = 4.7, 19.1$ Hz, 8H, βH) ppm. The NMR data were in agreement with the literature.

5-(3-Nitrophenyl)-10,15,20-triphenylporphyrin 100³²⁰

Benzaldehyde (35.4 g, 0.34 mol) and 3-nitrobenzaldehyde (25.25 g, 0.167 mol) were dissolved in hot glacial acetic acid (1 L) in a 2L, three-neck, round bottom flask. The mixture was brought to reflux and freshly distilled pyrrole (34.7 mL, 0.5 mol) was

added as quickly as possible, without causing an uncontrollable exothermic reaction (10 min). The resulting black solution was heated to reflux for 20 min before being cooled to 35 °C and filtered through a coarse sintered glass funnel and washed with methanol. A purple powder was obtained which was purified by column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent. The first fraction contained H₂TPP **58** (2.28 g, 3%): The second fraction contained the title compound (1.38 g, 5%); $R_f = 0.63$ (SiO₂, dichloromethane/*n*-hexane, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta = -2.77$ (s, 2H, NH), 7.80 (m, 9H, Ar-H), 7.97 (t, ³*J* = 7.9 Hz, 1H, Ar-H), 8.24 (d, ³*J* = 6.2 Hz, 6H, Ar-H), 8.57 (³*J* = 7.6 Hz, 1H, Ar-H), 8.70 (m, 1H, Ar-H), 8.74 (d, ³*J* = 4.7 Hz, 2H, β -H), 8.88 (s, 4H, β -H), 8.92 (d, ³*J* = 4.6 Hz, 2H, β -H), 9.11 (s, 1H, Ar-H) ppm. The 5,10- and 5,15-bis-(3-nitrophenyl)porphyrins were obtained as a mixture in the third fraction (2.7 g, 3%); 5,10,15-tris-(3-nitrophenyl)-20-phenylporphyrin was obtained as the fourth fraction (201.6 mg, 0.2%); $R_f = 0.3$ (SiO₂, dichloromethane/*n*-hexane, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta = -2.79$ (s, 2H, NH), 7.83 (m, 3H, Ar-H), 8.01 (t, ³*J* = 7.5 Hz, 3H, Ar-H), 8.25 (m, 2H, Ar-H), 8.56 (br, 3H, Ar-H), 8.73 (m, 3H, Ar-H), 8.79 (d, ³*J* = 4.5 Hz, 2H, β -H), 8.82 (s, 4H, β -H), 8.96 (d, ³*J* = 4.6 Hz, 2H, β -H), 9.11 (br, 3H, Ar-H) ppm. The analytical data were in agreement with the literature.

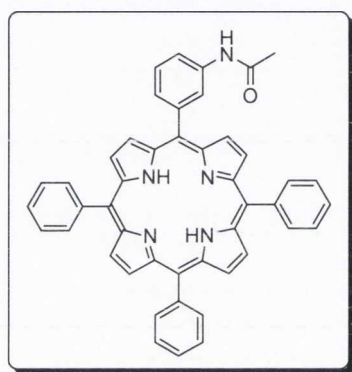
5-(3-*tert*-Butoxycarbonylaminoethylphenyl)-10,15,20-tritolylporphyrin **102**



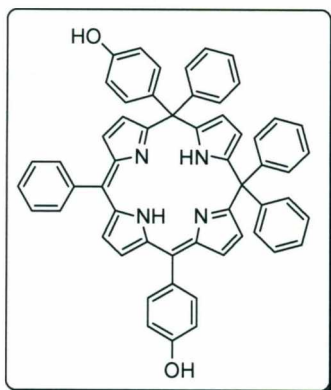
Prepared according to the procedure for a Suzuki coupling reaction using 5-bromo-10,15,20-tritolylporphyrin (66 mg, 0.1 mmol), potassium phosphate (424.6 mg, 2.0 mmol), 3-*tert*-butoxycarbonylaminoethylphenyl)boronic acid (251.2 mg, 1.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.01 mmol). The crude product was purified *via* column chromatography on silica gel using dichloromethane/*n*-hexane as eluent (2:1, v/v). The product was obtained as a purple solid (44 mg, 56%) mp 234 °C;

$R_f = 0.24$ (SiO_2 , dichloromethane/*n*-hexane, 1:1, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta = -2.74$ (s, 2H, NH), 1.47 (s, 9H, CH_3), 2.74 (s, 9H, CH_3), 4.66 (br, 2H, CH_2), 5.09 (s, 1H, NH), 7.59 (d, $^3J = 7.5$ Hz, 6H, Ar-*H*), 7.74 (m, 2H, Ar-*H*), 8.13 (m, 8H, Ar-*H*), 8.86 (m, 8H, βH) ppm; ^{13}C NMR (400 MHz, CDCl_3): $\delta = 21.4$ (CH_3), 28.2 (CH_3), 30.7 (qC), 43.7 (CH_2), 119.3 (qC), 120.1 (qC), 126.8 (qC), 127.3 (Ar-C), 133.2 (Ar-C), 134.4 (Ar-C), 137.2 (qC), 139.2 (qC), 142.5 (qC) ppm; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ) = 416 (5.5), 515 (4.3), 549 (4.2), 593 (4.1), 648 (4.0) nm; HRMS (ES^+) [$\text{C}_{58}\text{H}_{57}\text{N}_6\text{O}_4 + \text{H}$]: calcd 786.3808, found 786.3813.

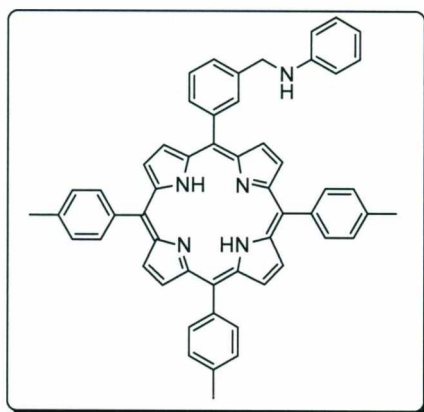
5-(3-Acetylaminophenyl)-10,15,20-triphenylporphyrin 103



Prepared according to the procedure for a Suzuki coupling reaction using 5-bromo-10,15,20-triphenylporphyrin (61.6 mg, 0.1 mmol), potassium phosphate (424.6 mg, 2 mmol), 3-acetylaminophenylboronic acid (89.5 mg, 0.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.01 mmol). The crude product was purified *via* column chromatography on silica gel using dichloromethane/*n*-hexane (2:1, v/v) as eluent. After recrystallisation from dichloromethane/methanol, the title compound was obtained as purple crystals (41.3 mg, 60%); mp >300 °C; $R_f = 0.28$ (SiO_2 , dichloromethane); ^1H NMR (400 MHz, CDCl_3): $\delta = -2.75$ s (2H, NH), 2.29 (s, 3H, CH_3), 7.41 (s, 1H, NH), 7.78 (m, 9H, Ar-*H*), 8.01 (d, $^3J = 6.7$ Hz, 1H, Ar-*H*), 8.19 (m, 2H, Ar-*H*), 8.24 (d, $^3J = 6.8$ Hz, 6H, Ar-*H*), 8.87 (m, 8H, βH) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): $\delta = 24.6$ (CH_3), 119.0 (Ar-C), 120.1 (Ar-C), 125.8 (qC), 126.5 (Ar-C), 127.3 (qC), 127.6 (Ar-C), 130.7 (Ar-C), 134.4 (Ar-C), 136.2 (qC), 142.0 (qC), 142.8 (qC), 168.4 (qC) ppm; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ) = 418 (5.6), 514 (4.4), 550 (4.2), 592 (4.1), 647 (4.1) nm; HRMS (ES^+) [$\text{C}_{46}\text{H}_{34}\text{N}_5\text{O} + \text{H}$]: calcd 672.2763, found 672.2761.

5,15-Bis(4-hydroxyphenyl)-5',10,10',20-tetraphenylporphyrin 104

Following the procedure developed for the synthesis of 5,10-disubstituted porphodimethenes in Section 7.1, **99** (50 mg, 0.08 mmol) and phenyl lithium (0.43 mL of a 1.8 M solution in dibutyl ether, 0.78 mmol) were reacted and subjected to purification *via* column chromatography on silica gel using ethyl acetate/*n*-hexane (1:5, v/v) as eluent. The first fraction contained starting material (13.1 mg, 26%). The second fraction contained the title compound **104** (20 mg, 16%); $R_f = 0.43$ (SiO₂, ethyl acetate/*n*-hexane 2:3, v/v); ¹H NMR (400 MHz, CDCl₃) δ = 5.46 (s, 2H, β H), 6.06 (m, 2H, β H), 6.16 (d, ³ J = 4.1 Hz, 2H, β H), 6.59 (d, ³ J = 4.6 Hz, β H), 6.68 (m, 4H, Ar-*H*), 6.86 (d, ³ J = 8.4 Hz, 2H, Ar-*H*), 6.91 (d, ³ J = 8.6 Hz, 2H, Ar-*H*), 7.06 (m, 6H, Ar-*H*), 7.24 (m, 9H, Ar-*H*), 7.42 (m, 5H, Ar-*H*), 7.56 (m, 2H, Ar-*H*), 7.73 (m, 2H, Ar-*H*) 10.53 (s, 1H, NH), 12.56 (s, 1H, NH) ppm; HRMS (ES⁺) [C₅₆H₄₁N₄O₂+H]: calcd 801.3230, found 801.3266.

