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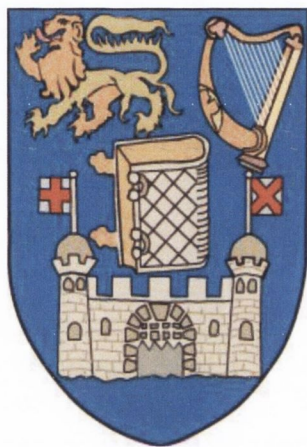
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Development of Synthetic Strategies Towards Multiporphyrin Arrays



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

Doctor of Philosophy

University of Dublin, Trinity College

December 2011

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Summary

The aim of this research was to develop synthetic strategies for the construction of multiporphyrin arrays with enhanced π -conjugation. Porphyrin oligomers with extended conjugation display a bathochromic shift in their absorption profiles and thus have a diverse range of potential optical applications. As Prof. Senge's group has interest in the areas of photodynamic therapy (PDT) and non-linear optics (NLO), the design of such oligomers took these into account.

One method to enhance the bathochromic shift is via the creation of conjugatively linked porphyrin oligomers. In our work, a series of symmetric and unsymmetric dimeric and trimeric porphyrin systems which are connected via conjugated linkers, namely alkyne and phenylacetylene, were synthesised via palladium catalysed C-C coupling reactions. These novel unsymmetric dimers and symmetric trimers were synthesised via the incorporation of all substituents on the monomeric components prior to coupling. The majority of these conjugated arrays exhibited a significant bathochromic shift in their UV/vis absorption profiles, in particular the alkyne linked arrays which showed absorption greater than 720 nm. The mass spectrometry spectra for phenylacetylene and diphenylbutadiene linked zinc arrays exhibited detachment of zinc from the porphyrin core in their spectra. These unusual results are both linker and metal dependent, usually only seen for more labile metals.

To further extend the absorption profile, a series of symmetric and unsymmetric dimeric and oligomeric porphyrin β - β , meso-meso, β '- β ' triply fused systems were synthesised via oxidative coupling methods. These arrays exhibit a dramatic bathochromic shift into the near-infrared region, many displaying absorption of greater than 1050 nm. Again, a library of bisporphyrins were synthesised in moderate to good yields, employing a diverse range of substituents on the porphyrin peripheries. Adopting a stepwise synthetic strategy, unsymmetric directly linked dimers were synthesised, both fully substituted as well as dimers containing a free meso position. Attempts to triply fuse these bisporphyrins had mixed results, with the isolation of the free meso arrays being difficult. A tetrameric fused array, incorporating alkynyl linked porphyrins was synthesised, the first known example, to our knowledge, of such an array and it exhibited unusual photophysical results. Encouraging preliminary biological studies of a symmetric triply-fused dimer indicate that these may be applicable to the field of PDT.

To enable the fine-tuning of the bisporphyrins synthesised, the reactivity of such was investigated via bromination, nitration, cycloaddition and organolithium reactions. Further post-fusing chemical transformations, namely organolithium, cycloaddition and transition-metal catalysed reactions, at the meso- and β -positions enables the fine-tuning of such arrays with the aim of enhancing the bathochromic shift and their potential optical applications. Via organolithium methods, a chlorin fused dimer was synthesised, few of which are known in the literature.

Finally, a series of porphyrin-carbazole conjugates were synthesised for OLED studies via a novel synthetic strategy. Carbazole linked porphyrin dimers were synthesised in good to excellent yields via stepwise Suzuki coupling reactions using bromoporphyrins and borylated carbazoles as the precursors, the latter of which were synthesised via known procedures from biphenyl derivatives. For comparative purposes porphyrin-carbazole monomers with different metal centres were synthesised. Single layer organic light emitting diodes (OLEDs) were created to demonstrate the optical properties of these materials. Light emission from these carbazole substituted porphyrins showed better results compared to previously examined bromo substituted porphyrins with better electroluminescence and lower turn-on voltages. Dimers exhibited turn-on voltages of 3V compared to 6V for monomeric porphyrin-carbazoles. Such results display the potential of porphyrin oligomers as OLEDs.

Publications

Ryan, A., Gehrold, A., Perusitti, R., Pintea, M., Fazekas, M., Locos, O. B., Blaikie, F., Senge, M. O. "Porphyrin dimers and arrays" *Eur. J. Org. Chem.*, **2011**, 5817-5844.

Cover Picture "Porphyrin dimers and arrays" *Eur. J. Org. Chem.*, **2011**, 5817-5844.

Ryan, A., Tuffy, B., Horn, S., Blau, W., Senge, M. O. "Carbazole-linked porphyrin dimers as organic light emitting diodes: Synthesis and initial photophysical studies" *Tetrahedron*, **2011**, 67, 8248-8254.

Senge, M. O., Pintea, M., Ryan, A. "Synthesis and crystal structure of a meso-meso directly linked bisporphyrin" *Zeitschrift für Naturforschung*, **2011**, 66b, 553-558.

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Senge M.O., Richter J., Bischoff I., Ryan A. "Highly substituted 2,3,7,8,12,13,17,18-octaethylporphyrins with meso aryl residues" *Tetrahedron*, **2010**, 66, 3508–3524.

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Rogers, L., Ryan, A., Senge, M. O. "Synthetic strategies for unsymmetrical porphyrins and porphyrin arrays for QSAR studies in photodynamic therapy" *TCD Medical School Tercentenary Symposium*. TCBI, Trinity College Dublin, Ireland. 04th November **2011**.

Rogers, L., Ryan, A., Senge, M. O. "Synthetic strategies for unsymmetrical porphyrins and porphyrin arrays for QSAR studies in photodynamic therapy" *14th Congress of the European Society for Photobiology.*, Geneva, Switzerland. 01st – 06th September **2011**.

Korodi, I. G, Lehmann, D., Pop, S., Ryan, A., Senge, M. O., Zahn, D. R. T. "Characterisation of organic field-effect transistors using zinc tetraphenylporphyrin monomers and dimers as active layers" *75th Annual Meeting of the DPG*, Dresden, Germany. 13th – 18th March **2011**.

Pop, S., Kate, P., Ryan, A., Zhang, X., Rappich, J., Esser, N., Hinrich, K., Senge, M. O. "Thin films of ethyne-linked porphyrin dimers investigated by spectroscopic ellipsometry" *75th Annual Meeting of the DPG*, Dresden, Germany. 13th – 18th March **2011**.

Ryan, A., Senge, M. O. "Synthesis of Porphyrin Oligomers for Applications in Photodynamic Therapy" *Recent Advances in Synthesis & Chemical Biology VII, CSCB Symposium*, TCD, Dublin, Ireland. 10th December **2010**.

Ryan, A., Senge, M. O. "Synthesis of Porphyrin Oligomers for Applications in Photodynamic Therapy" *Tetrapyrrole Discussion Group, TPDG*, Berlin, Germany. 15th – 16th September, **2010**.

Ryan, A., Horn, S., Senge, M. O. "Synthesis of Porphyrin Oligomers for Applications in Photodynamic Therapy" *Sixth International Conference on Porphyrins and Phthalocyanines, ICPP*, New Mexico, USA. 04th -09th July **2010**.

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Abbreviations

acac	acetylacetonate
AcOH	glacial acetic acid
BAHA	tris(4-bromophenyl)aminiumhexachloroantimonate
BChl	bacteriochlorophyll
Bu	butyl
calcd	calculated
COSY	correlation spectroscopy
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
dd	double doublet
DCE	1,2-dichloroethane
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DME	dimethoxyethane
DMF	<i>N,N'</i> -dimethylformamide
DPM	dipyrromethane
EAS	electrophilic aromatic substitution
equiv	equivalents
ESI	electrospray ionisation
GM	Goeppert Mayer
Hex	hexyl
HOMO	highest occupied molecular orbital
HpD	haematoporphyrin derivative
HRMS	high resolution mass spectrometry
IR	infrared
LH2	light harvesting complex II
LUMO	lowest unoccupied molecular orbital
m	multiplet
mp	melting point
MALDI	matrix assisted laser desorption ionisation
Me	methyl
MeOH	methanol

MW	microwave
m/z	mass-to-charge ratio
NBS	<i>N</i> -bromosuccinimide
NIR	near infrared
NLO	non-linear optics
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
OAc	acetate
OELD	organic electroluminescent device
OEP	2,3,7,8,12,17,18-octaethylporphyrin
OLED	organic light emitting diode
OTf	triflate
PFO	polyfluorene
PhLi	phenyllithium
PhOLED	phosphorescent organic light emitting diode
PIFA	phenyliodine(bis-trifluoroacetate)
PPh ₃	triphenylphosphine
ppm	parts per million
PVK	poly(<i>N</i> -vinylvarbazole)
q	quartet
RC	reaction centre
R _f	retention factor
rt	room temperature
s	singlet
t	triplet
TEA	triethylamine
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TOCSY	total correlation spectroscopy
tol	tolyl
2PA	two-photon absorption
TPP	5,10,15,20-tetraphenylporphyrin
UV	ultraviolet

vis

visible

v/v

volume to volume

CHAPTER 1:

Introduction

1. Introduction

1.1 Porphyrins - Basic structure and roles in nature

Porphyrin is the name given to a family of compounds whose common structural feature is a tetrapyrrole macrocyclic ring. They are intensely coloured compounds and the name porphyrin is derived from the Greek word *porphura*, which was used to describe the colour purple in ancient times.^[1] The macrocyclic ring is made up of four pyrrole-type ring units linked together by four methine bridging groups whose structure was first proposed by Küster in 1912^[2] and proved by Fischer in 1929 upon his synthesis of heme, the iron porphyrin which occurs in hemoproteins.^[3-4] Of the 22 conjugated π -electrons in the parent porphyrin structure, shown in Figure 1, only 18 π -electrons take part in the aromatic system, thus obeying Hückel's law for aromaticity ($4n+2$).^[5] The other four π -electrons possess more double bond character and are not involved in the aromatic system.

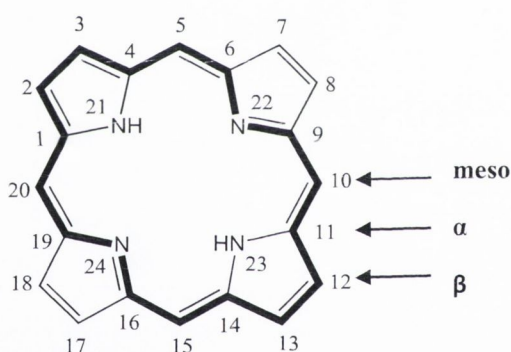
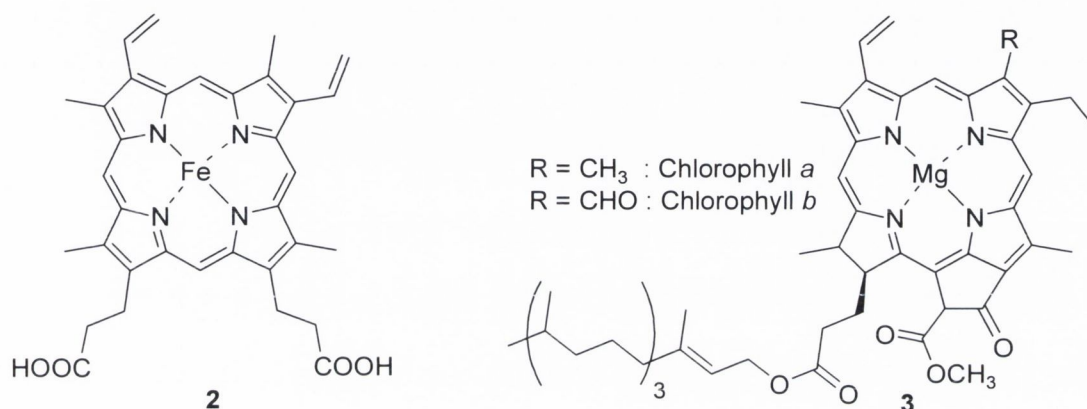


Figure 1.1: Porphyrin structure **1** and the IUPAC numbering system.^[6,7]

There are three different types of carbon atom in the porphyrin structure: α , β , and meso carbons. α -carbons refer to those at positions 1, 4, 6, 9, 11, 14, 16 and 19, β -carbons to those at positions 2, 3, 7, 8, 12, 13, 17 and 18 and meso-carbons to those at positions 5, 10, 15 and 20. The meso and β -carbons can undergo various addition and substitution reactions. The inner nitrogen atoms can either lose or gain protons to form a dianionic or dicationic species respectively. Metal ions can insert readily into the porphyrin core to form metalloporphyrins.^[8] Porphyrins can undergo many characteristic aromatic electrophilic substitution reactions, for example halogenations and acylation. The reactive sites on the porphyrin macrocycle are the meso- and β -positions, and depending on how electronegative the porphyrin is, either site can be activated. The introduction of a divalent metal into the porphyrin core activates the meso position to nucleophilic

attack, although this also occurs with free base porphyrins. Electrophilic metals deactivate the meso-positions and activate the β -positions. Generally, based on frontier orbital theory, all electrophilic, nucleophilic and radical addition reactions should preferentially occur on the meso-positions. Electrophilic addition reactions at the β -positions form chlorins and bacteriochlorins whilst addition reactions at the meso positions generate phlorins or porphodimethenes.^[1]



The primary focus of porphyrins in nature is to chelate metals and these metal complexes of porphyrins play a vital role in biochemical processes. These include oxygen transport in the blood stream whereby the protein haemoglobin, which incorporates the iron(II) protoporphyrin IX **2**, reversibly binds oxygen, allowing its transport. Multiporphyrin systems are involved in the catalysis of biochemical reactions and in photosynthesis (energy transfer) in plants as they make up components of cytochromes b and c and chlorophylls **3**.^[9] Chlorophyll is a reduced magnesium(II) porphyrin or chlorin with different substituents at the periphery, as seen with chlorophylls *a* and *b* **3**, and is crucial for the photosynthetic process. In green plants and photosynthetic organisms, some chlorophyll molecules make up part of the photochemical reaction centre which transduces absorbed light into chemical energy. The other pigment molecules act as light-harvesting molecules or antennae.^[10]

This light harvesting complex absorbs light energy to generate singlet excitation energy from the donor molecule, which consists of a dimeric bacteriochlorophyll or ‘special pair’ (Figure 1.3). The donor transfers the energy stepwise, via an acceptor bacteriopheophytin to the quinone acceptors, which in turn relay it to the photochemical reaction centre, through a process of electron transfer.^[11] The electron transfer from the special pair to the pheophytin is extremely rapid and it is in the reaction centre whereby

the light energy is converted into a separation of charge, thus initiating this oxidation-reduction chain.

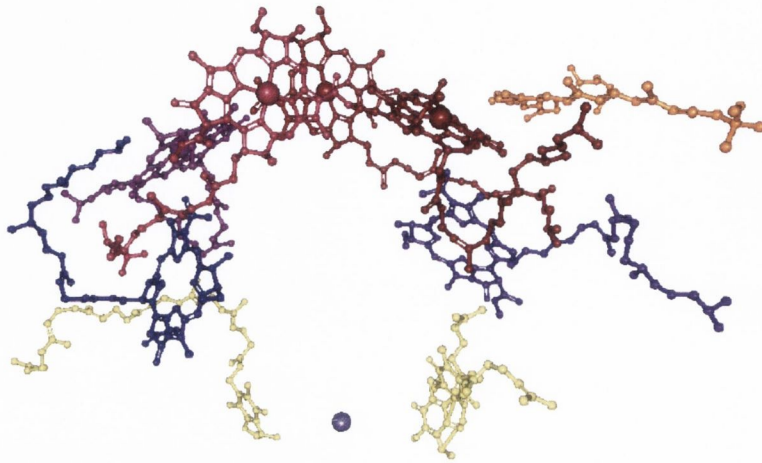


Figure 1.2: X-ray crystal structure of the photosynthetic reaction centre from *Rhodobacter sphaeroides* showing the special pair in red.^[12]

Through 3D crystal structures of the photosynthetic reaction centres and light-harvesting complexes of cyanobacterial photosystems,^[13-15] it is obvious to see the significant and vital role which chlorophyll molecules play in photosynthesis and these structures provide a deep insight into the understanding of the electron transfer events within the reaction centre (Figure 1.3).