5-(3-Phenylaminomethylphenyl)-10,15,20-tritolylporphyrin 105

Prepared according to the procedure for the synthesis of 5,10-porphodimethenes outlined in Section 7.1. 5-(3-*tert*butoxycarbonylaminomethylphenyl)-10,15,20-tritolylporphyrin (40 mg, 0.05 mmol) and phenyllithium (0.6 mL of a 1.8 M solution in

dibutyl ether, 1.0 mmol). The product was purified *via* column chromatography on silica gel using ethyl acetate/*n*-hexane as eluent (3:1, v/v). The product was obtained as a purple solid (17.2 mg, 44%); mp >300 °C; R_f = 0.28 (SiO₂, ethyl acetate/*n*-hexane, 3:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ = -2.74 (s, 2H, NH), 2.74 (s, 9H, CH₃), 5.00(d, ³*J* = 5.6 Hz, 2H, CH₂), 6.65 (s, 1H, NH), 7.44 (m, 3H, Ar-H), 7.51 (m, 1H, Ar-H), 7.59 (³*J* = 7.4 Hz, 7.77 (t, ³*J* = 7.4 Hz, 1H, Ar-H), 7.82 (m, 2H, Ar-H), 7.86 (d, ³*J* = 7.4 Hz, 1H, Ar-H), 8.12 (d, ³*J* = 7.4 Hz, 6H, Ar-H), 8.21 (m, [2+1]H, Ar-H), 8.88 (m, 8H, β -H) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ = 21.0 (qC), 21.4 (CH₃), 44.9 (CH₂), 46.6 (qC), 76.7 (qC), 119.6 (qC), 126.5 (qC), 126.8 (qC), 126.9 (Ar-C), 127.3 (Ar-C), 128.4 (Ar-C), 131.0 (qC), 131.6 (Ar-C), 133.3 (qC), 133.7 (Ar-C), 134.5 (Ar-C), 136.1 (qC), 136.8 (qC), 138.7 (qC), 142.3 (qc), 167.0 (qC) ppm;

6.5 Spectroscopic data of porphyrin dications

[5,15-Diphenylporphyrin][CF₃COO]₂

¹H NMR (400 MHz, CDCl₃): δ = 1.28 (s, 2H, NH), 7.96 (s, 6H, Ar-*H*), 8.46 (s, 4H, Ar-*H*), 9.02 (s, 4H, β *H*), 9.45 (s, 4H, β *H*), 10.70 (s, 2H, *meso H*) ppm; UV-vis (CH₂Cl₂ + 5% CF₃COOH): $\lambda_{\max}$ (lg ϵ) 420 (5.3), 569 (4.1), 614 (4.2) nm.

5,10,15-Triphenylporphyrin][CF₃COO]₂

¹H NMR (400 MHz, CDCl₃): δ = 1.30 (s, 2H, NH), 8.53 (m, 9H, Ar-*H*), 9.02 (m, 6H, Ar-*H*), 9.35 (m, 4H, β *H*), 9.68 (d, ³*J* = 4.7 Hz, 2H, β *H*), 10.06 (d, ³*J* = 4.8 Hz, 2H, β *H*), 11.32 (s, *meso H*) ppm; UV-vis (CH₂Cl₂ + 5% CF₃COOH): $\lambda_{\max}$ (lg ϵ) 429 (5.4), 581 (4.1), 633 (4.4) nm.

[5,10,15,20-Tetraphenylporphyrin][CF₃COO]₂

¹H NMR (400 MHz, CDCl₃): δ = -0.49 (s, 4H, NH, N⁺*H*), 8.03 (m, 12H, Ar-*H*), 8.60 (d, ³*J* = 6.2 Hz, 8H, Ar-*H*), 8.70 (s, 8H, β *H*) ppm; UV-vis (CH₂Cl₂ + 5% CF₃COOH): $\lambda_{\max}$ (lg ϵ) 449 (5.6), 683 (4.8) nm.

[5(1-Ethylpropyl)porphyrin][CF₃COO]₂

¹H NMR (400 MHz, CDCl₃): δ = -0.17 (br, 2H, NH), 1.06 (t, ³*J* = 7.4 Hz, CHCH₂CH₃), 2.91-3.11 (m, 4H, CHCH₂CH₃), 5.03 (m, 1H, CHCH₂CH₃), 9.44 (s, 2H, β *H*), 9.55 (m,

6H, βH), 10.56 (s, 1H, *meso H*), 10.68 (s, 2H, *meso H*) ppm; UV-vis (CH_2Cl_2 + 5% CF_3COOH): λ_{max} (lg ϵ) 404 (5.6), 551 (4.5), 643 (4.2) nm

[5,15-Bis(1-ethylpropyl)porphyrin][CF_3COO]₂

^1H NMR (400 MHz, CDCl_3): δ = -1.01 (s, 4H, NH , N^+H), 1.05 (t, 3J = 4.7 Hz, 12H, CHCH_2CH_3), 2.85-3.06 (m, 8H, CHCH_2CH_3), 4.90 (m, 2H, CHCH_2CH_3), 9.33 (m, 4H, βH), 9.11 (m, 4H, βH), 10.59 (s, 2H, *meso H*) ppm; UV-vis (CH_2Cl_2 + 5% CF_3COOH): λ_{max} (lg ϵ) 411 (5.5), 562 (4.3), 608 (4.3) nm.

[5,10,15-Tris(1-ethylpropyl)porphyrin][CF_3COO]₂

^1H NMR (400 MHz, CDCl_3): δ = -0.40 (br, 4H, NH , N^+H), 1.07 (m, 18H, CHCH_2CH_3), 2.77-2.96 (m, 12H, CHCH_2CH_3), 4.64 (m, 3H, CHCH_2CH_3), 9.09 (m, 8H, βH), 10.12 (s, 1H, *meso H*) ppm; UV-vis (CH_2Cl_2 + 5% CF_3COOH): λ_{max} (lg ϵ) 421 (5.4), 574 (4.1), 623 (4.2) nm.

[5,10,15,20-Tetrakis(1-ethylpropyl)porphyrin][CF_3COO]₂

^1H NMR (400 MHz, CDCl_3): δ = 0.97 (m, 24H, CHCH_2CH_3), 3.37 (m, 16H, CHCH_2CH_3), 5.11 (m, 4H, CHCH_2CH_3), 9.66 (s, 8H, βH) ppm; UV-vis (CH_2Cl_2 + 5% CF_3COOH): λ_{max} (lg ϵ) 428 (5.3), 593 (4.0), 643 (4.2) nm.

6.6 Spectroscopic data of porphodimethene dications

UV-vis titrations were performed with a Perkin Elmer, Lambda 1050 spectrophotometer. Solutions of porphyrins **58**, **82** and PDMs **86** and **87** were prepared in spectrophotometric grade dichloromethane (Sigma). MeSO_3H , TFA solutions were also prepared in spectrophotometric grade dichloromethane, however, as not all materials were soluble in dichloromethane, HCl , HBr and HClO_4 were dissolved in spectrophotometric grade methanol. In order to assure that the protonation constant in dichloromethane was not dramatically affected by small amounts of methanol, a test titration was carried out with TFA in methanol. No noticeable differences were evident in the resulting spectra when compared to the corresponding titration with TFA in dichloromethane. NMR titrations were either carried out in deuterated chloroform or deuterated dichloromethane, HCl and HClO_4 were dissolved in deuterated methanol. To rule out effects from the use of methanol, $[\text{H}_4\text{TPP}](\text{Cl})_2$ was compared to previous results reported in the literature whereby protonation was achieved with TFA and

subsequent anion coordination was accomplished with TBA-Cl to observe binding.²⁵⁸ The resonances were comparable.

[5,5',10,10'15,20-Hexaphenylporphyrin][MeSO₃]₂

¹H NMR (600 MHz, CDCl₃): δ = 5.77 (s, 2H, βH), 6.79 (d, ³J = 4.6 Hz, 2H, βH), 6.86 (s, 2H, βH), 7.11 (d, ³J = 4.7 Hz, βH), 7.33 (m, 20H, Ar-H), 7.67 (d, ³J = 7.2 Hz, 4H, Ar-H), 7.75 (t, ³J = 7.2 HZ, Ar-H), 10.57 (s, 1H, NH), 14.15 (m, 3H, NH, N⁺H) ppm; ¹³C (150.9 MHz, CDCl₃): 110.7 (β-C), 125.5 (β-C), 127.4 (Ar-C), 128.2 (Ar-C), 128.3 (Ar-C), 128.5 (qC), 128.7 (β-C), 129.5 (Ar-C), 129.7 (qC), 130.7 (qC), 132.2 (qC), 133.0 (Ar-C), 134.6 (qC), 134.7 (Ar-C), 137.0 (qC), 137.9 (qC), 138.6 (qC), 142.3 (qC), 142.5 (qC), 148.2 (qC), 167.4 (qC), 172.6(qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 408 (4.9), 639 (4.5) nm.

[5,5',10,10'15,20-Hexaphenylporphyrin][CF₃COO]₂

¹H NMR (600 MHz, CD₂Cl₂): δ = 5.94 (d, ³J = 2.2 Hz, βH), 6.82 (m, 4H, βH), 7.20 (m, [2+8]H, βH, Ar-H), 7.31 (m, 12H, Ar-H, 7.61 (m, 8H, Ar-H), 7.80 (t, ³J = 7.0 Hz, 2H, Ar-H), 9.65 (s, 1H, NH) ppm; ¹³C NMR (150.9 MHz, CD₂Cl₂): δ = 111.2 (β-C), 126.2 (β-C), 127.7 (Ar-C), 128.3 (β-C), 128.4 Ar-C), 128.6 (Ar-C), 129.1 (Ar-C), 133.7 (qC), 133.8 (Ar-C), 134.8 (Ar-C), 136.4 (qC), 138.0 (β-C), 138.2 (qC), 141.5 (qC), 141.5 (qC), 148.7 (qC), 173.6 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 410 (4.8), 629 (4.5) nm.

[5,5',10,10'15,20-Hexaphenylporphyrin][ClO₄]₂

¹H NMR (600 MHz, CDCl₃): δ = 6.08 (d, 2H, ³J = 2.0 Hz, βH), 6.85 (d, ³J = 4.9 Hz, βH), 7.24 (m, [8+2]H, βH, Ar-H), 7.28 (m, 12H, Ar-H), 7.60 (m, 8H, Ar-H), 7.77 (m, 2H, Ar-H), 8.94 (s, 1H, NH) ppm; ¹³C, NMR, (150.9 MHz, CD₂Cl₂): δ = 111.2 (β-C), 126.3 (β-C), 127.9, (Ar-C), 128.6 (Ar-C), 129.1 (Ar-C), 129.8 (β-C), 133.9 (Ar-C), 134.6 (qC), 134.9 (Ar-C), 136.3 (qC), 137.8 (qC), 139.2 (β-C), 140.7 (qC), 148.5 (qC), 152.0 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 414 (4.9), 631 (4.5) nm.

[5,5',10,10'15,20-Hexaphenylporphyrin][Cl]₂

¹H NMR (400 MHz, CD₂Cl₂): δ = 5.87 (d, ³J = 4.9Hz, 2H, βH), 6.73 (d, ³J = 4.9 Hz, 2H, βH), 6.76 (s, 2H, βH), 6.97 (s, ³J = 4.9 Hz, 2H, βH), 7.17 (m, 12H, Ar-H), 7.50 (m, 8H,

Ar-*H*), 7.65 (m, 2H, Ar-*H*), 10.94 (s, 1H, *NH*) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 412 (4.8), 640 (4.5) nm.

[5,10,15,20-Tetrakis(4-methoxyphenyl)-5'10'-diphenylporphyrin][MeSO₃]₂

¹H NMR (400 MHz, CDCl₃): δ = 3.84 (s, 6H, OCH₃), 3.96 (s, 6H, OCH₃), 5.78 (br, 2H, β*H*), 6.71 (m, 2H, β*H*), 6.83 (d, d, ³*J* = 8.9 Hz, 4H, Ar-*H*), 6.94 (s, 2H, β*H*), 7.06 (d, ³*J* = 8.5 Hz, Ar-*H*), 7.09 (d, ³*J* = 4.0 Hz, β*H*), 7.22 (m, 4H, Ar-*H*), 7.31 (m, 10H, Ar-*H*), 7.63 (d, ³*J* = 8.3 Hz, 4H, Ar-*H*), 10.24 (br, 3H, *NH*, *N*⁺*H*), 13.61 (br, 6H, CH₃SO₃⁻) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ = 55.3(OCH₃), 55.8 (OCH₃), 110.8 (β-C), 113.7 (Ar-C), 114.4 (Ar-C), 124.4 (β-C), 127.4 (Ar-C), 128.4 (Ar-C), 129.3 (β-C), 130.8 (Ar-C), 134.6 (qC), 137.2 (qC), 137.6 (β-C), 138.1 (Ar-C), 142.4 (qC), 158.8 (qC), 165.0 (qC), 171.1 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} = 423 (4.8), 485 (4.5), 636 (4.4) nm.

[5,10,15,20-Tetrakis(4-methoxyphenyl)-5'10'-diphenylporphyrin][CF₃COO]₂

¹H NMR (400 MHz, CDCl₃): δ = 3.84 (m, 6H, OCH₃), 3.99 (s, 6H, OCH₃), 5.89 (d, ³*J* = 2.6 Hz, 2H, β*H*), 6.72 (d, ³*J* = 4.8 Hz, 2H, β*H*), 6.79 (d, d, ³*J* = 9.0 Hz, 4H, Ar-*H*), 6.83 (s, 2H, β*H*), 7.11 (m, 14H, Ar-*H*), 7.54 (d, ³*J* = 8.8 Hz, 4H, Ar-*H*), 9.50 (s, 1H, *NH*), 13.45 (s, 2H, *N*⁺*H*), 13.60 (s, 1H, *NH*) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ = 55.0 (OCH₃), 55.7 (OCH₃), 110.5 (β-C), 113.7 (Ar-C), 114.5 (Ar-C), 124.8 (β-C), 127.3 (Ar-C), 127.7 (β-C), 128.3 (Ar-C), 129.0 (Ar-C), 130.4 (Ar-C), 133.9 (qC), 136.8 (β-C), 137.6 (Ar-C), 141.3 (qC), 148.2 (qC), 158.7 (qC), 165.1 (qC), 171.2 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} = 423 (4.8), 480 (4.5), 627 (4.4) nm.

[5,10,15,20-Tetrakis(4-methoxyphenyl)-5'10'-diphenylporphyrin][ClO₄]₂

¹H NMR (600 MHz, CDCl₃): δ = 3.83 (s, 6H, OCH₃), 3.98 (s, 6H, OCH₃), 6.16 (s, 2H, β*H*), 6.72 (m, 2H, β*H*), 6.77, 6.81 (d, d, ³*J* = 8.2 Hz, Ar-*H*), 6.93 (s, 2H, β*H*), 7.08 (d, ³*J* = 8.6 Hz, Ar-*H*), 7.13 (d, ³*J* = 3.5 Hz, β*H*), 7.26 (m, 6H, Ar-*H*), 7.34 (m, 4H, Ar-*H*), 7.55 (d, ³*J* = 8.6 Hz, Ar-*H*), 8.67 (s, 1H, *NH*), 11.92 (s, 2H, *N*⁺*H*), 12.16 (s, 1H, *NH*) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ = 55.2 (OCH₃), 55.8 (OCH₃), 111.2 (β-C), 114.0 (Ar-C), 114.6 (Ar-C), 125.2 (β-C), 127.5 (Ar-C), 128.7 (Ar-C), 129.1 (Ar-C), 129.3 (β-C), 130.6 (Ar-C), 133.3 (qC), 134.4 (qC), 136.5 (qC), 137.7 (Ar-C), 138.2 (β-C), 141.7 (qC), 147.7 (qC), 158.8 (qC), 165.1 (qC), 171.4 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} = 425 (4.8), 499 (4.6), 636 (4.3) nm.

[5,10,15,20-Tetrakis(4-methoxyphenyl)-5'10'-diphenylporphyrin][Cl]₂

¹H NMR (600 MHz, CDCl₃): δ = 3.84 (m, 6H, OCH₃), 3.98 (s, 6H,)CH₃), 5.76 (s, 2H, βH), 6.78-6.83 (d, d, ³J = 4.4, 8.0 Hz, 2H, βH, 4H, Ar-H), 6.90 (s, 2H, βH), 7.07 (d, ³J = 4.4 Hz, 2H, βH), 7.11 (d, ²J = 8.6 Hz, 4H, Ar-H), 7.27 (m, 6H, Ar-H), 7.38 (br, 5H, Ar-H), 7.46 (m, 4H, Ar-H), 7.58 (d, ³J = 8.4 Hz, 4H, Ar-H), 11.28 (br, 1H, NH), 14.52 (s, 2H, N⁺H), 14.75 (s, 1H, NH) ppm; ¹³C NMR(150.9 MHz, CDCl₃): δ = 55.5 (OCH₃), 56.2 (OCH₃), 109.6 (β-C), 113.7 (Ar-C), 114.7 (Ar-C), 124.9 (β-C), 127.3 (qC), 127.7 (β-C), 128.4 (Ar-C), 130.0 (Ar-C), 130.2 (qC), 131.2 (qC), 131.4 (Ar-C), 132.8 (qC), 135.3 (qC), 136.1 (qC), 136.8 (β-C), 138.1 (Ar-C), 142.2 (qC), 143.7 (qC), 147.4 (qC), 158.9 (qC), 165.1 (qC), 167.8 (qC), 171.9 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} = 426 (4.8), 474 (4.5), 639 (4.4) nm.