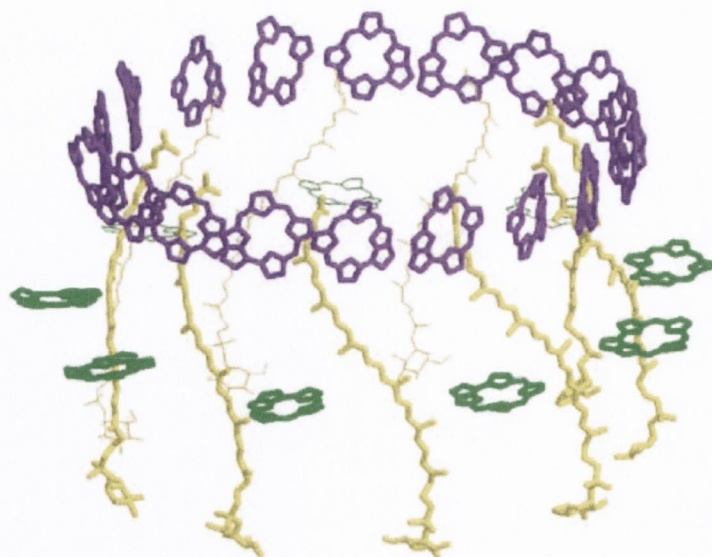


Figure 1.3: Crystal structure of LH2 complex in *Rhodobacter acidophila*. Bacteriochlorophyll (BChl) B800 is shown in green, BChl B850 in purple, and carotenoids in yellow^[13] adapted from.^[16]

As multichromophoric arrays are involved in this process, multiporphyrin arrays have potential to be used in “artificial photosynthesis” and solar energy generation due to their electrochemical and photoactive properties. Porphyrins absorb strongly in the visible region and thus can form part of an artificial photosynthetic system. Artificial models of porphyrin arrays with distinct geometries can provide a useful insight into the mechanisms of electron and energy transfers within these photosynthetic systems and also could duplicate light harvesting and electron transfer characteristics.^[17-22] As these models are of significance, it is crucial to develop synthetic strategies towards the development of such arrays.

1.2 Multiporphyrin Arrays – Synthetic Considerations

There has been vast advancement in the synthetic strategies towards the functionalisation and synthesis of monomeric porphyrins over the past few decades. For the synthesis of simple meso-substituted porphyrins, a variety of condensation reactions can be carried out, namely the Rothmund^[23-25] and Lindsey methods^[26-27] whereby numerous tetrasubstituted A₄ porphyrins can be synthesised from the acid-catalysed condensation of pyrrole with various aldehydes. For the synthesis of A₂ and A₂B₂ systems, dipyrrolyl and tripyrrolyl analogues, namely MacDonald [2+2] condensation,^[28] which utilises dipyrromethane derivatives^[29-31] and an aldehyde to give the 5,15-A₂ and A₂B₂ porphyrins and also [3+1] condensations, whereby tripyrrane is utilised to give access to 5-A and 5,10-A₂/A₂B₂ substituted porphyrins. For unsymmetric tetra substituted porphyrins, i.e. ABCD porphyrins, numerous strategies can be adopted, namely mixed condensations and organolithium methods. Mixed aldehyde condensations are not favoured, as the purification for such is quite tedious and low yielding via this route. Unsymmetric porphyrins can also be achieved via acyl dipyrrolyl analogues, a method developed by Lindsey and co-workers,^[32-33] and more recently, the synthesis of ABCD porphyrins has been achieved via bilane precursors^[34-36] in respectable yields, although the synthesis by such means requires several intermediary steps. For the synthesis of ABCD unsymmetric porphyrins from porphine **1**, A, A₂ and A₂B₂ precursors, methods whereby meso-substituents can be incorporated in a stepwise fashion can be adopted. This allows for a variety of substituents to be added to the porphyrin in good yields. This includes the novel meso functionalisations via organolithium reagents, developed by Senge and co-workers to generate unsymmetrical ABCD porphyrins from the parent porphine **1**.^[37-40]

This approach is favourable as the mild conditions adopted enable a wide variety of substituents to be introduced, without prior activation of the porphyrin macrocycle.

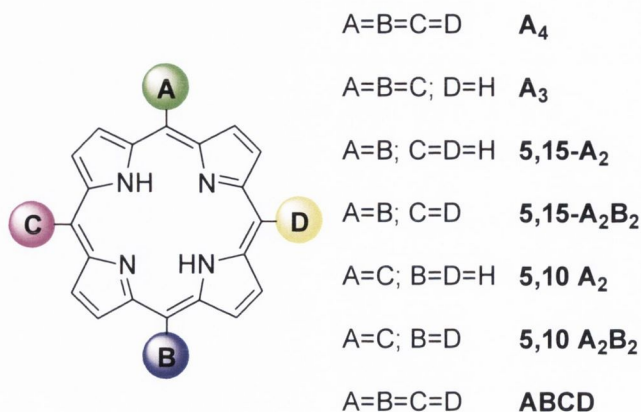


Figure 1.4: meso-Substitution patterns adopting the ABCD nomenclature.

In addition to this method, numerous palladium catalysed coupling reactions can be applied to porphyrins, enabling almost any substituent to be incorporated into the porphyrin periphery.^[41-43] These require prior activation via halogenation and these haloporphyrins provide an essential entry to meso functionalisations.^[44-45] The most utilised palladium catalysed reactions on porphyrins are namely the Suzuki-Miyaura, Heck, Stille and Sonogashira couplings, which involve the coupling of haloporphyrins with the desired substituent to be incorporated into the periphery.^[46] The main issue with such functionalisations is regioselectivity. As the meso position is more reactive towards electrophilic substitution reactions over the β -pyrrolic position, due to a higher electron density at the meso position, control over the regioselectivity of halogenation and other reactions such as nitration is difficult. Recent advancements in transition metal catalysed reactions on porphyrins by Osuka and co-workers has enabled functionalisation at β positions over meso, via iridium catalysed reactions.^[47] Such advancements in the organic transformations of porphyrins have opened the door to the synthesis of a range of functionalised and fine-tuned porphyrins, which can act as precursors towards the synthesis of multiporphyrinic arrays. There has been comprehensive research into the development of synthetic strategies towards such arrays and palladium catalysed couplings, amongst other strategies will be described.

Multiporphyrinic arrays are important in nature and much work is being undertaken to create arrays which mimic such biological processes present in light harvesting complexes for applications in solar energy conversion, etc. (Section 1.1). Multiporphyrin

arrays can be generated by various routes^[48] and the strategy adopted will depend on how the array is connected, i.e. whether it is non-covalently linked or covalently linked, and also on the type of linker or spacer group between the porphyrin sub-units which form the array. Many different types of linkages exist, namely non-covalent and covalent. Non-covalent refer to those arrays linked via self-association, e.g., hydrogen bonding and metal co-ordination. These self-assembled supramolecular arrays provide a useful insight into photosynthetic light-harvesting arrays as these highly ordered systems can serve as mimics to the natural arrays, which are held together in a protein matrix via non-covalent bonds.^[49-50] However, for the scope of this introduction, the focus will be on covalently linked arrays as this is the motivation for our research. Emphasis will be placed on carbon-carbon covalently linked porphyrin arrays and the different classes of linkages which exist, with the main focus being on aromatic, direct and conjugatively linked porphyrins. Other heteroatomic linked porphyrins, such as ether, ester and amide, exist, but will not be discussed further. Also, attention will be directed to meso-meso linked arrays, although there will be some references to other connectivity's, for example, meso- β linked arrays.

We envisaged developing porphyrinic arrays which display enhanced π -conjugation with the aim of employing these materials to optical applications such as photodynamic therapy (PDT), organic light emitting diodes (OLEDs) and non-linear optics (NLO). Such enhancement can be achieved via various strategies and most optical applications require this feature for improved efficiency. As we are concerned with the electronic properties of multiporphyrin arrays, it is important to understand the basic theory for such characteristics.

1.3 Electronic properties of multiporphyrin arrays

Porphyrins have characteristic UV-visible spectra and this provides a useful and powerful means of identifying different types of porphyrins. Their absorption spectra are similar to other aromatic compounds in that they have two distinct absorption regions, however, they absorb in the near-ultraviolet and visible regions unlike other aromatics. The intense colour of porphyrins is due to this characteristic.

The first region is the Soret band (or B band), named after its discoverer,^[51] lies in the 390-425 nm region and this represents the allowed π - π^* transition state. In the 480-700 nm region, the weaker Q bands are situated. These consist of between two and four

bands, depending on the substitution pattern of the porphyrin and whether or not it is in the free base or metallated form. Free base porphyrins have four Q bands due to their lower symmetry compared to metallated porphyrins and thus the elimination of degenerated excited states. Metalloporphyrins have higher symmetry and as a result they generally only exhibit two Q bands. Gouterman's four-orbital model (Figure 1.6) is a theory commonly used to explain the origin of the UV-vis spectra of porphyrins,^[52-54] allowing for the two highest occupied molecular orbitals (HOMOs) and the two lowest unoccupied molecular orbitals (LUMOs) of the porphyrin macrocycle to be considered.

The HOMOs (a_{1u} and a_{2u}) are singly degenerate whilst the LUMOs (e_{gy} and e_{gx}) are doubly degenerate. The one electron transitions between these molecular orbitals generate four excited states, with their symmetry being the same and thus causes them to overlap and interact with one another, both constructively and destructively. The constructive interaction results in the more intense short-wavelength Soret bands and the destructive interaction results in 'forbidden' transitions giving the less intense long-wavelength Q bands. The Q bands, according to Gouterman theory, are forbidden but exist due to molecular vibrations within the macrocycle.

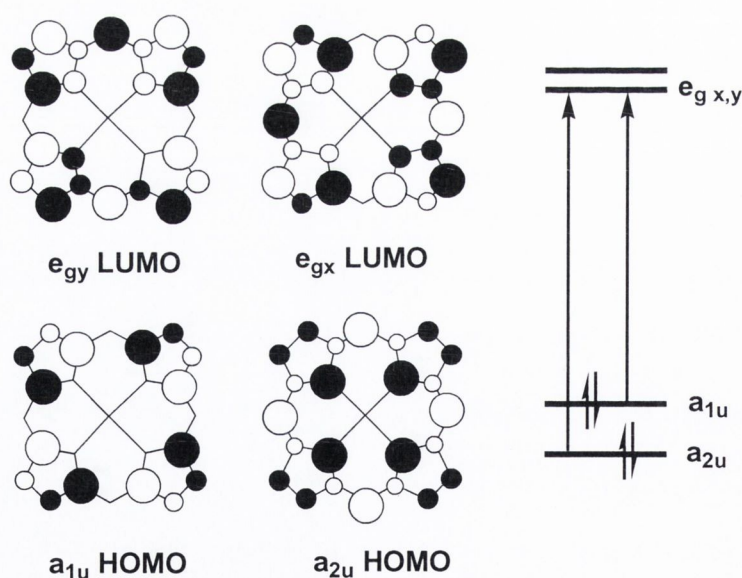


Figure 1.5: Representation of the Gouterman four-orbital theory.

In multiporphyrin arrays, excitonic coupling theory can be used to explain their absorption spectra. Depending on how the porphyrin subunits are arranged and how they are linked, different absorption spectra will result. Point-dipole exciton coupling theory, developed by Kasha *et al.*,^[55-56] may be used to account for spectral changes by

interporphyrin interactions where the strength of the dipole interaction is signified by Coulombic interactions. These interactions are dependent on oscillator strength and orientation and distance relative to one another. ‘Head-to-tail’ orientation results in J-type excitonic coupling, which is an allowed lower energy transition. ‘Parallel’ orientation results in H-type coupling, which is of higher energy. Most multiporphyrinic arrays exhibit split Soret bands and this is due to J-type exciton coupling between adjacent porphyrins.^[57] The most pronounced interactions between porphyrins is observed when they are directly linked, either singly or triply. Also, the extension of the porphyrin conjugation results in the decrease in the HOMO-LUMO gap and this is due to the change in the electron density distribution on the porphyrin.^[58] The absorption spectra of the porphyrin oligomers depends on the type of linker used, the substituents on the porphyrin macrocycle and where the porphyrins are linked, which in our case is predominantly at the meso position. Any enhancement of conjugation will result in a bathochromic shift in the absorption spectrum of the lowest energy Q band, i.e. $\lambda_{\max}$. As mentioned, the geometry of the array controls the communication between sub-units and efficiency of electron transfer. For directly meso-meso singly linked arrays, the porphyrin units are geometrically orthogonal to each other, resulting in a disruption to the π -electron conjugation and thus little or no bathochromic shift in absorption. Any spectral changes with respect to monomeric components are induced by Coulombic interactions of the dipole moments i.e. excitonic interactions.^[59] Triply fused β - β , meso-meso, β - β linked porphyrin are geometrically co-planar and these arrays exhibit a substantial red shift in absorption due to the enhanced π -conjugation, which greatly reduces the HOMO-LUMO energy band gap.^[57] Arrays linked via conjugated linkers such as alkynyl and phenylacetylene, exhibit a bathochromic shift due to enhanced π -electron conjugation. Those linked via aromatic linkers such as phenylene have a more rigid geometry and lack bathochromic shifts in their absorption profiles. Such arrays are suitable as photosynthetic mimics as the rigid geometry acts as the structural motif for the protein matrix in biological light-harvesting systems.

1.4 Applications of multiporphyrin arrays

Due to the highly conjugated macrocyclic system, the absorption profile and the stability of porphyrins, they have a diverse range of applications. These applications include photodynamic therapy (PDT), catalysis, sensors and applications in materials chemistry, such as non-linear optics (NLO) and organic light emitting diodes (OLEDs). Highly

conjugated porphyrin arrays also have potential applications in such areas.^[9] A selection of these applications will be discussed in more detail and also how these porphyrin arrays can be employed for such applications.

1.4.1 Non-linear optics

Optical limiting is a protection method against high-intensity visible light source damage to the human eye and porphyrins are a target choice as optical limiters. It is a process of attenuating high intensity light whilst allowing the efficient transmittance of low intensity ambient light. Non-linear optics (NLO) describes the behaviour of light in non-linear media and NLO materials have also been widely investigated for potential use in data storage, telecommunications, computers and display technologies.

Porphyrins have numerous properties which make them desirable materials for the use in optoelectronics.^[58, 60-61] These properties include: 1) the fact that the porphyrin structure can be modified to enhance their optoelectronic effect, 2) the delocalisation of π -electrons in the conjugated macrocyclic ring which gives the large non-linear optical effects and 3) the thermal-, chemical- and photostability of porphyrins is greater than for those of “typical” organic chromophores. Conjugated multiporphyrin arrays are of interest due to their extended π -systems and thus potentially enhanced NLO effect.^[62-64] Two-photon absorption is a third-order non-linear optical response and TPA-PDT is an emerging area for cancer-treatment (Section 1.4.3).

1.4.2 Photoinduced electron-transfer (Light-harvesting)

Photosynthetic light-harvesting antennae consist of circularly arranged chromophores^[13] where the exciton transfer processes of photosynthesis take place. In photo-induced electron transfer, the electrons in the ground state are paired in the HOMO. One electron transfers into the LUMO in the excited state after the absorption of light. In order to be efficient, the antenna must absorb in a similar region to that of the light source. Also, as the singlet excited states do not have a long lifetime, the transfer of energy within and from the antenna must be rapid. In generating multiporphyrin arrays for this purpose, electronic communication between the chromophores must be rapid and efficient. Conjugative linkers are appropriate for such artificial antennas as there is a strong delocalisation of electrons between the porphyrin units, potentially allowing the necessary communication.^[65]

The simplest model consists of a porphyrin covalently linked to an electron donor or acceptor and such two-component systems are known as a dyad. These dyads can undergo photo-initiated charge transfer under appropriate conditions and their irradiation leads to the formation of the excited singlet state of the porphyrin. The singlet state, which is very short lived, may then donate an electron to the attached acceptor to form a charge separated state. However, this state is also short-lived so does not adequately mimic the photosynthetic reaction centre which gives long-lived charge separation. Triad units covalently linked and containing donor and acceptor moieties may provide a better mimic for the natural photosynthetic process which occurs in a number of steps. The charge separation for such triads has a longer lifetime and thus provides a better model. Larger covalently linked cyclic arrays and self-assembled supramolecular constructs effectively mimic the light-harvesting systems, with electron transfer rates comparable to those in natural systems.^[20, 66-67]

1.4.3 Photodynamic therapy (PDT)

Photodynamic therapy is a branch of cancer treatment which utilises the combination of a drug and light to induce a cytotoxic effect in cancerous or other unwanted tissue. A drug, or photosensitiser, is administered to the body and it accumulates in the malignant tissue.^[68] The diseased tissue is then illuminated with light of an appropriate wavelength which activates the accumulated drug to the excited singlet state (S_1).

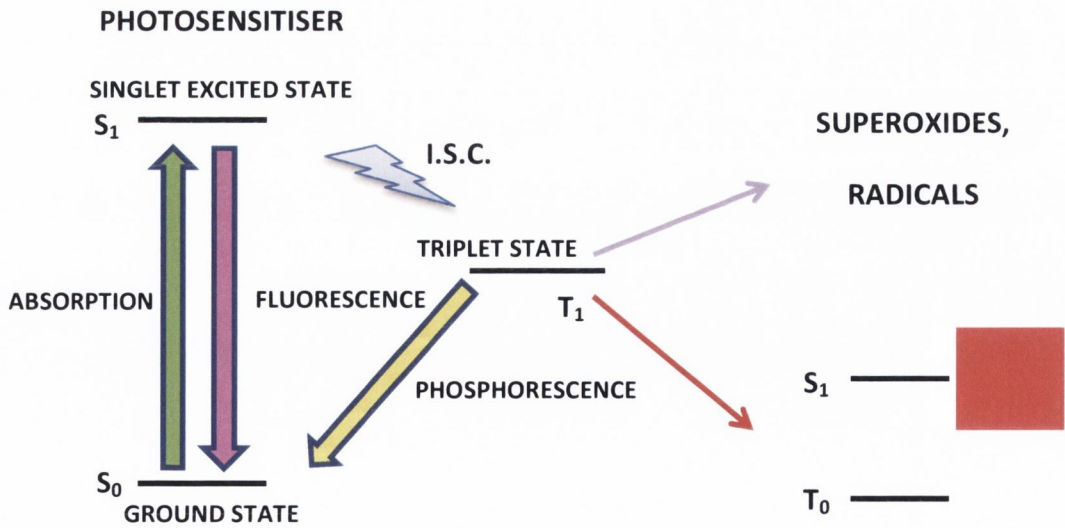


Figure 1.6: Generation of singlet oxygen through photosensitisation.

This can undergo intersystem-crossing to the triplet state (T_1) and this is the species which can react with ground state oxygen to generate singlet oxygen (Figure 1.6). This, along with superoxides and radicals, are the cytotoxic species. Generally it is accepted that the predominant mode of cell death is via singlet oxygen (Type I), with some contribution from the superoxides and radicals generated (Type II).^[68] As porphyrins absorb strongly in the visible region, and have excited states with sufficient lifetimes, they can be easily activated by light and thus can be used as such photosensitisers.^[1]

The photodynamic effect of porphyrins was first illustrated in 1913 when Meyer-Betz injected himself with “hematoporphyrin derivative” or HpD. HpD is derived from hematoporphyrin and is a mixture of porphyrin compounds.^[69] It was the most commonly used PDT agent until the 1980’s, when it was purified and partially identified. The active fraction of HpD, known as Photofrin®, is now used as it has been shown to be twice as active as HpD.^[9] Photofrin® is a mixture of porphyrin dimers and oligomers, joined together by a variety of covalent bonds, Figure 1.7 showing an active dimeric component **4**. A number of porphyrin based photosensitisers, primarily monomeric derivatives, have since been developed as potential PDT agents, for example the commercially available 5,10,15,20-tetrakis(3-hydroxyphenyl)chlorin, Temoporfin **5** (Foscan®).^[70-71]

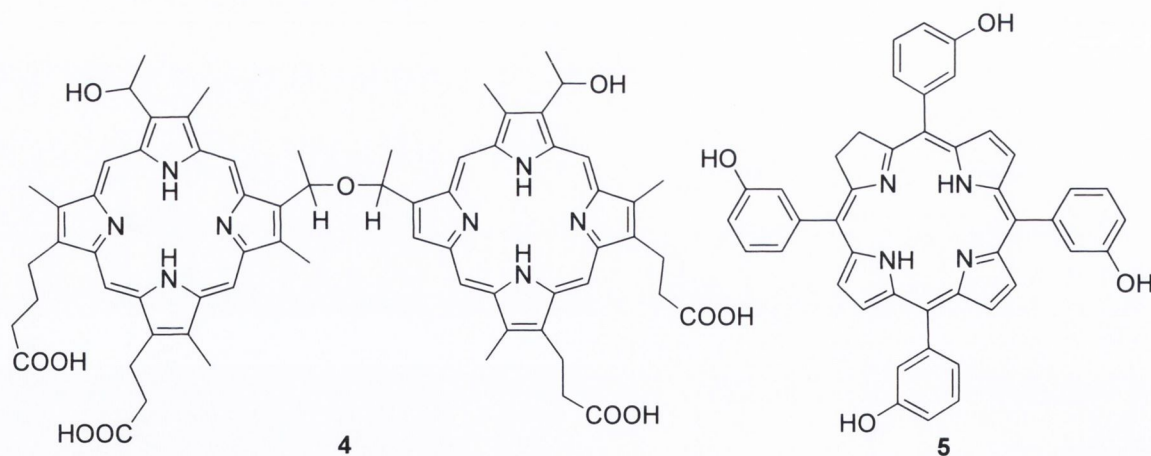


Figure 1.7: Structure of a dimeric component of Photofrin® **4** and Foscan® **5**.

Chlorins and bacteriochlorins are advantageous for PDT due to their longer wavelength absorbance compared to porphyrin counterparts. Covalently linked porphyrin dimers have been synthesised and tested for cytotoxicity as models for understanding the mechanism of action of Photofrin®.^[72-74]

A major drawback of these agents is the limitation of the cancer types which they can treat, due to the wavelength dependency of the penetration of light.^[75] One method to overcome this is the extension of the π -conjugation of the porphyrin, and as mentioned a convenient approach to this is the development of conjugated porphyrin arrays. Conjugated butadiyne linked dimers have recently been shown to be efficient as photosensitisers *in vitro*.^[76] These dimers exhibit large two-photon absorption (2PA) and interest in 2PA PDT is on the increase. Described as an ‘emerging area’ in a recent medical review,^[77] 2PA is a third-order non-linear occurrence, whereby there is excitation of a molecule by the simultaneous absorption of two photons using strong laser pulses (Section 1.4.1). With one-photon absorption, the penetration of biological tissue by light is low as absorption is in the 400-700 nm region, where tissues absorb strongly.^[78-79] With 2PA, irradiation at longer wavelengths, into the near IR region of 700-1300 nm, is possible and thus light can penetrate deeper as biological tissues absorb less in this region. This potentially could enable the targeting of deeper tumors, making PDT attractive for a wide range of cancers.^[80] Also, the light source required is a focused laser beam which enables a higher selectivity for the tumour and minimises damage to healthy cells. The efficiency of 2PA is quantified by two-photon absorption cross-section values (σ) and molecules exhibiting high σ values are of interest to this area. Monomeric porphyrin compounds without any donor-acceptor groups show low efficiency and thus are poor candidates for 2PA-PDT. However, by increasing the π -conjugation, the efficiency can be greatly improved. As mentioned, an attractive route to execute this is to link porphyrins via conjugated linkers or by triply fusing porphyrins together. Such an increase in π -conjugation results in a substantial increase in σ values, as seen with Anderson’s butadiyne linked dimers^[81] which have σ values of 1×10^4 GM and are proving to be promising candidates for PDT application. Using these materials as ‘molecular rotors’, due to the rotation about the alkynyl bonds, they have also quantified intracellular viscosity alterations in cells via fluorescent imaging and the effect which this has on PDT treatment.^[82]

Although the materials mentioned are of benefit to PDT, a major drawback is the general poor solubility of porphyrins, but there are many means to overcome this issue. One such route is via the incorporation of water-solubilising groups into the porphyrin periphery, such as alkoxy chains,^[81] sugar moieties,^[83] ^[84] or bile acids^[85] or by constructing amphiphilic arrays, i.e. constructs with lipophilic and hydrophilic entities. An example of

this has been given recently with conjugated glycosyl dimers.^[86] In the cases of sugars and bile acids, these not only enhance the solubility of the array, but also assist with tumour targeting. As there is lectin overexpression of tumor cell surfaces, which are sugar binding proteins, glycosyl-porphyrin conjugates can target specific tumors, enabling better incorporation and thus efficacy. It also has been shown that bile acids can promote PDT efficacy by potentiating apoptosis.^[87] Another method to overcome the poor solubility of porphyrins is the development of liposomal formulations, whereby the porphyrin is incorporated into the liposome as a drug delivery system. Liposomes consist of a lipid bilayer and therefore can permeate the cell and release the drug within. Known Foscan®-liposomal formulations,^[88] such as Foslip®^[89] and Fospeg®^[90] have not shown enhanced PDT effects but with regard to multiporphyrin arrays, liposomal formulations could provide a solution to their poor solubilities, enabling their incorporation into the cell and thus their application in PDT. A very recent development in this area was the discovery of ‘porphyrin hybrid cerasome’ whereby lipid substituted porphyrins self-assembled to form a liposomal type structure and possessing many advantages over traditional liposomal formulations.^[91-92] Other than the dimers mentioned above, there has been little focus on the development of porphyrin arrays as potential photosensitisers but promising *in vitro* results^[76] have shown this to be an emerging area for PDT enhancement.

1.4.4 Organic Light Emitting Diodes (OLEDs)

The field of organic light emitting diodes (OLEDs), also known as organic electroluminescent devices, has been developed substantially over the past 25 years, due to their importance in flat panel displays and electrical devices.^[93-94] OLEDs are multi-layered structures consisting of two electrodes, an emissive and conductive layer, as shown in the schematic representation in Figure 1.8. The electroluminescent layer consists of organic semiconducting materials which emit light in response to electric current flowing through it and are of use in everyday devices such as television screens, mobile phones and computer monitors.^[95] These OLEDs also have the potential to act as emitters into the near-IR region, depending on the organic material employed.^[96] Such near-IR OLEDs could have diverse optical applications such as in PDT and night vision.

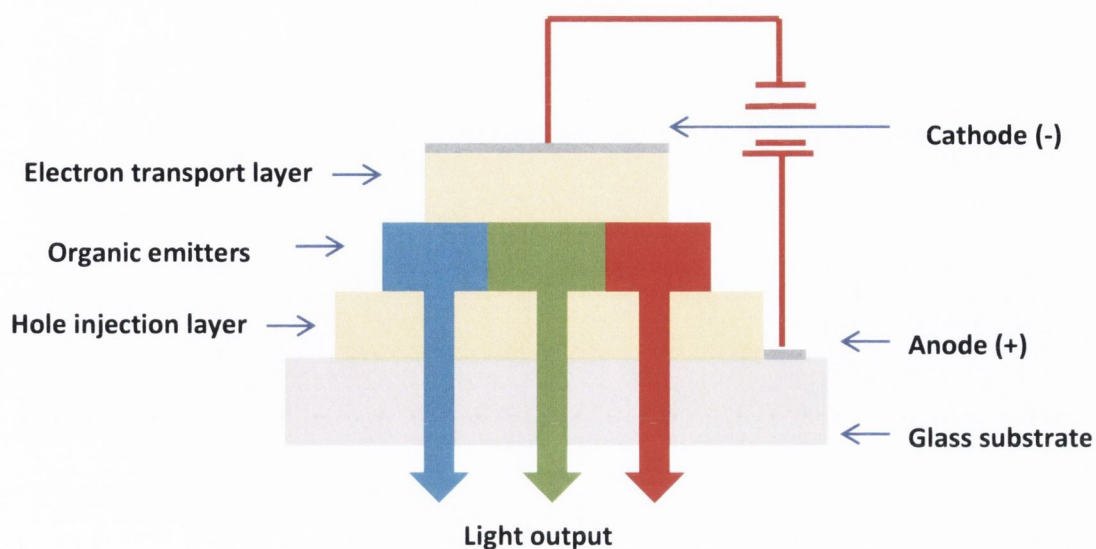
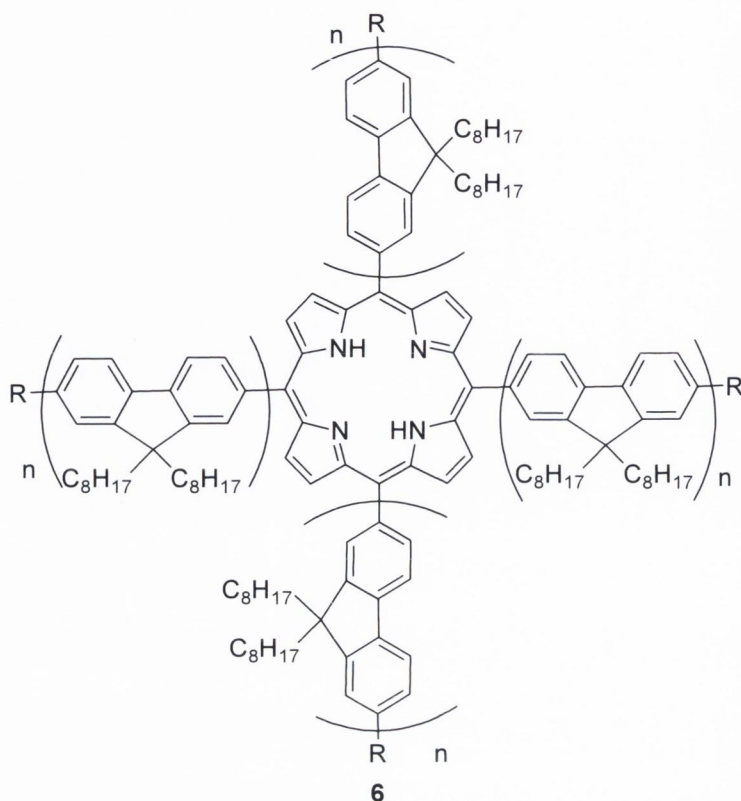


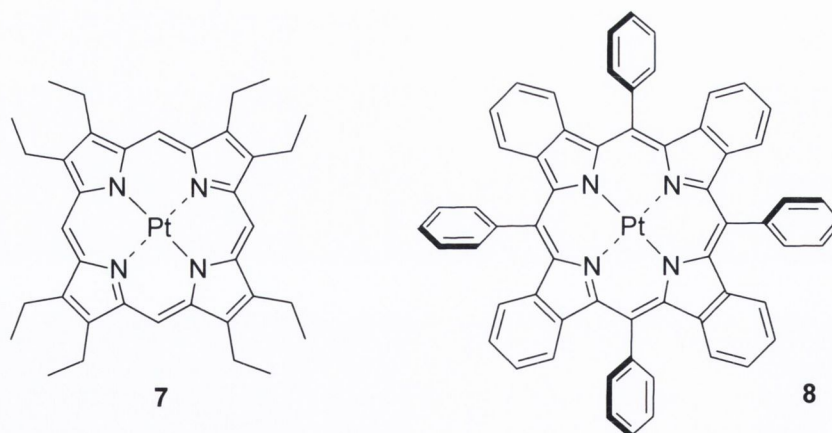
Figure 1.8: Diagram of a working OLED device

When a voltage is applied to the OLED device, the cathode pumps electrons into the emission layer whilst the anode pumps electron holes putting the dye material into an excited state. On return to the ground state, there is a release of energy from the dye in the form of light or electroluminescence, the colour of which is dependent on the difference in energy between the ground and excited energy levels.^[93] There are many different types of OLED devices, the standard of which adopts fluorescent dyes. By incorporating phosphorescent dyes, phosphorescent OLED devices can be created which have an added advantage of longer emission lifetime.^[97-98] As the colour of light depends on the differences in energy levels, the structure of the dye molecule will affect this. Porphyrins are highly chromophoric materials, thus emit light in the red-region and have a narrow emission width. Therefore, their incorporation into OLED host matrix materials as dopants is of interest for the development of improved displays. As a result, research into developing porphyrins for use in OLEDs is expanding.^[94, 99-101]

Porphyrins can be fine-tuned by the substitution pattern on the periphery and through the modification of their central metal ion, depending on the type of OLED required. Generally, the host matrices consist of conjugated polymers such as polyfluorene (PFO) and poly(*N*-vinylcarbazole) (PVK) which themselves act as strong green and blue emitters.^[102] These conjugated polymers are attractive as OLED materials as they have good hole transporting abilities and they have high triplet energy.^[94-95]