[5,10,15,20-Tetraphenylporphyrin][MeSO₃]₂

¹H NMR (400 MHz, CD₂Cl₂): δ = -0.69 (s, 3H), -0.35 (s, 6H), 0.92 (br, 2H, NH), 8.08 (m, 12H, Ar-H), 8.70 (d, ³J = 6.7 Hz, 8H, Ar-H), 8.74 (s, 8H, βH) ppm; UV-vis (CH₂Cl₂): λ_{max} = 440 (5.6), 655 (4.7) nm.

[5,10,15,20-Tetraphenylporphyrin][ClO₄]₂

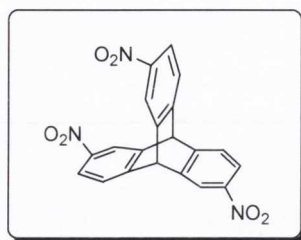
¹H NMR (400 MHz, CD₂Cl₂): δ = -2.10 (s, 1H, NH), 8.01 (m, 12H, Ar-H), 8.62 (d, ³J = 6.3 Hz, 8H, Ar-H), 8.81 (s, 8H, βH) ppm; UV-vis (CH₂Cl₂): λ_{max} = 454 (5.5), 695 (4.8) nm.

[5,10,15,20-Tetraphenylporphyrin][Cl]₂

¹H NMR (400 MHz, CD₂Cl₂): δ = -0.12 (s, 1H, NH), 0.84 (m, 3H, NH, N⁺H), 8.04 (m, 12H, Ar-H), 8.64 (m, 16H, Ar-H, βH) nm; UV-vis (CH₂Cl₂): λ_{max} = 454 (5.6), 693 (4.5) nm.

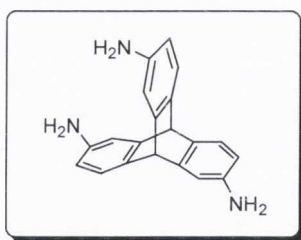
6.7 Triptycene-linked porphyrin trimers

2,6,14-Trinitrotriptycene **124**²⁶⁵

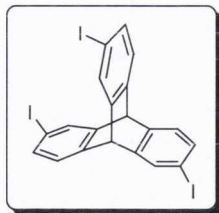


Triptycene (2.5 g, 10 mmol) was dissolved in concentrated HNO₃ (100 mL, 65%), and heated to 75 °C for 24 h. The brown solution was cooled to rt, poured into H₂O (1 L) and stirred. The precipitate was collected, washed with cold water and dried in air. The crude product was separated by column chromatography using dichloromethane/*n*-hexane (1:1, v/v) as eluent, to afford the title compound (3.3 g, 85%); ¹H NMR (400 MHz, CDCl₃): δ = 5.85 (s, 1H, CH), 5.87 (s, 1H, CH), 7.67 (m, 3H, Ar-H), 8.08 (dd, ⁴*J* = 2.1, ³*J* = 8.1 Hz, 3H, Ar-H), 8.36 (m, 3H, Ar-H) ppm. The NMR data were in agreement with the literature.

2,6,14-Triaminotriptycene **125**²⁶⁵



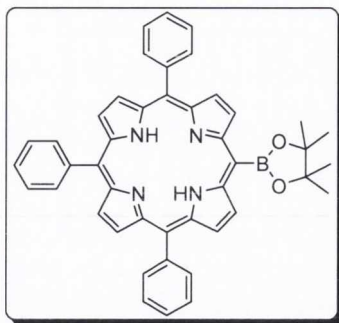
2,6,14-Trinitrotriptycene (1 g, 2.6 mmol) was dissolved in dry dichloromethane (20 mL) and dry methanol (20 mL) and palladium on carbon (1.4 g, 10 wt.%) was added. The suspension was placed in an ice bath and sodium borohydride (2.44 g, 65 mmol) was added slowly. After 30 min, the reaction mixture was filtered and washed with dichloromethane. The organic phase was washed with water (40 mL x 2) and brine (40 mL x 2). The organic solvent was removed *in vacuo* to yield a white solid in quantitative yield; ¹H NMR (400 MHz, CDCl₃): δ = 3.50 (b, 6H, NH₂), 5.05 (s, 1H, CH), 5.07 (s, 1H, CH), 6.74 (m, 3H, Ar-H), 6.27 (m, 3H, Ar-H), 6.74 (m, 3H, Ar-H) ppm. The NMR data were in agreement with literature data.

2,6,14-Triiodotriptycene 126²⁶⁵

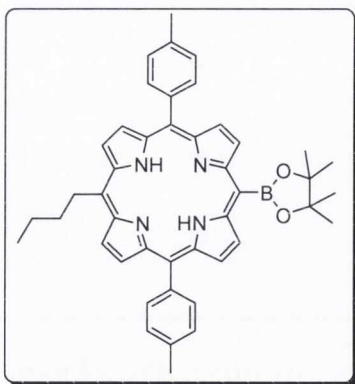
2,6,14-Triaminotriptycene (660 mg, 2.20 mmol) was dissolved in hydrochloric acid (5 mL) and water (10 mL). The reaction mixture was cooled in an ice bath. Sodium nitrite (501 mg, 7.3 mmol) was dissolved in water and added to the reaction mixture over a period of 10 min. Potassium iodide (2.75 g, 16.5 mmol) was dissolved in H₂O (5 mL) and added over 30 min. The mixture was heated to 80 °C for 2 h, cooled, and then extracted with dichloromethane (30 mL x 3). The combined extracts were washed with sodium bisulfate (20 mL x 2), dried over anhydrous sodium sulfate and concentrated to remove the organic solvents. The crude product was subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:3, v/v) as eluent to give the product as a white solid (372.5 mg, 27%). ¹H NMR (400 MHz, CDCl₃): δ = 5.29 (m, 2H, CH), 7.14 (d, ³J = 7.8 Hz, 3H, Ar-H), 7.38 (d, ³J = 7.5 Hz, 3H, Ar-H), 7.74 (b, 3H, Ar-H) ppm. The NMR data were in agreement with the literature.

General procedure for the boronylation of bromoporphyrins

A 100 mL Schlenk flask was charged with 5-bromo-10,15,20-trisubstitutedporphyrin or [5-bromo-10,15,20-trisubstitutedporphyrin]zinc (1 equiv.) and dried under vacuum. Dry 1,2-dichloroethane (20 mL) and dry triethylamine (13 equiv.) were added under argon. The solution was degassed *via* 3 freeze-pump-thaw cycles before the vessel was purged with argon. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (10 equiv.) and dichlorobis(triphenylphosphine)palladium(II) (0.03 equiv.) were added. The Schlenk tube was sealed and heated to 90 °C overnight. The reaction was cooled and quenched with a saturated KCl (10 mL) solution, washed with water and dried over anhydrous sodium sulfate. The organic solvents were removed *in vacuo* and subjected to purification *via* column chromatography.

5-(4',4',5',5'-Tetramethyl-[1',3',2']-dioxaborolan-2'-yl)-10,15,20-triphenylporphyrin 133

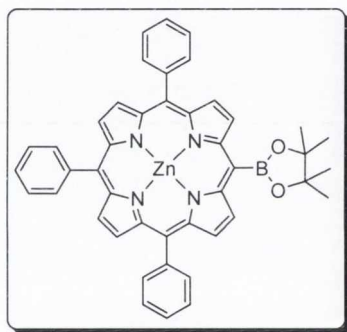
5-Bromo-10,15,20-triphenylporphyrin **131** (400 mg, 0.65 mmol), triethylamine (1.17 mL, 8.42 mmol), borolane (0.94 mL, 6.48 mmol) and dichlorobis(triphenylphosphine)-palladium(II) (13.6 mg, 0.02 mmol) were reacted according to the procedure outlined above and subjected to column chromatography using dichloromethane as eluent, to yield a purple solid (241.1 mg, 56%); mp >300 °C; R_f = 0.2 (SiO₂, dichloromethane/*n*-hexane 1:2, v/v); ¹H NMR (600 MHz, CDCl₃) δ = -2.75 (s, 2H, NH), 1.87 (s, 12H, CH₃), 7.78 (m, 9H, Ar-*H*), 8.24 (m, 6H, Ar-*H*), 8.85 (dd, ³*J* = 4.4, 14.2 Hz, 4H, β *H*), 9.00 (d, ³*J* = 4.6 Hz, 2H, β *H*), 9.89 (d, ³*J* = 4.6 Hz, 2H, β *H*) ppm; ¹³C NMR (150.9 MHz, CDCl₃) δ = 23.3(CH₃), 85.2 (qC), 120.0 (qC), 121.8 (qC), 126.6 (Ar-C), 127.7 (Ar-C), 134.5 (Ar-C), 142.0. (qC), 142.4 (qC) ppm; δ = $\lambda_{\max}$ (lg ϵ) 417 (5.4), 514 (4.3), 546 (4.0), 588 (4.0), 649 (3.9) nm; HRMS(ES⁺) [C₄₄H₃₈N₄+H] calcd. 665.3088, found 665.3109.