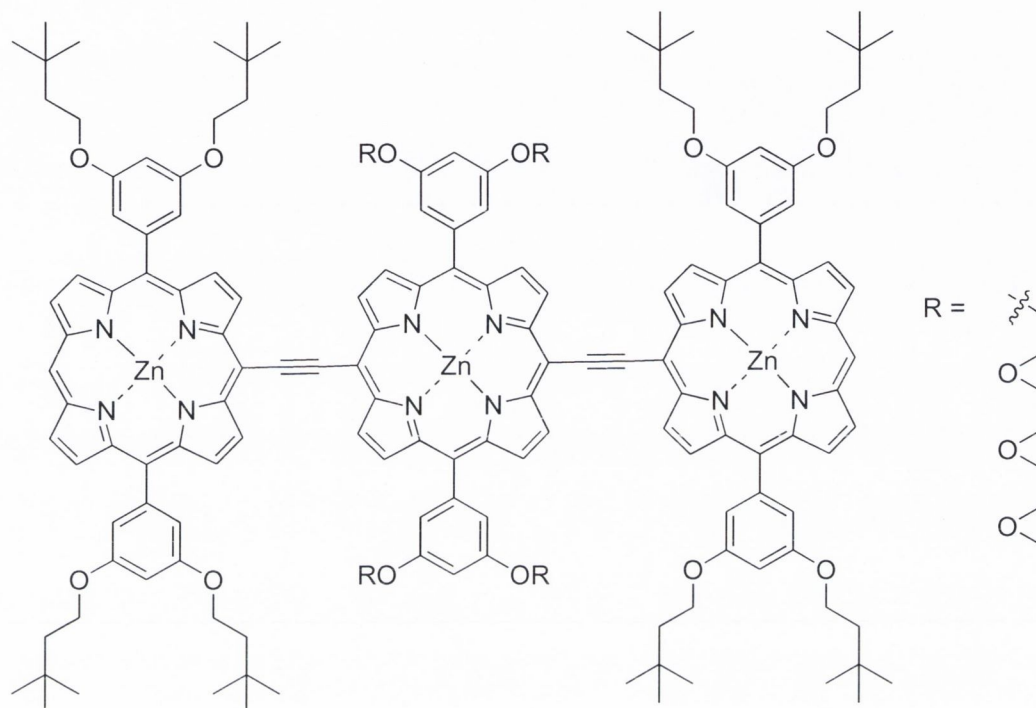


Recently, the incorporation of these aromatic moieties into porphyrins has become attractive for OLED purposes so as to enhance the efficiency of the host, as seen in porphyrin **6**.^[97, 103-106] Platinum porphyrins **7** and **8** have also been shown to have high external quantum efficiencies when doped into OLED devices.^[107-108]



With **8**, the fused aromatic groups at the beta-pyrrolic positions enhance the bathochromic shift of the absorption and emission profiles due to the extended π -conjugation of the structure. Also, the non-planarity of the structure enhances this shift making the dye a NIR emitter.^[109-110] Phosphorescent OLEDs are desired as they emit light for longer periods of time and porphyrin trimer **9** has been shown to be an efficient

phosphorescent dopant in PhOLED devices with an external quantum efficiency of 6 %. These NIR emitters are of use in applications such as night-vision displays and PDT and display the potential which conjugated porphyrin arrays have in the field of OLEDs.^[96]



9

1.5 Porphyrin arrays with conjugated linkers

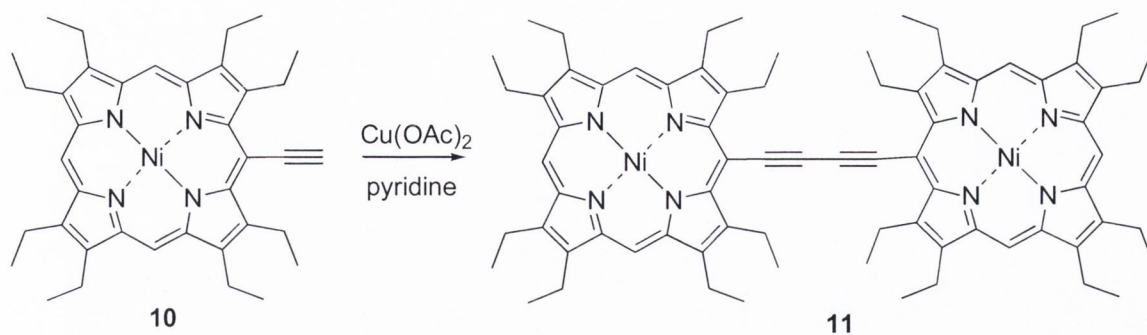
Multiporphyrin arrays can be connected through a variety of covalent linkers and depending on the linker used, the array will function in different applications. The primary purpose for developing multiporphyrin arrays is for applications in artificial photosynthesis, to gain a deeper insight into light-harvesting and photo-induced energy transfer in plants by mimicking such processes.^[111] Additionally, multiporphyrin arrays, if exhibiting enhanced delocalised π -conjugation, can serve as materials for NLO, PDT and other optical applications, which require long-wavelength absorption. The electronic properties of these arrays can be fine-tuned via structural modifications of the porphyrin sub-units either at the monomeric stage or through post array construction modifications; for example by variation of the central metal or by alteration of meso and β substituents. For the scope of this section, focus will be on ethynyl, butadiyne, aromatic and hybrid ethynyl-aromatic linkers. Multiporphyrin arrays containing other conjugated linkers such

as alkenyl and azido exist, but will not be further described. There are numerous synthetic strategies towards the synthesis of such conjugatively linked porphyrin oligomers. The most predominant are condensation strategies, whereby the necessary aldehyde precursors are synthesised in a multistep fashion. Stepwise synthesis involving functionalisations of monomeric porphyrins are also used, culminating in an ultimate palladium catalysed coupling reaction to form the desired oligomer. The type of coupling employed is dependent on linker involved and the shape of the architecture, it being linear, cyclic, star-shaped or dendritic.^[48]

1.5.1 Ethynyl, aromatic and hybrid linked multiporphyrin arrays

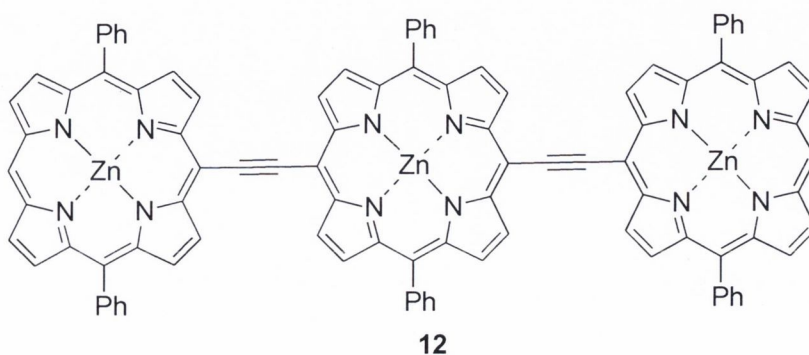
Ethynyl linked porphyrin arrays and derivatives of such a conjugated linker such as phenylethyne and butadiyne linkers, are widely known in the literature. As a result of the conjugation through the linker, there is strong excitonic and electronic coupling between the porphyrin units and this causes a pronounced shift in absorption profiles into the visible and near infra-red regions. With alkynyl units, there is rotational freedom about the triple bonds giving rise to rotational isomers or so-called conformational isomers. In porphyrin arrays linked via alkynyl groups, this gives rise to complicated optical properties as the electronic nature of the array is dependent on its conformation in the ground state. These properties were investigated by Anderson and co-workers,^[112] whereby butadiyne linked porphyrin arrays exhibited two limiting conformations: the twisted conformation and the co-planar conformation. The coupling between the porphyrinic units is strongest when they are co-planar and steadily decreases to a minimum when they are perpendicular. In other words, the alkynyl linked arrays adopt multiple conformations resulting in unique photophysical properties. The overall π -conjugation in these arrays is enhanced and this results in an enhanced absorption spectrum or red-shift, desirable for many optical applications.

The first alkynyl linked porphyrin array was that of butadiyne linked dimer **11**, synthesised in 1978 by Arnold *et al.*^[113] This was formed via the Eglington reaction of 5-ethynyl-octaethylporphyrin **10**, which is the oxidative homo-coupling of terminal alkynes to form bis-acetylenes.^[114] This type of homo-coupling can also be achieved under Glaser-Hay coupling conditions, whereby catalytic quantities of copper(I) can be used, as opposed to stoichiometric amounts for the Eglington reaction.



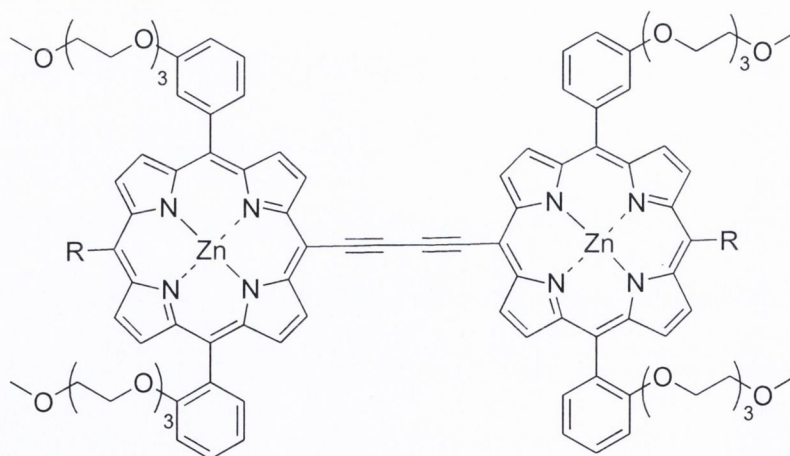
Scheme 1.1: Synthesis of first acetylene linked bis-porphyrin.^[113]

The development of palladium catalysed coupling chemistry has opened the door to numerous syntheses of alkynyl linked multiporphyrins, with the most utilised method adopting Sonogashira coupling conditions, or modified versions thereof. These palladium catalysed coupling reactions require the activation of the porphyrin via halogenation, the most common precursors of which are bromo-porphyrins. Brominations at the meso-positions are readily achieved using NBS in excellent yields, although lower if a free meso-position is necessitated.^[44] The incorporation of the alkynyl moiety to the porphyrin periphery can also be achieved using a condensation reaction with propargyl aldehyde,^[115] along with the organolithium approach^[116] to introduce phenylacetylene which removes the activation step and eliminates any selectivity issues. A recently developed method, yet to be applied to porphyrins, uses calcium carbide to generate acetylene *in situ* from hydrogenbromide (derived from aryl-bromides) in the presence of an amino-phosphine ligand.^[117] This forms symmetric diaryl alkynes in one-pot excellent yields and could be applied to the bromo-porphyrins to synthesise alkynyl linked porphyrins. Another alternative is via the condensation methods described in Section 1.2.^[118]



Therien and co-workers synthesised meso-meso dimeric and trimeric and meso- β ethynyl linked dimeric linear porphyrins via palladium catalysed Sonogashira coupling conditions in yields of 33-72 %, the lower yield being that of trimer **12**. Butadiyne bridged dimeric derivatives of **12** were synthesised in yields of up to 74 %, employing Eglington reaction conditions. Such arrays were used as model systems for light-harvesting antennae.^[119-120] ‘Porphyrin ladders’ were developed by Anderson and co-workers, whereby dimeric butadiyne linked linear porphyrins were synthesised via Glaser coupling conditions. Ladder type complexes were formed via aggregation and the co-ordination of 1,4-diazabicyclo[2.2.2]octane (DABCO) with the central zinc metals.^[121] These double-stranded ladder-type assemblies control the conformation of the arrays, reducing the rotation barrier along the triple bonds, thus adopting a planar conformation which has been shown to improve their potential to be employed in optical applications as enhanced π -conjugation is observed.^[122-123]

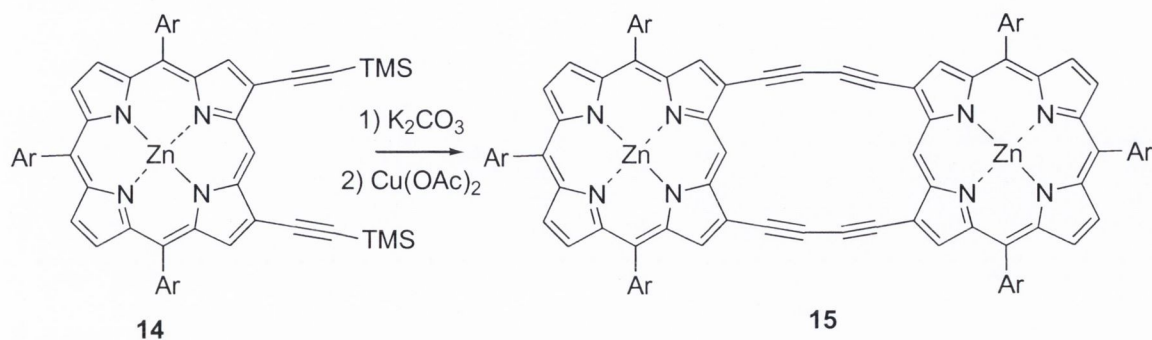
Further research by Anderson and co-workers on butadiyne linked arrays has yielded hydrophilic dimers **13** which are currently being tested *in vitro* for photodynamic therapy^[76, 82] (Section 1.4.3). These dimers display high singlet oxygen quantum yields, strong fluorescence in the 700-800 nm region and large two-photon absorption cross-sections in the near-IR region, all of which are of importance to PDT.^[81]



13

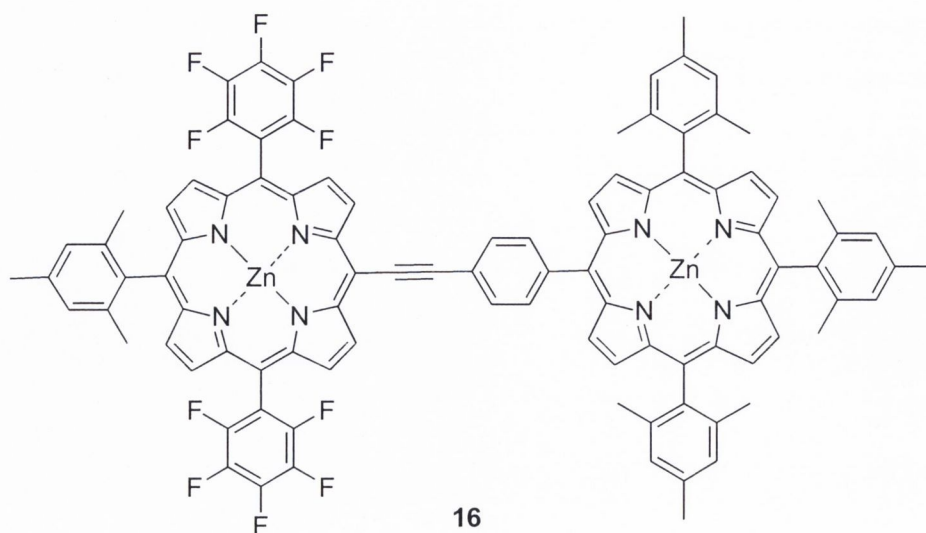
Also, Osuka and co-workers have developed butadiyne bridged dimers with large 2PA cross-section values. In contrast to **13**, these dimers are bridged at the β -positions, made possible through selective β -borylations via iridium catalysed reactions,^[47] leaving the meso-position free. Subsequent transformation of the boryl groups to trifluorosulfonyl

derivatives and Sonogashira coupling provided the precursor **14**. Deprotection and Glaser-Hay coupling yields the butadiyne bridged dimer **15** in good yield.^[124-125]

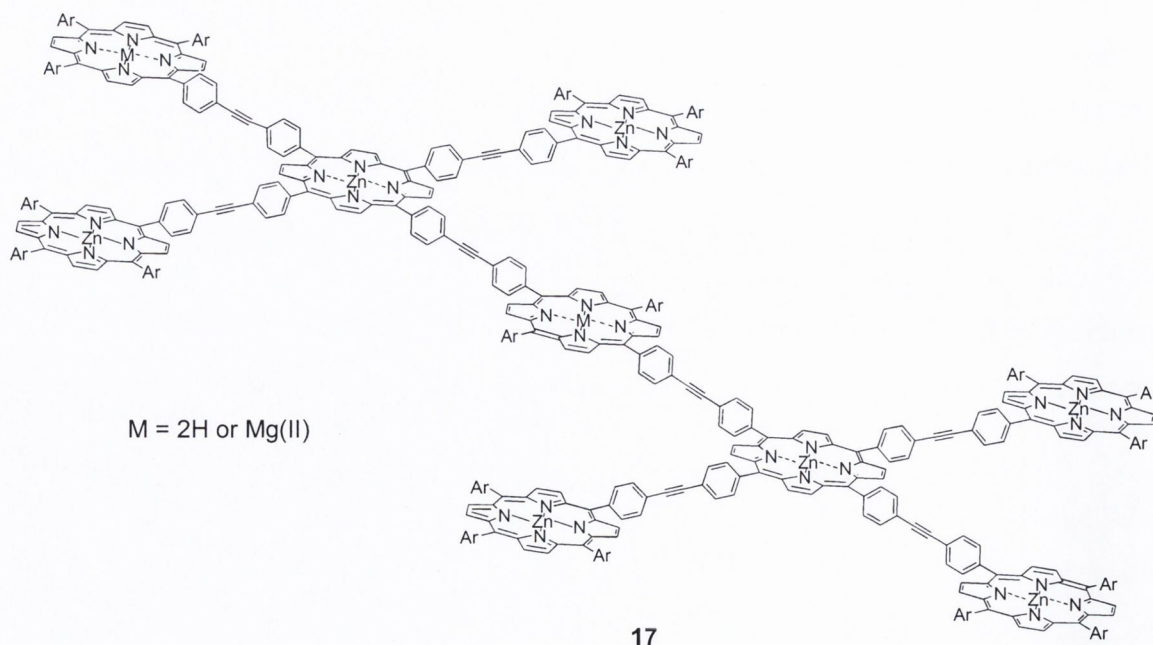


Scheme 1.2: Synthesis of β - β butadiyne linked bisporphyrins.