5-Butyl-15-(4',4',5',5'-tetramethyl-[1',3',2']dioxaborolan-2'-yl)-10,20-bis(4-methylphenyl)porphyrin 134

5-Bromo-15-butyl-10,20-ditolylporphyrin **132** (400 mg, 0.64 mmol), triethylamine (1.16 mL, 8.31 mmol), borolane (0.93 mL, 6.39 mmol) and dichlorobis(triphenylphosphine)-palladium(II) (13.5 mg, 0.02 mmol) were reacted according to the procedure outlined above and subjected to column chromatography

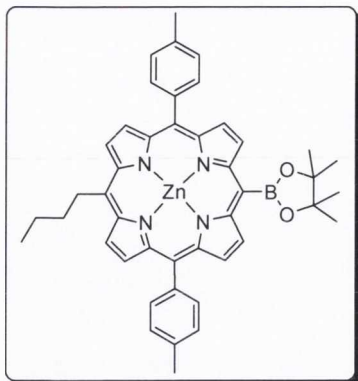
using dichloromethane as eluent, to yield a purple solid (283.9 mg, 66%); mp 191 °C; R_f = 0.32 (SiO₂, dichloromethane/*n*-hexane 1:2, v/v); ¹H NMR (400 MHz, CDCl₃) δ = -2.61 (s, 2H, NH), 1.15 (t, ³*J* = 7.4 Hz, 3H, CH₂CH₂CH₂CH₃), 1.85 (m, 14H, CH₃, CH₂CH₂CH₂CH₃), 2.56 (m, 2H, CH₂CH₂CH₂CH₃), 2.77 (s, 6H, tolyl-CH₃), 5.03 (t, ³*J* = 7.9 Hz, 2H, CH₂CH₂CH₂CH₃), 7.60 (d, ³*J* = 7.6 Hz, 4H, Ar-H), 8.12 (d, ³*J* = 7.6 Hz, 4H, Ar-H), 8.97 (dd, ³*J* = 4.6 Hz, 12.2, 4H, β H), 9.50 (d, ³*J* = 4.7 Hz, 2H, β H), 9.84 (d, ³*J* = 4.6 Hz, 2H, β H) ppm; ¹³C NMR (150.9 MHz, CDCl₃) δ = 14.2 (CH₃), 21.5 (CH₃), 23.7 (CH₂), 25.3 (CH₃), 35.2 (CH₂), 40.9 (CH₂), 85.0 (qC), 119.5 (qC), 122.5 (qC), 127.1 (β -C), 127.2 (Ar-C), 131.1 (β -C), 131.6 (β -C), 134.4 (Ar-C), 137.2 (qC), 139.7 (qC) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) 417 nm (5.35), 517 (4.22), 549 (3.79), 589 (3.77), 644 (3.53); HRMS (ES⁺) [C₄₄H₄₅BN₄O₂+H]: calcd 673.3714, found 673.3685.

[5-(4',4'',5',5''-Tetramethyl-[1',3',2]-dioxaborolan-2'-yl)-10,15,20-triphenylporphyrinato]zinc(II) 135



5-Bromo-10,15,20-triphenylporphyrin **131** (400 mg, 0.65 mmol), Et₃N (1.17 mL, 8.42 mmol), borolane (0.94 mL, 6.48 mmol) and dichlorobis(triphenylphosphine)-palladium(II) (13.6 mg, 0.02 mmol) were reacted according to the procedure outlined above to yield a purple solid (241.1 mg, 56%); mp >300 °C R_f = 0.14 (SiO₂, dichloromethane/*n*-hexane, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ = 1.90 (s, 12H, CH₃), 7.82 (m, 9H, Ar-H), 8.27 (m, 6H, Ar-H), 9.00 (m, 4H, β H), 9.14 (d, ³*J* = 4.6 Hz, 2H, β H), 9.97 (d, ³*J* = 4.6 Hz, 2H, β H) ppm; ¹³C NMR (150.9 MHz, CDCl₃) δ = 25.2 (CH₃), 85.1 (qC), 120.8 (qC), 122.4 (qC), 126.3 (Ar-C), 127.3 (ar-C), 131.3 (β -C), 132.0 (β -C), 137.8 (β -C), 134.2 (Ar-C), 142.7 (qC), 149.8 (qC), 150.3 (qC), 154.3 (qC) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) 414 (5.6), 548 (4.4), 585 (4.0) nm; HRMS(ES⁺) [C₄₄H₃₅N₄O₂Zn+H] calcd. 726.2145, found 726.2165.

[5-Butyl-15-(4',4',5',5'-Tetramethyl-[1',3',2']dioxaborolan-2'-yl)-10,20-bis(4-methylphenyl)porphyrin]zinc 136



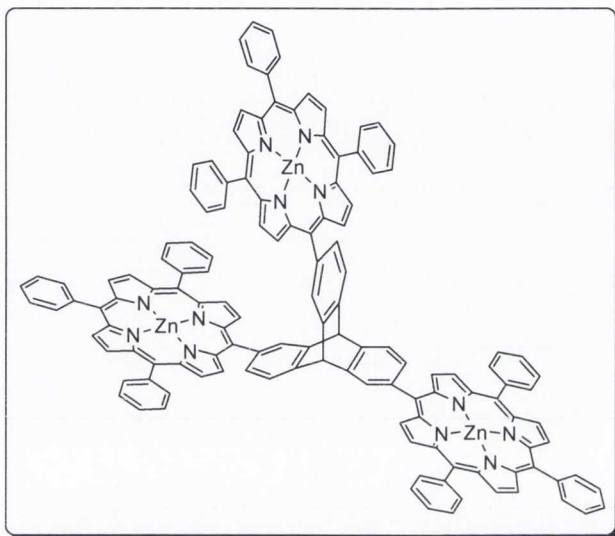
Metallation was performed on the crude product of the above reaction (before column chromatography). Filtration through a frit using silica gel and dichloromethane/*n*-hexane (1/1, v/v) isolated the debrominated porphyrin side product. Changing the eluent to dichloromethane yielded the title compound **136** as a purple solid (390.4 mg, 80% for two steps); mp >300 °C; R_f = 0.51 (SiO₂, dichloromethane/*n*-hexane 3:1, v/v) ¹H NMR (400 MHz, CDCl₃) δ = 1.17 (t, ³*J* = 7.4 Hz, 3H, CH₂CH₂CH₂CH₃), 1.90 (m, 14H, CH₃, CH₂CH₂CH₂CH₃), 2.54 (m, 2H, CH₂CH₂CH₂CH₃), 2.79 (s, 6H, tolyl-CH₃), 4.92 (m, 2H, CH₂CH₂CH₂CH₃), 7.62 (d, ³*J* = 7.2 Hz, 4H, Ar-H), 8.13 (d, ³*J* = 7.3 Hz, 4H, Ar-H), 9.05 (m, 4H, β H), 9.50 (m, 2H, β H), 9.91 (m, 2H, β H) ppm; ¹³C NMR (150.9 MHz, CDCl₃) δ = 14.2 (CH₃), 21.5(CH₃), 23.8 (CH₂), 25.3 (CH₃), 35.6 (CH₂), 41.2 (CH₂), 85.1 (qC), 120.4 (qC), 123.2 (qC), 127.7 (Ar-C), 128.9 (β -C), 131.8 (β -C), 132.9 (β -C), 134.4 (Ar-C), 137.0 (qC), 140.1 (qC), 149.2 (qC), 149.7 (qC), 150.0 (qC), 154.6 (qC) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 419 (5.7), 548 (4.5), 585 (4.1) nm; HRMS(ES⁺) [C₄₄H₄₃N₄O₂Zn+H] calcd. 734.2771, found 734.2749.

Suzuki-Miyaura coupling reaction

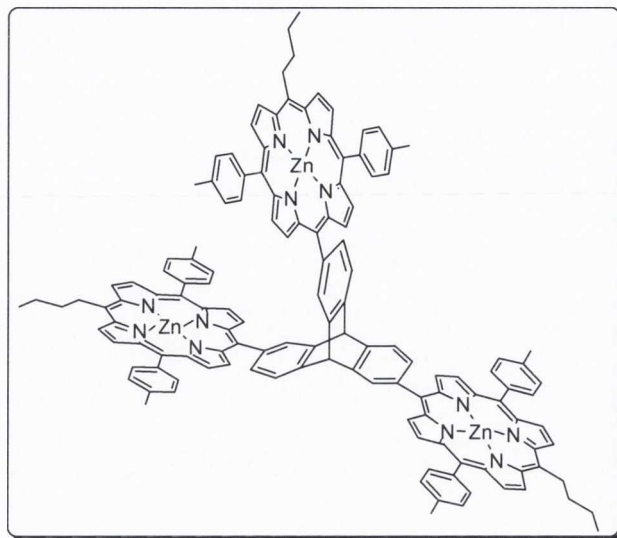
Boronate porphyrin (1 equiv.), 2,6,14-triiodotriptycene (0.3 equiv.) and potassium phosphate (4 equiv.) were added to a 100 mL Schlenk flask and dried under vacuum. The vacuum was released to allow the addition of dry dimethylformamide (25 mL). The mixture was degassed *via* three freeze-pump-thaw cycles before the vessel was purged with argon and tetrakis(triphenylphosphine)palladium(0) (0.1 equiv.) was added. The Schlenk flask was sealed and heated to 100 °C overnight (TLC control; dichloromethane/*n*-hexane 1:1, v/v). Then, the solvent was removed and the residue was

redissolved in dichloromethane, washed with aqueous sodium hydrogen carbonate. The crude porphyrin mixture was dried *in vacuo* and subjected to purification *via* column chromatography.

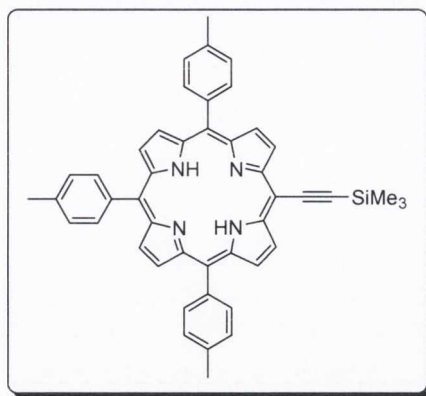
2,6,14-[Tris(5,10,15-triphenylporphyrin-20-ylato)zinc(II)]triptycene 140



Following the above procedure [5-(4',4',5',5'-tetramethyl-[1',3',2]-dioxaborolan-2'-yl)-10,15,20-triphenylporphyrinato]zinc(II) **135** (200 mg, 0.27 mmol), 2,6,14-triiodotriptycene (52.1 mg, 0.08 mmol), potassium phosphate (233.3 mg, 1.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (31.6 mg, 0.03 mmol) were reacted and subjected to purification *via* column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent. The title compound was obtained in a yield of 27% (44.4 mg); mp >300 °C; R_f = 0.21 (SiO₂, dichloromethane/*n*-hexane 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ = 6.16 (s, 1H, CH), 6.31 (s, 1H, CH), 7.82 (m, 27H, Ar-H), 8.01 (d, ³*J* = 7.1 Hz, 1H, Ar-H), 8.13 (d, ³*J* = 7.3 Hz, 1H, Ar-H), 8.17 (m, 1H, Ar-H), 8.30 (m, 20H, Ar-H), 8.52 (s, 1H, Ar-H), 8.61 (s, 1H, Ar-H), 8.70 (s, 1H, Ar-H), 8.99-9.11 (m, 18H, βH), 9.22 (m, 6H, βH) ppm; ¹³C (150.9 MHz, CDCl₃): δ = 56.2 (Ar-C), 120.7 (AR-C), 122.4 (Ar-C), 126.6 (Ar-C), 127.5 (Ar-C), 130.6 (Ar-C), 132.0 (Ar-C), 132.1 (β-C), 132.4 (β-C), 134.5 (Ar-C) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) 424 (5.9), 548 (4.6), 587 (4.0) nm; HRMS (MALDI LD⁺) [C₁₃₄H₈₀N₁₂Zn₃+H]: calcd. 2048.4503, found 2048.4529.

2,6,14-[Tris(5-*n*-butyl-10,20-ditolylporphyrin-20-ylato)zinc(II)]tritycene 141

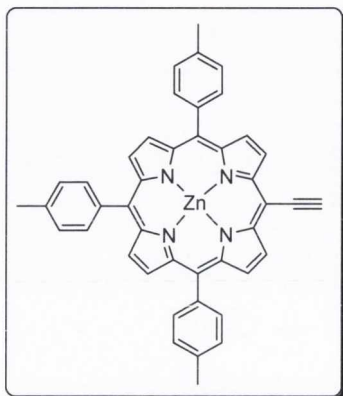
Following the above procedure [5-Butyl-15-(4',4',5',5'-tetramethyl-[1',3',2']dioxaborolan-2'-yl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) **136** (200 mg, 0.27 mmol), 2,6,14-triodotriptycene (51.5 mg, 0.08 mmol), potassium phosphate (230.7 mg, 1.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (31.4 mg, 0.03 mmol) were reacted and subjected to purification *via* column chromatography on silica gel using dichloromethane/*n*-hexane (2:1, v/v) as eluent. The title compound was obtained in a yield of 22% (22 mg, 27%); $>300^{\circ}\text{C}$; $R_f = 0.41$ (SiO_2 , dichloromethane/*n*-hexane 1:2, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.18$ (t, $^3J = 7.3$ Hz, 9H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.90 (m, 6H $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.60 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.77 (s, 6H, tolyl- CH_3), 2.79 (s, 12H, tolyl- CH_3), 5.04 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 6.10 (s, 1H, Ar-H), 6.26 (s, 1H, Ar-H), 7.62 (m, 12H, Ar-H), 7.97 (d, $^3J = 7.3$ Hz, 1H, Ar-H), 8.14 (m, 18H, Ar-H), 8.54 (s, 1H, Ar-H), 8.63 (s, 1H, Ar-H), 9.07 (m, 18H, βH), 9.58 (m, 6H, βH) ppm; ^{13}C (150.9 MHz), CDCl_3): 13.9 (CH_3), 21.4 (CH_3), 23.6 (CH_2), 35.4 (CH_2), 41.0 (CH_2), 46.2 (qC), 54.3 (Ar-C), 120.5 (qC), 122.2 (Ar-C), 127.2 (Ar-C), 128.6 ($\beta\text{-C}$), 130.4 (Ar-C), 130.7 (Ar-C), 131.7 ($\beta\text{-C}$), 132.1 ($\beta\text{-C}$), 132.3 ($\beta\text{-C}$), 134.2 (Ar-C), 136.9 (qC), 139.9 (qC), 149.9 (qC), 150.4 (qC) ppm; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ) 424 (6.0), 552 (4.8), 593 (4.6) nm. HRMS (MALDI LD^+) [$\text{C}_{134}\text{H}_{104}\text{N}_{12}\text{Zn}_3+\text{H}$]: calcd. 2072.6381, found 2072.6462.

5,10,15-Tritolyl-20-trimethylsilylethynylporphyrin **146**⁴²

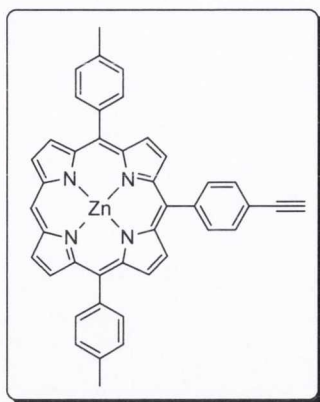
Pyrrole (1.38 mL, 22 mmol), *p*-toluladehyde (1.42 mL, 11.6 mmol) and 3-trimethylsilylpro-2-pynal (1.18 mL, 10.8 mmol) were dissolved in dry chloroform (1.8 L), in a three-neck, 2 L, round-bottom flask equipped with an argon inlet. The flask was shielded from ambient light before trifluoroboron etherate (0.26 mL, 1.58 mmol) was added. The reaction was stirred at rt overnight, after which DDQ (3.4 g, 15 mmol) was added. The reaction mixture was stirred for a further hour. Triethylamine (3 mL) was added before the crude mixture was filtered through a layer of silica gel using dichloromethane as eluent. The organic solvents were evaporated *in vacuo* and the crude product was subjected to purification *via* column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent. The first fraction contained trace amounts of 5,10,15,20-tetra(trimethylsilylethynyl)porphyrin **142**. The second fraction contained 5-tolyl-10,15,20-tri(trimethylsilylethynyl)porphyrin **143** (60 mg, 2%): $R_f = 0.75$ (SiO₂, dichloromethane/*n*-hexane 1:1, v/v); ¹H NMR (400 MHz, CDCl₃) $\delta = -2.12$ (s, 2H, NH), 0.66 (s, 18H, SiCH₃), 0.68 (s, 9H, SiCH₃), 2.75 (s, 3H, tolyl-CH₃), 7.60 (d, ³ $J = 7.6$ Hz, 3H, Ar-H), 8.06 (d, ³ $J = 7.6$ Hz, 2H, Ar-H), 8.80 (d (³ $J = 4.6$ Hz, 2H, βH), 9.52 (d, ³ $J = 4.6$ Hz, 2H, βH), 9.58 (dd, ³ $J = 8.5, 4.6$ Hz, 4H, βH) ppm. The third fraction contained a mixture of 5,10-ditolyl-15-,20-di(trimethylsilylethynyl)porphyrin and 5,15-ditolyl-10,20-di(trimethylsilylethynyl)-porphyrin **144** and **145** (168 mg 4%): $R_f = 0.67$ (SiO₂, dichloromethane/*n*-hexane 1:1, v/v). The fourth fraction contained the title compound **146** (310 mg, 8%): $R_f = 0.59$ (SiO₂, dichloromethane/*n*-hexane 1:1, v/v); ¹H NMR (400 MHz, CDCl₃) $\delta = -2.37$ (s, 2H, NH), 0.65 (s, 9H, SiCH₃), 2.73 (s, 3H, tolyl-CH₃), 2.75 (s, 6H, tolyl-CH₃), 7.57 (d, ³ $J = 7.9$ Hz, 2H, Ar-H), 7.61 (d, ³ $J = 7.8$ Hz, 4H, Ar-H), 8.09 (d, ³ $J = 8.0$ Hz, 2H, Ar-H), 8.11 (d, ³ $J = 7.8$ Hz, 4H, Ar-H), 8.82 (s, 4H βH), 8.95 (d, ³ $J = 4.7$ Hz, 2H, βH), 9.67 (d, ³ $J = 4.7$ Hz, 2H, βH) ppm; UV-vis (CH₂Cl₂):