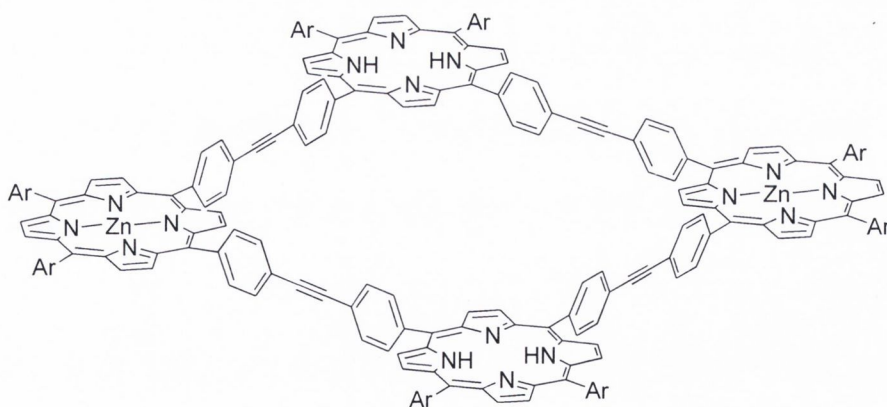
For light harvesting applications, the phenylene, phenylacetylene and diphenylacetylene linkers are predominantly used as these provide architectural control which mimics the protein matrix. With the phenylacetylene linker, the ethyne component serves as the acceptor whilst the phenyl unit acts as the donor in symmetric porphyrin arrays, thereby allowing the mediation of excited state energy transfer, which occurs in the photosynthetic antennae complexes. The incorporation of the phenylacetylene moiety can be achieved via organolithium reactions,^[116] Sonogashira coupling and subsequent deprotection^[126] and also via condensation approaches.^[127-128] Lindsey and co-workers fine-tuned these phenylacetylene linked dimers for this purpose, for example by the incorporation of pentafluorophenyl substituents in dimer **16**. With these substituents, the energy levels of the porphyrin can be tuned, thereby facilitating charge-separation.^[129] This energy-transfer can also be mediated by the incorporation of free-base and zinc metallated porphyrins into the array. Trimeric variations of these arrays have also been developed for similar purposes.^[130] Such arrays were synthesised via Sonogashira coupling of the free phenylacetylene monomer with halogenated porphyrin in yields of up to 62 %.



The diphenylacetylene linker is semi-rigid with some limited rotation about the alkynyl bond and also allows for weak excitonic coupling between the two porphyrin components. Thus, due to this weak coupling, the electronic properties of the array equal the sum of the individual porphyrins. A similar effect is observed in phenylene linked porphyrin arrays but here, due to a shorter distance between porphyrin units, energy transfer is enhanced. As the phenyl ring lies orthogonal to the plane of the porphyrin ring, phenylene linked arrays will adopt a rigid conformation and thus are of interest for biological model studies.^[131] In constructing such phenylene and diphenylacetylene linked arrays, many considerations must be taken into account.



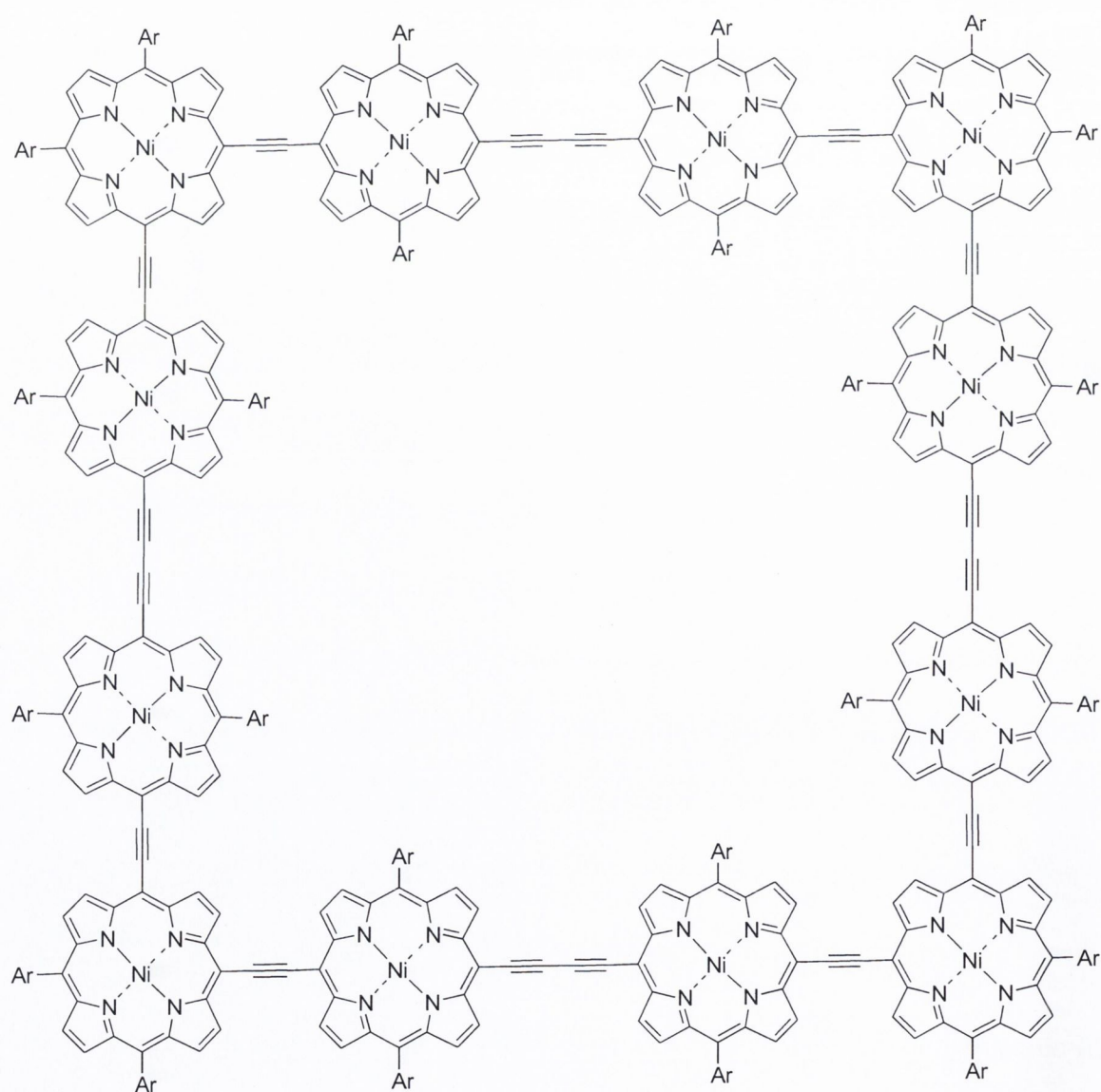
Lindsey and co-workers have led the field in the development of such linked porphyrins for light-harvesting applications and provided insight into the effects various modifications have on energy transfer within the arrays.^[131] Generally, the copper-free Sonogashira conditions are employed for the preparation of such oligomers. With porphyrin nonamer **17**, a coupling yield of 20 % was obtained and these large arrays exhibit efficient singlet energy transfer, particularly when mixed metal porphyrin components were used.^[132] Investigations into the torsional mobility of the linker and its effect on the electronic communication between the porphyrin units have been assessed. It was proven that as the torsional constraint increases, the rate and efficiency of energy transfer decreases, thus having a diphenylacetylene linker with modest flexibility is advantageous. Also investigated was the substituent pattern on the porphyrin periphery and the effects, if any, these have on energy transfer rates. It was discovered that meso-aryl and other electron donating substituents result in an a_{2u} HOMO and thus electron density is localised on the meso-carbon where the linker is attached. In contrast to this, β -alkyl substituents and meso electron withdrawing substituents result in an a_{1u} HOMO which localises electron density on the pyrrolic carbons. Optical communication between porphyrin units of multiporphyrin arrays is seen with an a_{1u} HOMO for β -linked arrays and an a_{2u} HOMO for meso linked arrays. Thus, the importance of the substitution pattern on the porphyrin periphery, in terms of energy transfer, is evident and can play an important role in the design of such arrays.



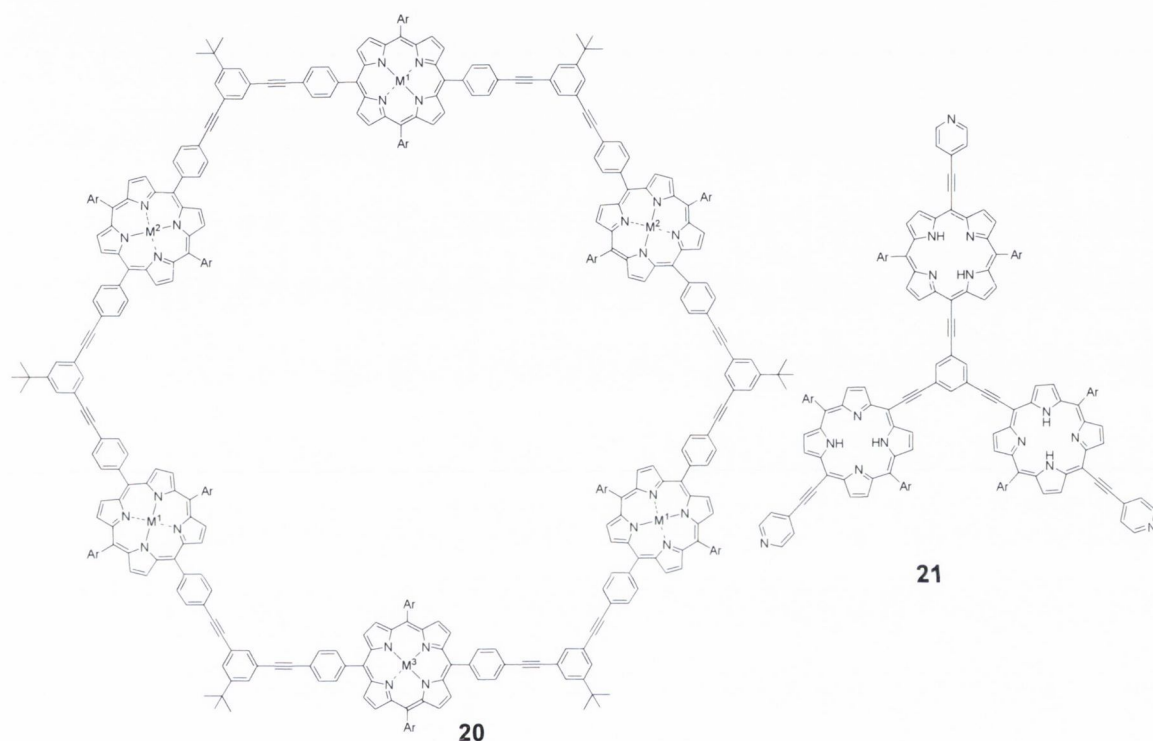
18

In attempts to mimic the cylindrical structure of the light harvesting complex in natural systems, cyclic and square^[133-134] covalently linked arrays have also been developed. These incorporate ethyne, butadiyne, phenylene, diphenylacetylene and phenyl acetylene linkers and, in some cases, require the template-directed synthesis for optimum

yields of the desired array. Depending on the linker adopted, these large arrays can have complete or incomplete π -conjugation. Those lacking complete conjugation have been extensively investigated and generally incorporate hybrid aromatic-ethynyl linkers, as show with square-shaped tetramer **18**,^[135] synthesised via copper-free Sonogashira coupling of 5,10 A_2B_2 monomeric porphyrins. Arrays of 1,3-phenyl linked porphyrins have been employed to generate porphyrin wheels by Osuka and co-workers,^[136] from a 1,3-phenylene linked dimer with free-meso positions and subsequent oxidative oligomerisation using $AgPF_6$ with an ultimate oxidative coupling under dilute conditions to give the desired porphyrin wheel-like array containing up 12 or 24 porphyrin units, in yields of 34 and 60 %, respectively.

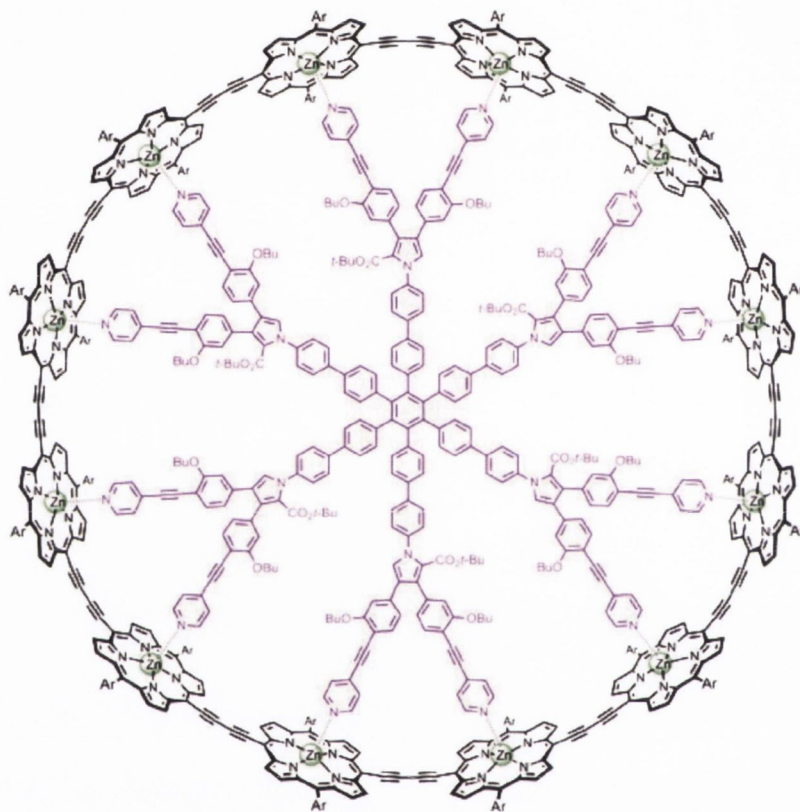


However, incorporating ethynyl and butadiyne linkers, as shown in square shaped tetrameric^[133] and dodecameric arrays **19**,^[134] creates the porphyrin dodecamer array as fully conjugated system, functioning like a molecular wire and making it applicable to the field of molecular devices and also for as a host-guest material. These arrays are generally synthesised via an ultimate Sonogashira or Glaser-Hay type coupling step, with overall yields being low to moderate, in the case of **19**, 9 %.



To enhance yields of these “cyclic porphyrin oligomers” and direct the desired oligomer formation, templates can be employed in the synthetic strategy via a supramolecular approach.^[137] Oligophenyleneacetylene linked cyclic hexamer **20** was synthesised in 59 % yield using the template **21** by Gossauer and co-workers.^[138] Without this template low yields of 8-31 % were obtained.^[139] Recently, the template-assisted synthesis of nano-ring **22** was obtained in a coupling yield of 96 % by Anderson and co-workers. Vernier templating was adopted to generate this 12-porphyrin nano-ring with a diameter of 4.7 nm, the template of which can easily be removed. These nano-rings of porphyrin macrocycles are of interest due to their resemblance to the natural light-harvesting complexes and no doubt will serve as mimics for insight into light-harvesting processes.^[140] Also, Anderson and co-workers developed the 6-membered porphyrin

nano-ring derivative of **22** and this has been shown to have promising OLED properties, whereby the cyclic array minimises aggregation in the electroluminescent layer.^[141] These supramolecular type constructions exhibit the benefits of using template-directed synthesis for the generation of new and potentially more efficient light-harvesting arrays, molecular wires and arrays for other optical applications.