$\lambda_{\max}$ (lg ϵ) = 453 (5.4), 568 (4.3), 607 (4.7), 648 (4.2), 670 (4.1) nm. The final fraction contained 5,10,15,20-tetratolylporphyrin **147** (515.5 mg, 14%) R_f = 0.48 (SiO₂, dichloromethane/*n*-hexane 1:1, v/v); UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 420 (5.7), 517 (4.4), 553 (4.2), 593 (4.1), 659 (4.0) nm. The spectroscopic data were in agreement with the literature.

[5-Ethynyl-10,15,20-tritolylporphyrinato]zinc(II) **149**⁴²



A 50 mL round bottom flask was charged with [5,10,15-tritolyl-20-(trimethylsilyl-ethynyl)porphyrinato]zinc(II) **146** (335 mg, 0.45 mmol) and tetrabutylammonium fluoride (0.6 mL of a 1 M solution in THF 0.6 mmol). The reaction mixture was stirred at rt for 30 min (TLC control). The crude product was then filtered through a short layer of silica gel using dichloromethane as eluent. The solvent was removed under reduced pressure and the product **149** was obtained in quantitative yield. R_f = 0.45 (SiO₂, dichloromethane/*n*-hexane 1:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ = 2.73 (s, 3H, tolyl-CH₃), 2.75 (s, 6H, tolyl-CH₃), 4.17 (s, 1H, C $\equiv$ CH), 7.58 (m, 6H, Ar-H), 8.09 (m, 6H, Ar-H), 8.93 (s, 4H, β H), 9.04 (d, ³*J* = 4.5 Hz, 2H, β H), 9.77 (d, ³*J* = 4.5 Hz, 2H, β H) ppm; ¹³C NMR (150.9 MHz, CDCl₃) δ = 21.3 (CH₃), 83.1 (CH), 127.2 (Ar-C), 130.6 (β -C), 131.6 (β -C), 132.9 (β -C), 134.1 (Ar-C), 137.1 (qC), 139.4 (qC), 149.9 (qC), 150.6 (qC), 152.5 (qC) ppm; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) 427 (5.7), 558 (4.5), 599 (4.3) nm. The NMR data were in agreement with the literature.

5-Phenylethynyl-10,20-ditolylporphyrin **154**⁶⁰

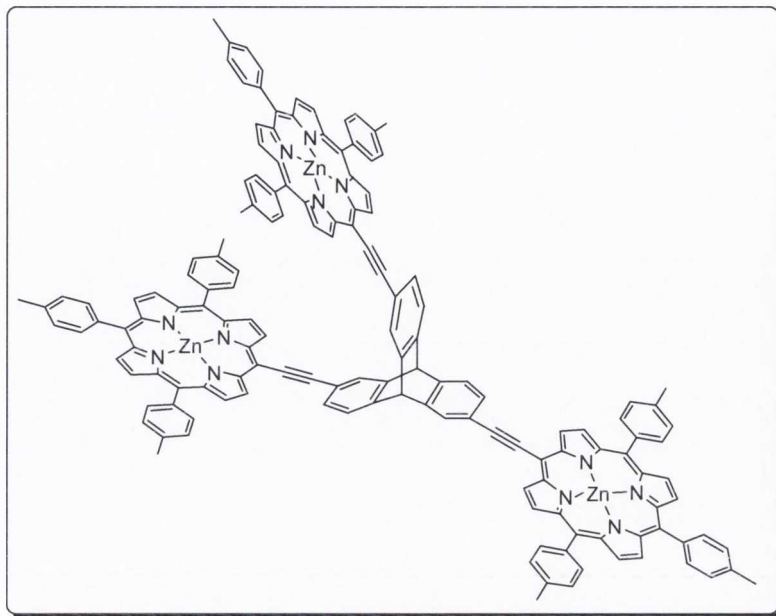
A 100 mL, 3-neck round-bottom flask was dried under high vacuum, purged with argon and charged with 1-bromo-4-ethynylbenzene (0.91 g, 5 mmol). Dry diethyl ether (<5 mL) was added and the solution was cooled to -70°C . *n*-Butyllithium (4 mL of a 2.5 M solution in hexanes, 10 mmol) was added dropwise over 1 h at -70°C . The reaction mixture was warmed to -40°C and dry THF was added until a white/pink suspension formed (~2 mL). Then, 5,15-ditolylporphyrin (200 mg, 0.41 mmol) dissolved in THF (80 mL), was added rapidly to the vigorously stirred solution and the reaction was stirred at rt for 4 h (colour change to brown). Saturated ammonium chloride (2 mL, colour change to green) and DDQ (280 mg, 1.23 mmol, colour change to red) were added. After 1 h, the crude product was filtered through a layer of silica gel using dichloromethane as eluent. Recrystallisation from dichloromethane/methanol yielded **153** (167 mg, 69%); $R_f = 0.5$ (SiO_2 , dichloromethane/*n*-hexane 1:1, v/v); ^1H NMR (400 MHz, CDCl_3) $\delta = -2.99$ (s, 2H, NH), 2.75 (s, 6H, tolyl- CH_3), 3.35 (s, 1H, $\text{C}\equiv\text{CH}$), 7.62 (d, $^3J = 7.7$ Hz, 4H, Ar-H), 7.91 (d, $^3J = 7.8$ Hz, 2H, Ar-H), 8.15 (d, $^3J = 7.7$ Hz, 4H, Ar-H), 8.20 (d, $^3J = 7.8$ Hz, 2H, Ar-H), 8.86 (d, $^3J = 4.8$ Hz, 2H, βH), 8.96 (d, $^3J = 4.8$ Hz, 2H, βH), 9.07 (d, $^3J = 4.7$ Hz, 2H, βH), 9.37 (d, $^3J = 4.6$ Hz, 2H, βH), 10.25 (s, 1H, *meso* CH) ppm. The NMR data were in agreement with the literature.

153 was dissolved in chloroform (50 mL) and added to a 100 mL round bottom flask equipped with a reflux condenser and brought to reflux. $\text{Zn}(\text{OAc})_2$ (10 equiv.) was dissolved in methanol and added to the refluxing solution. The progress of the reaction was monitored by TLC. After 15 min. the heat source was removed and the solution was allowed to cool before being passed through a plug of silica using dichloromethane as eluent. The product **154** was obtained as a pink solid in quantitative yield; mp >300