22 [140]

1.5.2 Directly linked multiporphyrin arrays

Directly linked multiporphyrin arrays, both singly and triply fused, have the potential to be utilised in applications such as optoelectronics and nanotechnology. These directly linked arrays exhibit extremely efficient and rapid electron transfer along the array as the porphyrin chromophores interact strongly with one another as they are closer together than arrays connected via covalent linkers. With meso-meso directly linked arrays, the porphyrins lie orthogonal to each other (Figure 1.9), whereby the electronic delocalisation is minimal, in contrast to the conjugatively linked arrays. Thus, these arrays can be applied as electron transfer mimics and much research has been invested into the synthesis and application of such arrays to electron transfer processes. In

contrast, β - β , meso-meso, β - β triply linked arrays exhibit a substantial increase in electronic delocalisation and the π -conjugation is greatly enhanced through the array. Such oligomers are suitable for a wide range of optical applications.

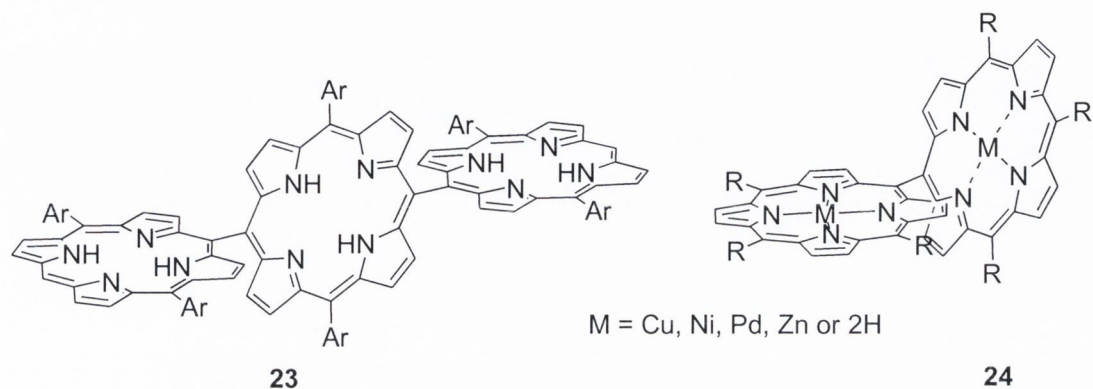
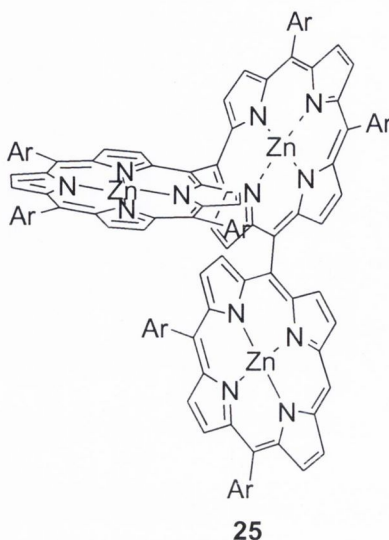


Figure 1.9: Directly linked porphyrin trimer **23** and dimer **24** showing perpendicular geometry.

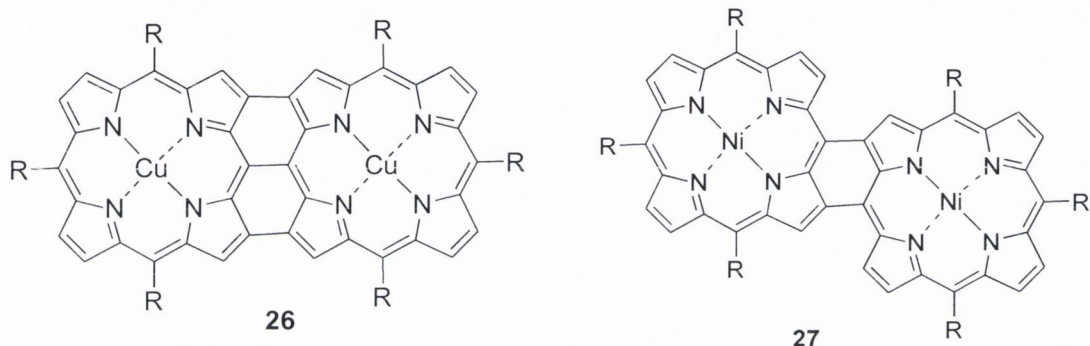
Since the first synthesis of meso-meso directly linked porphyrins by Susumu *et al.* in 1996 via a condensation reaction of a formyl porphyrin and a dipyrromethane derivative^[142] to yield trimer **23**, there have been numerous approaches towards the synthesis of such directly linked porphyrin arrays. As this condensation approach only yielded the directly linked array in low yield (<1 %), the development of alternative synthetic methods for the synthesis of such arrays was crucial. For singly linked arrays, these strategies include: total synthesis involving the condensation of a dipyrromethane with tetrakis(5-formyl-2-pyrrol)ethane,^[143] nickel-mediated Ullmann coupling,^[144] oxidative fusing of free meso porphyrins using various oxidants such as hypervalent iodine reagents (e.g., PIFA),^[145-146] silver salts (AgPF₆),^[147-151] and other strong oxidants such as DDQ/Sc(OTf)₃. Also, these arrays can be synthesised via electrochemical oxidation^[152-153] and via the oxidative dimerisation of porphyrin anions, a method developed by Senge and co-workers.^[154] The former method is advantageous as free base dimers are produced in one-step in excellent yields. Most other coupling methods require metallated porphyrins for fusing to occur. Additionally, a stepwise synthetic strategy can be adopted, which necessitates the prior activation of the C-H bond via bromination and borylation, with the ultimate palladium catalysed Suzuki coupling step to give the desired directly linked porphyrin array.^[155] Although prior activation of the meso position is needed, this stepwise synthesis is beneficial for the generation of unsymmetric and non-linear porphyrin arrays, such as L-shaped trimer **25**, which can act as precursors to more elaborate multiporphyrin arrays.^[156] These meso-meso directly linked porphyrin arrays

not only have importance in electron transfer studies as photosynthetic mimics but also are vital precursors to in the synthesis of triply fused porphyrinic arrays.



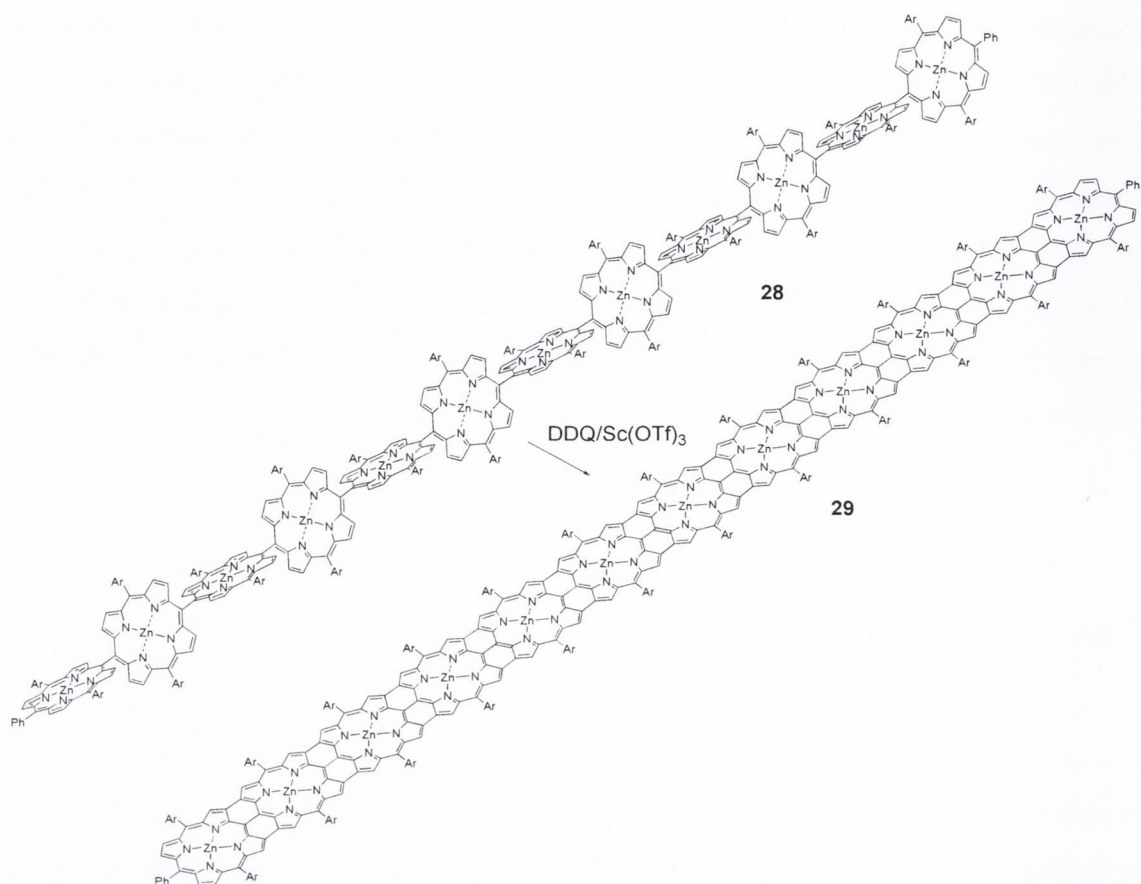
A large number of these oligoporphyrins have been synthesised and exhibit interesting photophysical properties. One convenient method is the Ag(I)-promoted oxidative coupling of 5,15-diarylporphyrins, discovered by Osuka and co-workers,^[157] one of the first methods developed towards directly linked porphyrin synthesis. This method involves the one-electron oxidation of metallocporphyrins at the free meso positions to give a radical cation^[158-159] which reacts with a neutral 5,15-porphyrin to give a directly linked bisporphyrin and higher oligomers. This approach opened the door to the use of other oxidants such as DDQ/Sc(OTf)₃ and hypervalent iodine to be employed as these reagents result in fewer side products. Using this single electron oxidation method, an oligomer consisting of 128 directly linked porphyrin units was synthesised,^[150] employing AgPF₆ as oxidant. The Ag(I) promoted oxidation can be improved by the addition of iodine and for 5,10,15-trisubstituted porphyrins, bisporphyrins can be synthesised in yields of up to 95%.^[160] To further prove the mechanism for oligoporphyrin formation, an electrochemical anodic oxidation was used for their synthesis. The regioselectivity for this oxidative coupling is strongly dependent on the central metal. For zinc(II) porphyrins, the a_{2u} HOMO predominates and as a result there is greater electron density at the meso carbon over the β-pyrrolic carbon.^[161] Thus, the cation radical generated is attacked by the neutral zinc(II) porphyrin at the meso position, which is the most nucleophilic site. With copper(II), palladium(II) and nickel(II), the a_{1u} HOMO is favoured, resulting in larger electron density at the β-pyrrolic carbon and thus

the meso- β linked arrays form with these metalated porphyrins. With hypervalent iodine(III) reagents such as bis(trifluoroacetate) (PIFA), a similar oxidative coupling pattern results. These reagents provide an alternative to the traditional metal oxidisers using mild conditions and can promote many coupling reactions due to the highly electrophilic iodine center.^[162-165] Their use in the synthesis of biaryl compounds via an efficient single-electron transfer mechanism^[166-167] ^[168] prompted the application of such reagents for the synthesis of directly linked porphyrin dimers in excellent yields with short reaction times.^[146]



Expanding from singly linked arrays, triply fused β - β , meso-meso, β - β triply linked arrays can also be synthesised using similar strategies, just employing larger quantities of oxidants. The first example of such fused arrays was that of copper(II) bisporphyrin **26**.^[169-170] This was synthesised from a meso trisubstituted precursor, using tris(4-bromophenyl)aminium hexachloroantimonate (BAHA) as oxidant.^[171-172] A drawback of this oxidant is that β -pyrrolic chlorinated side products formed, thereby limiting the applicability of this reagent. To eliminate this, other strong oxidants such as DDQ/Sc(OTf)₃^[173] and PIFA^[174] can be used. Again, the central metal determines the regioselectivities of these oxidations with β - β , meso-meso, β - β triply linked arrays forming with zinc(II) porphyrins and β - β , meso-meso doubly linked arrays forming with palladium(II) and nickel(II) porphyrins **26** and **27**.^[175] This can be attributed to electronic properties as discussed for the singly linked arrays.

Using 5,15-disubstituted porphyrins, porphyrin tapes **28** and **29**, of up to 12 porphyrin units, were synthesised^[173] employing DDQ/Sc(OTf)₃ as oxidant (Scheme 1.3). These planar structures have an absorption bathochromic shift due to their extensive π -conjugation, which increases with increasing porphyrin units, and have the potential for applications in non-linear optics and molecular electronics.



Scheme 1.3: Synthesis of porphyrin tape **29** via DDQ/Sc(OTf)₃ oxidation of **28**.

Other methods for the synthesis of such arrays adopt different oxidants, a recent one being that of gold(III) mediated oxidation using AuCl₃-AgOTf. This gold salt induces the oxidative coupling of free meso porphyrins, most likely through a one-electron oxidation as seen with other oxidants, albeit much more powerful, enabling the synthesis of nickel(II) β - β , meso-meso, β - β triply fused bisporphyrins of type **26**.^[176] Formation of the doubly fused bisporphyrin, typical with nickel(II) porphyrins using other oxidants, was observed only when oxidant equivalents were lowered. This gold mediated oxidation also enabled the synthesis of bromo substituted triply fused dimers in excellent yields, in comparison to yields of <15% when DDQ/Sc(OTf)₃ was employed as the oxidant. A limitation in this method, however, is the instability of zinc(II) porphyrins. There is significant demetallation from the starting material, restricting any possible oxidative coupling products. For the synthesis of more elaborate, non-linear constructs a stepwise strategy is needed.^[156] In general, the construction of the singly directly linked array is executed first and subsequent oxidation provides the desired fused array. A range of square, L-shaped, T-shaped **30**, square **31**, triangular and circular arrays have been

developed by Osuka and co-workers, all with interesting photophysical properties enabling their use in areas such as NLO and other optical applications (Figure 1.10).^[156]

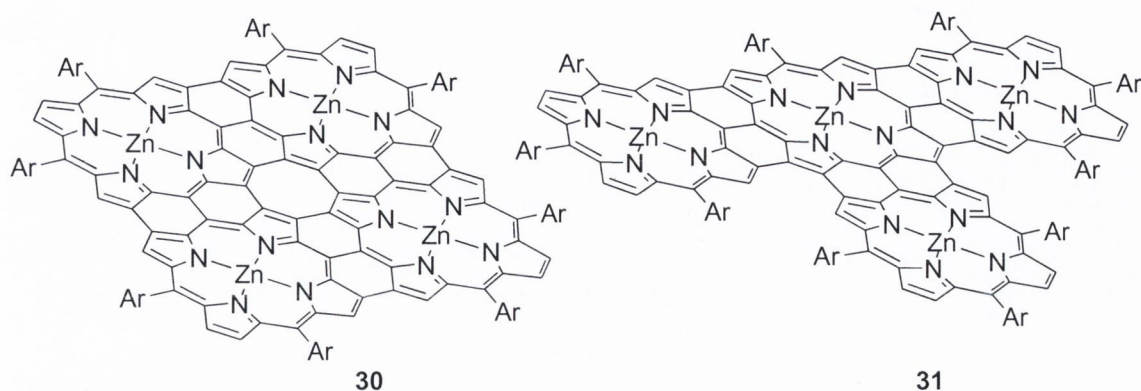
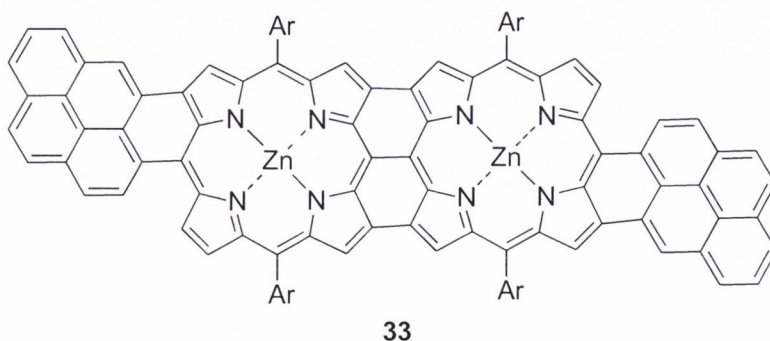
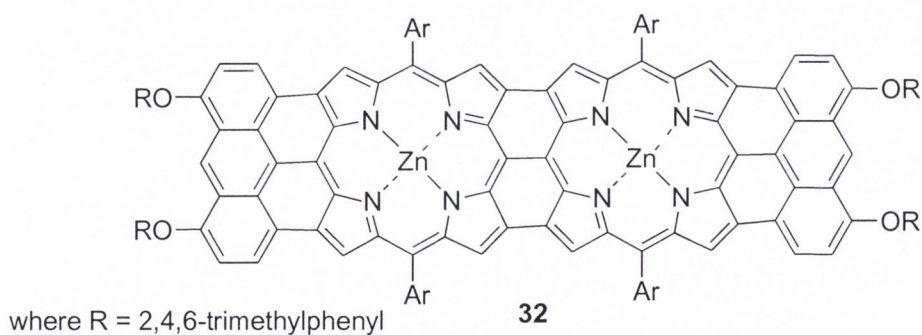
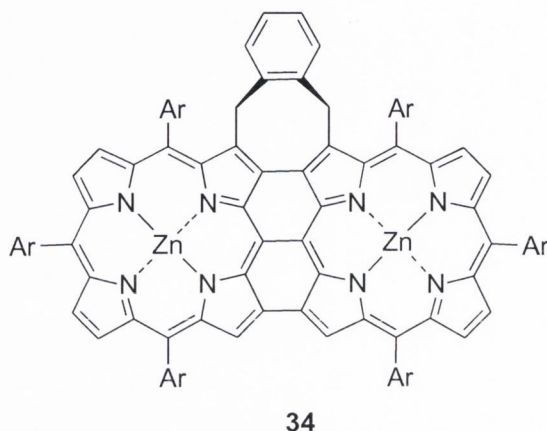


Figure 1.10: Square-shaped and T-shaped fused arrays **30** and **31** developed by Osuka and co-workers.

Work by Davis *et al.* has produced triply linked systems with anthracene fused at the porphyrin periphery using Osuka's oxidative method.^[177-178] This further enhances the absorption profile and electronic properties of the array. For this fusing to work, however, electron donating alkoxy substituents on the anthracene units were required and dimer **32** was prepared in 13 % yield. This dimer exhibited a pronounced bathochromic shift in absorption spectrum, well into the near-IR region, with a λ_{max} of 1495 nm. Other triply fused porphyrin arrays incorporating fused aromatic moieties, e.g., pyrene **33**^[179-180] and perylene,^[181] have been developed, with similar effects in comparison with anthracene derivative **32** on the overall electronic properties.



Limited research has focused on the reactivity of such triply fused systems, with Osuka and co-workers reporting ‘bay-area’ modifications when zinc(II) triply fused dimers were treated with azomethine ylide^[182] and *o*-xylene^[183] whereby cycloaddition occurred with the internal double bonds (“bay area”), to form chlorin intermediates which are subsequently oxidised to give the cycloadduct of type **34**.



Other modifications to directly linked porphyrins were generally carried out on singly fused arrays, prior to triply fusing, for example β -functionalisations using iridium catalysts. Such post-modifications of meso-meso linked arrays demonstrate the ability to fine-tune such oligomers for use in optical applications.^[184]

1.6 Objectives

The aim of this work was to develop novel strategies for the synthesis of covalently linked unsymmetrical multiporphyrin arrays, both conjugatively and directly linked, for the purpose of exerting a bathochromic shift in the absorption profile. These arrays have the potential to be used in optical applications, the focus here being on PDT, NLO and OLEDs.

For the synthesis of multiporphyrin arrays, the functionalisation of the porphyrin periphery was essential and therefore the introduction of substituents at the monomeric stage was executed adopting an extensive range of reactions, particularly organolithium reactions, which have been comprehensively developed by the Senge group, and palladium catalysed coupling reactions. These reactions enabled the introduction of the vital linker substituents for the synthesis of conjugated arrays.

Whilst many multiporphyrin arrays connected via conjugated linkers exist, the majority of these focus on symmetric systems and arrays that have saturated meso substitution patterns. Our approach was to develop unsymmetric conjugated dimers and linear trimers via a twofold strategy. The first involved the introduction of asymmetry at the monomeric stage, whilst the second was the synthesis of linear arrays bearing free meso positions which potentially act as sites for further chemical modifications. Adopting Sonogashira catalysed coupling reactions it was hoped to prepare a library of these compounds and to investigate their photophysical properties.

Fully conjugated porphyrin arrays were also sought after for further expansion of the absorption profile. The most efficient way of doing so is through triply fusing porphyrin units via oxidative methods generating fused porphyrin arrays, resulting in a significant bathochromic shift of the absorption into the near-infrared region. Although several investigations have been carried out on these arrays, these are limited to symmetric arrays incorporating similar substituents. Our aim was to develop a library of symmetric and unsymmetric porphyrin dimers and arrays, via known oxidative methods, for similar purposes as those for the conjugatively linked oligomers. It was also hoped to investigate the reactivity of the fused arrays, limited research of which exists in the literature.

Lastly, it was envisaged to develop a series of novel porphyrin-carbazole conjugates for OLED studies. Polymeric carbazoles are commonly used as host matrices in OLED devices. Via the incorporation of this moiety to the porphyrin macrocycle and the development of novel carbazole-linked porphyrins, it was hoped that an improvement of OLED properties would be observed. Implementing a novel stepwise synthetic strategy, such conjugates could be generated and their OLED properties investigated.

CHAPTER 2:
Synthesis of Monomeric Porphyrin
Precursors

2.1 Introduction

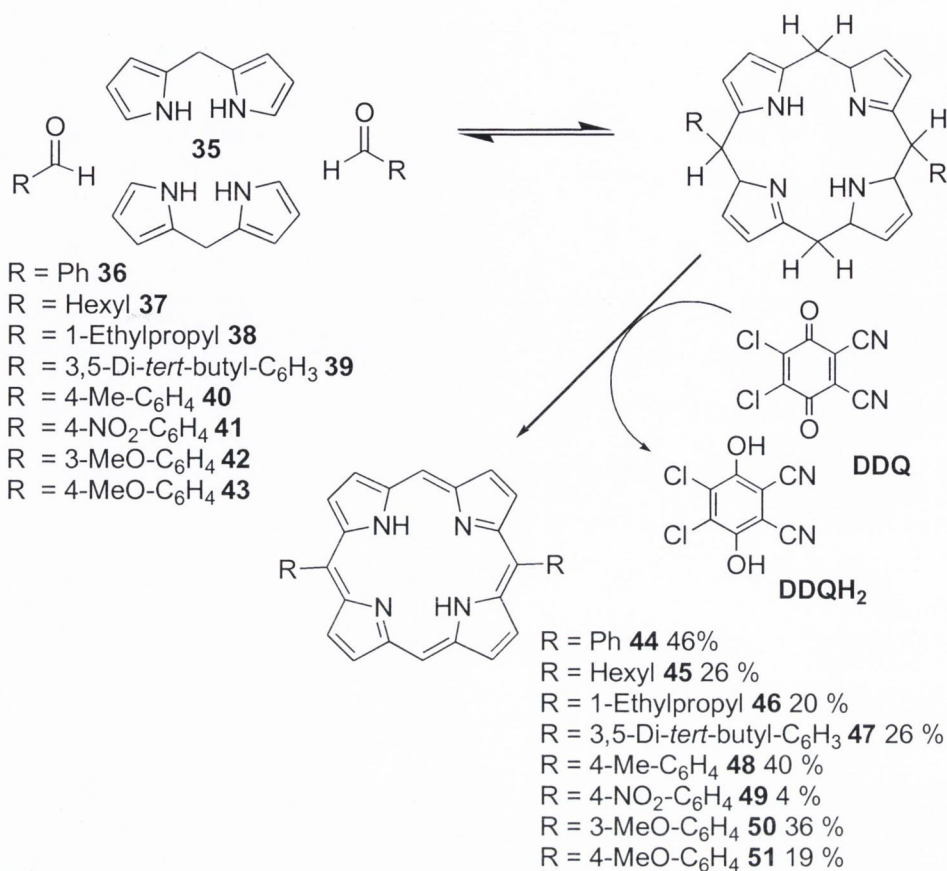
The synthesis of monomeric porphyrins is vital for the subsequent construction of multiporphyrin arrays. At the monomeric stage, synthetic strategy is of utmost importance, as it is at this point that the majority of functionalisations to the porphyrin periphery are executed. An example for this is the activation of the porphyrin via halogenation and the introduction of the conjugated linkers, such as ethyne and phenylacetylene, necessary for synthesis of linked porphyrin arrays. A range of different reactions can be adopted for these syntheses and this chapter will focus on the key steps in the construction of these monomeric precursor porphyrins.

2.2 Synthesis

2.2.1 Synthesis of 5,15- A_2 porphyrins

For the scope of this thesis, the porphyrin building block of main concern are the 5,15-disubstituted A_2 type porphyrin and the various meso functionalisations which were undertaken. To synthesise this type of A_2 -porphyrin, the [2+2] MacDonald synthetic strategy was adopted^[28, 185] (Scheme 2.1), whereby dipyrromethane **35** (DPM) was condensed with the desired aldehyde (**36-43**) to yield 5,15-disubstituted porphyrins **44**,^[186] **45**,^[187] **46**,^[188] **47**,^[142] **48**,^[189] **49**, **51**,^[185] **50**,^[190] in yields of 4-43 %, comparable to those in the literature. The mechanism for this acid-catalysed condensation proceeds via a thermodynamically favoured porphyrinogen intermediate,^[186] over the oligomerisation of DPM, which is subsequently oxidised to the desired porphyrin using DDQ as oxidant.^[26, 185, 191]

This mild synthetic approach is versatile for many functionalities, enabling the generation of 5,15-porphyrins in gram scale quantities and is advantageous over the harsher Rothemund^[23] and Adler-Longo^[25] condensation strategies. The equilibrium for porphyrinogen formation is highly dependent on the reaction concentration and the irreversible formation of porphyrin is achieved via oxidation with DDQ. Any oligomerised **35** will also be oxidised, the removal of which is easily executed via filtration through a plug of silica gel.



Scheme 2.1: MacDonald [2+2] Condensation: Synthesis of 5,15-A₂ porphyrins **44-51**. *Reagents and conditions:* i) **35**, aldehyde, CH₂Cl₂, TFA, rt, ii) DDQ, TEA.

For the synthesis of **35**, pyrrole was condensed with paraformaldehyde in a one-pot synthesis with pyrrole acting as both reagent and solvent, with a reaction temperature of 60 °C due to the poor solubility of paraformaldehyde at room temperature. Following Kugelrohr distillation **35** was obtained in a yield of 46%, following a widely utilised method, developed by Lindsey and co-workers.^[30] This method can also be adopted for the synthesis of substituted dipyrromethanes, allowing for the “*trans*” tetrasubstituted 5,15-A₂B₂ porphyrins to be synthesised,^[192] although scrambling issues from this synthetic route can prove problematic.^[192-194] Key to obtaining acceptable yields of these DPMs is the termination of the condensation at the DPM stage, minimising the formation of oligomerised products which is obtained by using a huge excess of pyrrole which suppresses oligomerisation. Also, acid-catalysation of pyrrole gives predominantly 2- and trace 3- substituted products leading to a *N*-confused dipyrromethane which can affect yields.^[30, 195] An array of other methods exist for the synthesis of **35**, generally only differing in quantities of pyrrole and reaction solvent used and the work-up conditions, without significant effect on the yield. The maximum reported yield of **35** in

51 % was from the Lindsey method, adapted recently by Anderson and co-workers,^[196] with modified quantities of pyrrole, using paraformaldehyde dissolved in water and carrying out the reaction at room temperature. Such conditions minimise oligomerisation and hence improve reaction yields. Alternative routes to these key DPM precursors include stepwise and directed syntheses. The yields of the A₂ substituted porphyrins **44-51** vary quite significantly depending on substituent and are generally affected by poor solubilities of the final compound, thus making isolation difficult. This was particularly noticeable for *para*-nitrophenylporphyrin **49**, where a condensation yield of only 4 % was obtained. These 5,15- A₂ porphyrins have two free meso positions whereby functionalisations and the introduction of crucial linker substituents can be executed.

2.2.2 Organolithium reactions

A versatile method for the introduction of meso substituents to the 5,15-A₂ porphyrins is the organolithium approach, developed by Senge and co-workers.^[37-39] As unsymmetrically substituted porphyrins are required by many applications, this method proves quite useful for their synthesis. Other strategies for the production of unsymmetric porphyrins involve challenging total syntheses^[35] which, from a practical viewpoint, are not viable. The organolithium approach involves a direct nucleophilic substitution of the porphyrin periphery, thereby eliminating any need for prior activation, and was first demonstrated by Callot and co-workers on TPP via butylation at the β -position and also meso-butylation of OEP giving stable phlorin products but in low yields.^[197-198] However, Senge and co-workers demonstrated the capability of nucleophilic substitution via organolithium reactions with OEP yielding 5-substituted porphyrins in yields of up to 95 %.^[37,199] When applied to β -unsubstituted 5,15-A₂ porphyrins, the synthesis of A₂B porphyrins in excellent yields was possible.^[116,200] This method is favorable as it is highly tolerant of a wide range of functionalities and involves either the direct reaction of organolithium reagent with the porphyrin, i.e. whereby these are commercially available, namely phenyllithium, hexyllithium and *n*-butyllithium, or, where the organolithium reagent must be first generated *in situ* and subsequently reacted with the porphyrin. This method enables the introduction of vital substituents and is key to the synthetic strategy for the generation of multiporphyrin arrays.

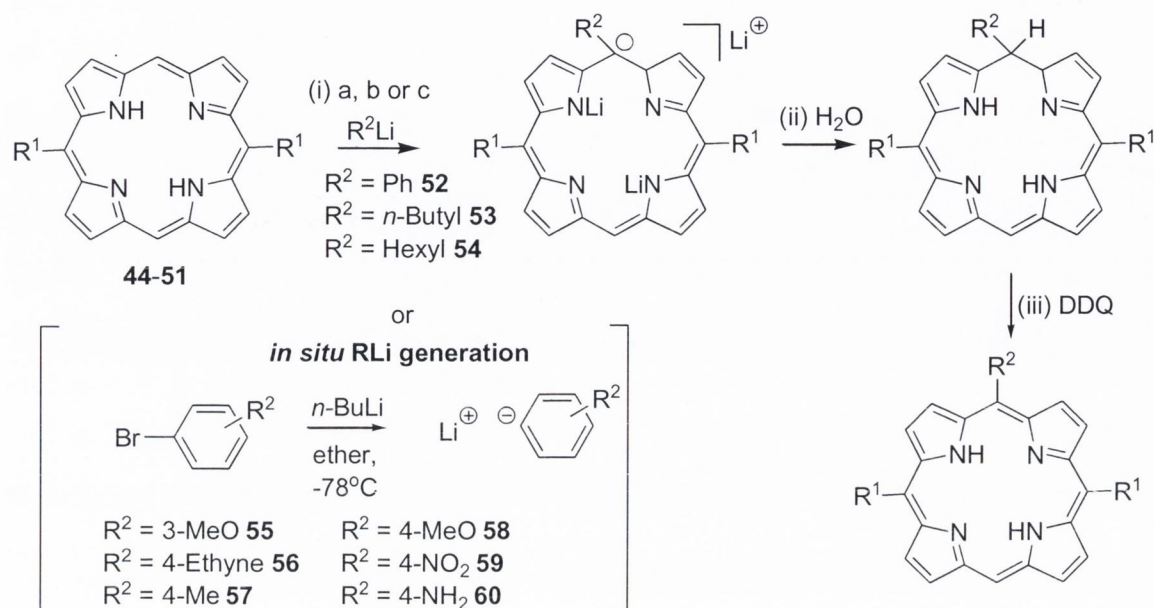
These organolithium reactions can be used to generate fully unsymmetrical ABCD porphyrins from porphine **1** or 5- A substituted porphyrins,^[201-202] but here emphasis will

be on the generation of trisubstituted A_3 and A_2B systems from A_2 precursors **44-51**. On reaction of a 5,15- A_2 porphyrin with the organolithium reagent (Scheme 2.2), a hydroporphyrin intermediate is generated. For free-base porphyrins the reaction proceeds via a dihydroporphyrin or phlorin intermediate, whilst for metalloporphyrins, the reaction proceeds via a porphodimethene species. The overall nucleophilic substitution via an addition-oxidation mechanism is similar to that of Ziegler alkylation,^[203] whereby the initial reaction of the organolithium reagent on the meso carbon generates an anionic species. This can be hydrolysed to the hydroporphyrin, with subsequent oxidation with DDQ yielding the desired A_3 or A_2B porphyrin^[116] or, the anionic species can be trapped with electrophilic reagents to generate unsymmetric A_2BC monomeric systems,^[204] but other routes are preferred.