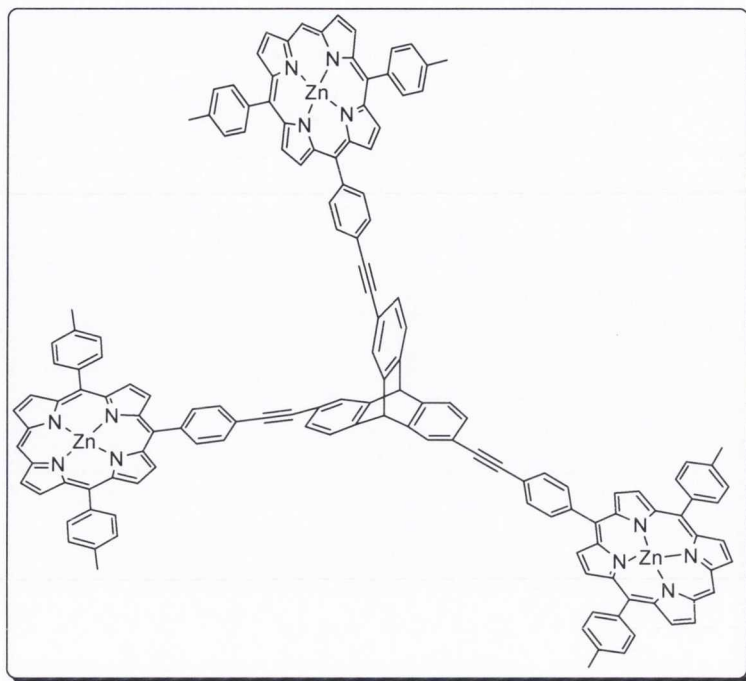
$^{\circ}\text{C}$; $R_f = 0.46$ (dichloromethane/*n*-hexane, 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 2.76$ (s, 6H, CH_3), 3.34 (s, 1H, $\text{C}\equiv\text{CH}$), 7.61 (d, $^3J = 7.6$ Hz, 4H, Ar-H), 7.92 (d, $^3J = 7.6$ Hz, 2H, Ar-H), 8.14 (d, $^3J = 8.2$ Hz, 4H, Ar-H), 8.21 (d, $^3J = 8.2$ Hz, 2H, Ar-H), 8.97 (d, $^3J = 4.7$ Hz, 2H, β -H), 9.06 (d, $^3J = 4.7$ Hz, 2H, β -H), 9.13 (d, $^3J = 4.7$ Hz, 2H, β -H), 9.38 (d, $^3J = 4.1$ Hz, 2H, β -H), 10.23 (s, 1H, *meso* CH) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 21.6, 83.8, 105.9, 120.2, 120.8, 121.3, 127.4, 130.3, 131.5, 131.7, 132.1, 132.7, 134.4, 134.5, 137.2, 139.6, 143.7, 149.3, 149.7, 150.3$ ppm; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ) = 415 (5.7), 542 (4.8) nm; HRMS (ES^+): $[\text{C}_{42}\text{H}_{30}\text{N}_4\text{M}^+]$: calcd 652.1605, found 652.1588.

General procedure for the Sonogashira coupling reaction

Ethynyl-substituted porphyrins (1.0 equiv.), 2,6,14-triiodotriptycene (0.33 equiv.) and triphenylarsine (2.0 equiv.) were added to a 100 mL Schlenk flask and dried under vacuum. The vacuum was released to allow for the addition of dry THF (10 mL) and dry triethylamine (5 mL). The mixture mixture was degassed *via* three freeze-pump-thaw cycles before the vessel was purged with argon and tris(dibenzylideneacetone)-dipalladium(0) was added. The Schlenk tube was sealed and the reaction mixture stirred overnight at 30°C . Then, dichloromethane (60 mL) was added, the mixture was washed with water (2 x 30 mL) and dried over sodium hydrogen carbonate. The solvent was evaporated under reduced pressure and the product purified by column chromatography on silica gel.

2,6,14-[Tris(10,15,20-tritolylporphyrin-20-ylato)zinc(II)]ethynetriptycene **156**

[5-Ethynyl-10,15,20-Tritolylporphyrinato]zinc(II) **149** (100 mg, 0.15 mmol) 2,6,14-triiodo-triptycene (31.5 mg, 0.05 mmol), triphenylarsine (91.7 mg, 0.3 mmol) and tris(dibenzylideneacetone)dipalladium(0) (27.4 mg, 0.03 mmol) were reacted according to the above procedure. The crude product was subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent to yield the title compound **156** (mg, 28%); mp >300 °C; R_f = 0.61 (SiO₂, dichloromethane/*n*-hexane 3:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ = 2.75 (m, 27H, tolyl-CH₃), 5.93 (s, 1H, Ar-H), 6.00 (s, 1H, Ar-H), 7.59 (m, 24H, Ar-H), 7.83 (m, 6H, Ar-H), 8.11 (m, 24H, Ar-H), 8.29 (s, 1H, Ar-H), 8.32 (s, 1H, Ar-H), 8.35 (s, 1H, Ar-H), 8.91 (m, 12H, βH), 9.06 (m, 6H, βH), 9.86 (m, 6H, βH) ppm; ¹³C (150.9 MHz, CDCl₃): δ = 21.4 (CH₃), 53.9 (Ar-C), 121.4 (qC), 124.2 (Ar-C), 127.2 (qC), 127.2 (Ar-C), 128.7 (Ar-C), 129.2 (Ar-C), 130.6 (Ar-C), 131.7 (Ar-C), 132.8 (Ar-C), 134.1 (Ar-C), 134.2 (qC), 137.1 (qC), 139.4 (qC), 144.9 (qC), 149.8 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) = 443 (6.0), 527 (4.2), 566 (4.7), 614 (4.9) nm; HRMS (MALDI LD⁺) [C₁₄₉H₉₈N₁₂Zn₃+H]: calcd. 2246.5912, found 2246.5916.

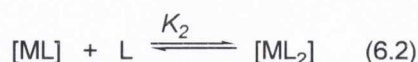
2,6,14[Tris(10,20-ditolylporphyrin-5-ylato)zinc(II)]phenylethyne triptycene 157

[5-Phenylethynyl-10,20-ditolylporphyrinato]zinc(II) **155** (100 mg, 0.15 mmol) 2,6,14-triiodotriptycene (32.2 mg, 0.05 mmol), triphenylarsine (93.6 mg, 0.3 mmol) and tris(dibenzylideneacetone)dipalladium(0) (28.0 mg, 0.03 mmol) were reacted according to the above procedure. The crude product was subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent to yield the title compound **156** (39.6 mg, 36%); mp >300 °C; R_f = 0.49 (SiO₂, dichloromethane/*n*-hexane 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ = 2.77 (m, 18H, tolyl-CH₃), 5.66 (s, 1H, Ar-H), 5.68 (s, 1H, Ar-H), 7.49 (d, ³*J* = 6.9 Hz, 3H, Ar-H), 7.62 (m, 12H, Ar-H), 7.74 (m, 3H, Ar-H), 7.87 (m, 3H, Ar-H), 7.96 (d, ³*J* = 7.9 Hz, 6H, Ar-H), 8.15 (m, 12H, Ar-H), 8.24 (d, ³*J* = 7.9 Hz, 6H, Ar-H), 9.04 (m, 12H, βH), 9.13 (m, 6H, βH), 9.37 (m, 6H, βH), 10.20 (m 3H, *meso*CH) ppm; ¹³C (150.9 MHz, CDCl₃): δ = 21.4 (CH₃), 53.7 (Ar-C), 106.0 (*meso*-CH), 124.7 (Ar-C), 125.2 (qC), 127.2 (Ar-C), 128.2 (Ar-C), 128.8 (Ar-C), 129.6 (Ar-C), 130.3 (qC), 131.6 (Ar-C), 132.0 (Ar-C), 132.6 (Ar-C), 134.3 (Ar-C), 137.0 (qC), 143.2 (qC) ppm; UV-vis (CH₂Cl₂): λ_{max} (lg ε) = 415 (6.0), 542 (4.6), 581 (3.5) nm; HRMS (MALDI LD⁺) [C₁₄₆H₉₂N₁₂Zn₃+H]: calcd. 2204.5442, found 2204.5479.

6.8 Determination of Binding Constants

UV-vis titrations were performed with a Perkin Elmer, Lambda 25 spectrophotometer. Solutions of porphyrin monomer **158** and trimers **140**, **156** and **157** were prepared in spectrophotometric grade dichloromethane (Sigma). 4-4'-bipyridine solutions were also prepared in spectrophotometric grade dichloromethane.

Within this thesis, the binding constants have been determined by using the nonlinear least-squares program SPECFIT/32TM, which is a multivariate data analysis program for modeling and fitting experimental data sets (such as chemical kinetics and equilibrium titrations) obtained from multivariate spectrophotometric measurements. The fitting methodology, which relies on the use of various mathematical parameters,³²¹ uses the Levenberg-Marquardt procedure to minimise the least-squares residuals between the data set and the model system.³²² In order to solve the number of species (speciation) present at equilibrium, SPECFIT takes advantage of the Newton-Raphson method. The model used specifies various states of interaction, for instance complexation between Host and Guest species, in terms of the overall stability constants (β). Considering the two stepwise equilibrium process involved in the binding interaction between a host (M) and a guest (L), the equilibrium constants K_1 and K_2 implicated in the interaction can be expressed using Equation 6.1 and Equation 6.2.



Brackets signify equilibrium molar concentrations. The stepwise binding constants K_1 and K_2 can be determined using Equations 6.3 and 6.4.

$$K_1 = \frac{[ML]}{[M][L]} \quad (6.3)$$

$$K_2 = \frac{[ML_2]}{[M][L]} \quad (6.4)$$

The overall equilibrium constant for this process, β , is the product of the two stepwise constants K_1 and K_2 ($\beta = K_1.K_2$). SPECFIT yields binding constants as cumulative $\log \beta$ values. So, for the 1:2 (M:L₂) equilibrium process this is translated by the $\log \beta_{1:2}$, which represents the sum of the individual constants ($\log \beta_{1:2} = \log K_1 + \log K_2$). Therefore, for any multi-step equilibrium, by subtraction of successive $\log \beta$ values, the $\log K$ for each equilibrium step can then be determined.

This program automatically scales its calculations with the supplied initial concentrations (allowing for dilution).

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