The mechanism shown in Scheme 2.2 is generally what can be applied for free-base precursors, whereby the lithiated intermediate generated on addition of R^2Li is hydrolysed to a phlorin, which is subsequently oxidised to the desired trisubstituted A_3 or A_2B porphyrin. From a strategic viewpoint, these organolithium reactions were critical as they enabled the introduction of the phenylacetylene linker to porphyrins **44**, **45** and **46** and these also enabled the incorporation of key substituents to the free meso positions of A_2 porphyrins **44-51** generating A_3 and A_2B porphyrins. Substituents such as methoxyphenyl have been shown to be beneficial for the localisation of photosensitisers in tumours in PDT treatment^[205] (Section 1.4.3), so it was envisaged that the introduction of these substituents would be advantageous for this application.

The introduction of phenyl, *n*-butyl and *n*-hexyl substituents to the porphyrin macrocycle is simply executed via the direct addition of **52**, **53** and **54** respectively to the specific porphyrin dissolved in THF under inert conditions. For organolithium reagent **52**, addition can be carried out at 0 °C but for **53** and **54**, addition is carried out at -78 °C and is implemented more slowly. This enabled the generation of a library of phenyl, *n*-butyl and hexyl substituted A_3 and A_2B porphyrins in good to excellent yields of 67-93 % for porphyrins **65**, **67**, **72**, **73-75**, **77** and **78** (Scheme 2.2). However, attempts to substitute 5,15-bis(4-nitrophenyl)porphyrin **49** with a phenyl group via the organolithium reaction, for the formation of **71**, were unsuccessful, most likely due to the poor solubility of **49** in THF. No reaction was observed and the starting material was recovered. *para*-Nitro

porphyrins are notoriously insoluble materials^[206] and thus functionalisation of **49** was abandoned.



R ¹	R ²	#	%
Ph	3-MeO-C ₆ H ₄	61 ^[40]	30
Ph		62 ^[116]	85
Ph	4-O ₂ N-C ₆ H ₄	63 ^[209]	n/d
Ph	4-H ₂ N-C ₆ H ₄	64 ^[116]	11
Hexyl	Hexyl	65 ^[211]	93
Hexyl		66	30
1-ethylpropyl	Ph	67	92
1-ethylpropyl		68	35
3-MeO-C ₆ H ₄	3-MeO-C ₆ H ₄	69 ^[190]	65
4-MeO-C ₆ H ₄	4-MeO-C ₆ H ₄	70 ^[212]	71
4-O ₂ N-C ₆ H ₄	Ph	71	n/d

R ¹	R ²	#	%
Ph	Ph	72 ^[207]	93
Ph	Hexyl	73 ^[208]	67
Ar	Ph	74 ^[210]	92
Ar	Hexyl	75	75
4-Me-C ₆ H ₄	4-Me-C ₆ H ₄	76 ^[129]	91
4-Me-C ₆ H ₄	<i>n</i> -Butyl	77	69
3-MeO-C ₆ H ₄	Ph	78 ^[40]	92
3-MeO-C ₆ H ₄	<i>n</i> -Butyl	79 ^[208]	26
4-MeO-C ₆ H ₄	<i>n</i> -Butyl	80	33

where Ar = 3,5-di-*tert*-butyl-C₆H₃

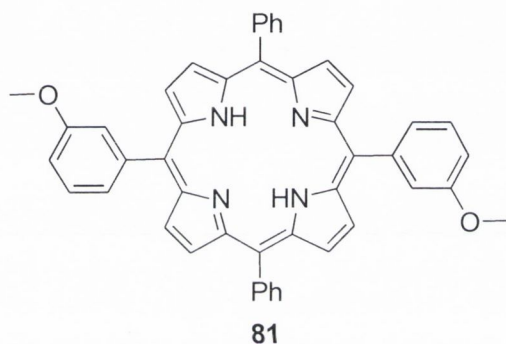
Scheme 2.2: Synthesis of A₃ and A₂B porphyrins **61–80**. *Reagents and conditions:* i) a) PhLi, THF, rt, 0.5 h. b) *n*-BuLi or *n*-HexLi, THF, -78 °C – rt, 0.5 – 1 h. c) *n*-BuLi, arylbromide, diethylether -78°C – rt, porphyrin, THF 0.5 – 1 h. ii) H₂O, 0.4 h. iii) DDQ, 1 h.

For substitutions where the organolithium reagent was not commercially available, these were obtained via the *in situ* lithiation of aryl bromides with *n*-BuLi, via a lithium-

halogen exchange. The generated organic nucleophiles were then reacted with the electrophilic porphyrin at a free meso position to form the desired trisubstituted product. For phenylacetylene introduction, on generation of RLi **56**, the reaction proceeded quite well with phenyl substituted porphyrins, forming **62**^[116] in 74% yield. However, this was not the case for the alkyl substituted porphyrins, which formed **66** and **68** in yields of 35 and 30 %, respectively. The best yield for **68** was obtained when the reaction was left overnight. This appeared initially to be a solubility problem of **46** in THF. However, when the solvent volume was increased no improvement was seen. Other alterations such as adjusting the *n*-BuLi equivalents and altering reaction time had no positive effect on the reaction yield. Starting materials **45** and **46** were recovered in approximate yields of 30 and 28%, respectively. Other methods employ mixed condensations for phenylacetylene substitution, but as arrays bearing a free meso substituent were of concern, this was not a feasible approach and thus the organolithium method was favoured.

To introduce a *para*-nitrophenyl substituent via organolithium reaction, test reactions were carried out using **44**. The generation of the organolithium reagent *in situ* from bromo-nitrophenyl **59** was challenging and although some generation was observed, with a white suspension forming, subsequent trapping via the porphyrin electrophile (**44** in THF) was unsuccessful. The desired compound **63** was not detected and the starting material **44** was recovered. The unsuccessful generation of organolithium **59** can most likely be attributed to the *para* electron withdrawing effect of the nitro group which destabilises carbanion formation, i.e the *ortho/para* deactivating effect. Therefore, for the introduction of such nitrophenyl groups, an alternative strategy was required (Section 2.2.5). For the 4-aminophenyl incorporation to the porphyrin periphery, for the synthesis of **64**, generation of the organolithium reagent again proved challenging. Although here, a *para* electron donating group is being used and thus, in theory, generation of **60** should not be problematic with porphyrin **64** has a literature yield of 82 %, ^[116] this was not the case. In practice, RLi **60** took longer than 5 hrs to generate and the subsequent reaction of **60** with porphyrin **44** had poor results. Generally, the butylated starting material was observed when a shorter generation time of RLi was used, only after a 5 h generation time and subsequent reaction time of 16 hrs was the desired porphyrin **64** observed in a low yield of 11 %. Such low yields may be attributed to the decomposition of **64** on silica gel during purification or due to incomplete generation of RLi **60**.

For 4-methylphenyl (tolyl) introduction, reactive species **57** was generated from 4-bromotoluene. Subsequent reaction with ditolyl porphyrin **48** gave the trisubstituted A₃ porphyrin **76** in an excellent yield of 92 %. The introduction of aryl-alkoxy substituents, however, was not as high yielding. Porphyrins **50** and **51** yielded the butylated side-products **79**^[208] and **80** in yields of 26 and 23%, respectively, along with the desired trisubstituted compounds **69**^[208] and **70** in yields of 65 and 71%. Also, for the synthesis of **61**, the tetrasubstituted product **81** was formed as a side product in 4% yield, and the desired trisubstituted porphyrin was only obtained in a 30 % yield. In spite of occurring as side products, the butylated materials were employed in subsequent reactions for the synthesis of porphyrin arrays.

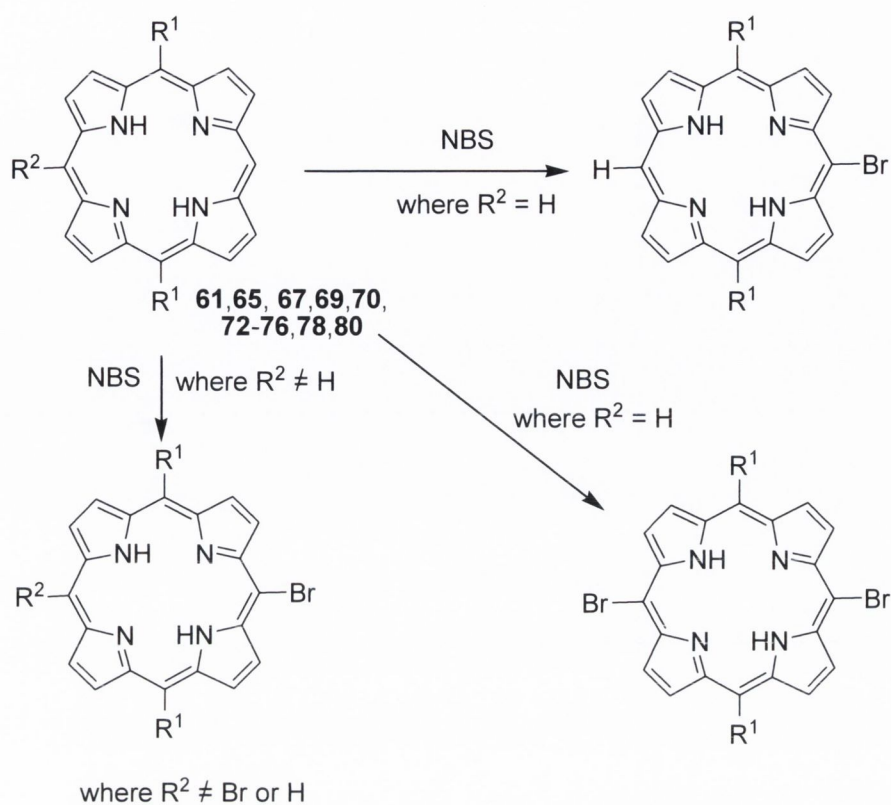


2.2.3 Bromination

Key precursors for the production of porphyrin oligomers are bromo-porphyrins. These activated porphyrins allow for many palladium catalysed cross-coupling reactions to be carried out, generating a new C-C or C-heteroatom bond, useful in both the synthesis of arrays, and also for the introduction of key substituents or linkers. Brominations of porphyrins can be carried out by numerous methods,^[213-214] and involve an electrophilic aromatic substitution (S_EAr). There are two sites where S_EAr in porphyrins can occur, the meso and β -positions, with preferential substitution at the more reactive meso positions. The most utilised bromination methods involve the use of molecular bromine (Br₂) or *N*-bromosuccinimide (NBS) in chlorinated solvents, the latter of which is preferred for meso-bromination. 5,15-A₂ **44-48** and **50**, and 5,10,15-A₂B **61**, **65**, **67**, **69**, **70**, **72-76** and **78-80** porphyrins were brominated using NBS following a standard procedure^[44] forming brominated porphyrins **82-102**^[215-217] in yields ranging from 55-95%, the lower yields being those of alkoxy substituted porphyrins **90** and **91**, along with monobrominated porphyrins **94**,^[215] **95**, **96**,^[218] **97**^[219] and **102**. The alkoxy-phenyl

porphyrins were more soluble in methanol than other substituted porphyrins, thus, product was lost during the work-up procedure, leading to a lowering of yields. For monobromination of 5,15-disubstituted porphyrins, the regioselectivity is quite difficult to control and thus leads to the formation of dibrominated porphyrins as side products, although optimised conditions enable isolation of monobrominated products in yields of up to 66 %. The separation of such bromo products via column chromatography is time-consuming and uneconomical. Thus, an alternative method to achieve such monobrominated precursors is through dibromination and subsequent mono debromination via dehydropalladisation, using a palladium catalyst and hydrogen source.^[176, 220-221] Such debromination procedures are of benefit as they enable the generation of mono-brominated porphyrins without the requisite of column chromatography and it also enables the bromo substituent to act as a protecting group in some reactions. This method was not investigated but could facilitate a superior and less time-consuming route towards the generation of mono-brominated porphyrins. One drawback of the procedure would be the possible palladium metal insertion so generally metallated porphyrins need to be employed for this method.

Despite this drawback, these monobrominated porphyrin monomers are essential in subsequent coupling reactions to form the linear oligomers with free meso positions, with dibrominated porphyrins being used for trimeric array synthesis. Surprisingly, the dibromo-dihexyl porphyrin **99**^[217] proved quite insoluble in many organic solvents, such as THF, and thus was not used for further reactions. Hence the 1-ethylpropyl derivative **101** was used as solubility was enhanced. All of the above bromo-porphyrins were used in subsequent coupling reactions, for the introduction of functionalised substituents and/or for the synthesis of porphyrin arrays.

**A₂B/A₃ bromo porphyrins**

R^1	R^2	#	Yield %
Ph	3-MeO-C ₆ H ₄	82	69
Ph	Ph	83 ^[210, 222]	93
Ph	Hexyl	84 ^[223]	89
Hexyl	Hexyl	85 ^[211]	88
Ar	Hexyl	86	93
Ar	Ph	87 ^[210]	91
1-Ethylpropyl	Ph	88	94
3-MeO-C ₆ H ₄	Ph	89	94
3-MeO-C ₆ H ₄	3-MeO-C ₆ H ₄	90	69
4-MeO-C ₆ H ₄	4-MeO-C ₆ H ₄	91	61
4-MeO-C ₆ H ₄	<i>n</i> -Butyl	92	55
4-Me-C ₆ H ₄	4-Me-C ₆ H ₄	93 ^[129]	92

A₂ mono and dibromoporphyrins

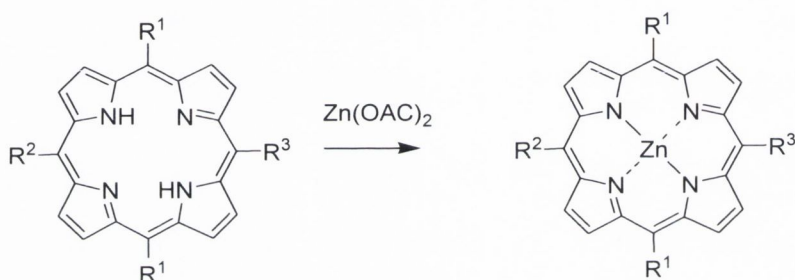
R^1	R^2	#	Yield %
Ph	H	94 ^[215]	58
1-Ethylpropyl	H	95	54
3-MeO-C ₆ H ₄	H	96 ^[218]	54
4-Me-C ₆ H ₄	H	97 ^[218]	57
Ph	Br	98 ^[216]	93
Hexyl	Br	99 ^[217]	88
Ar	Br	100 ^[224]	92
1-Ethylpropyl	Br	101	88
Ar	H	102	88

where Ar = 3,5-Di-*tert*-butyl-C₆H₃

Scheme 2.3: Synthesis of bromoporphyrins **82-102**. *Reagents and conditions:* NBS, pyridine, CHCl₃, 0 °C, 0.5 - 3 h.

2.2.4 Metallation

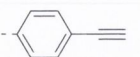
Metalloporphyrins exist where a metal ion coordinates with the lone-pairs on the inner nitrogen atoms in the porphyrin core, with the loss of the two inner hydrogen atoms. An extensive range of metal ions can be inserted, the method of which is dependent on the metal ion involved.^[225] Metal insertions into the porphyrin core are very straightforward and high yielding.^[226] Tactically, metallations were undertaken to protect the porphyrin core from undesired metal insertions during coupling reactions, for comparative studies with free-base counterparts and also for the fine-tuning of electronic properties for optical applications, such as electron transfer to mimic biological systems.^[227]



Where $R^3 = \text{Br}$

R^1	R^2	#	%
Hexyl	Hexyl	103	89
Ph	Ph	104 ^[129]	95
	H	105 ^[119]	90
	Hexyl	106	84
	Br	107 ^[216]	92
4-Me-C ₆ H ₄	H	108	85
	4-Me-C ₆ H ₄	109 ^[129]	93
3-MeO-C ₆ H ₄	H	110	82
	Ph	111	89
Ar	Ph	112 ^[46]	90
	Ph	113	92
1-Ethylpropyl	Ph	113	92
	Br	114	88

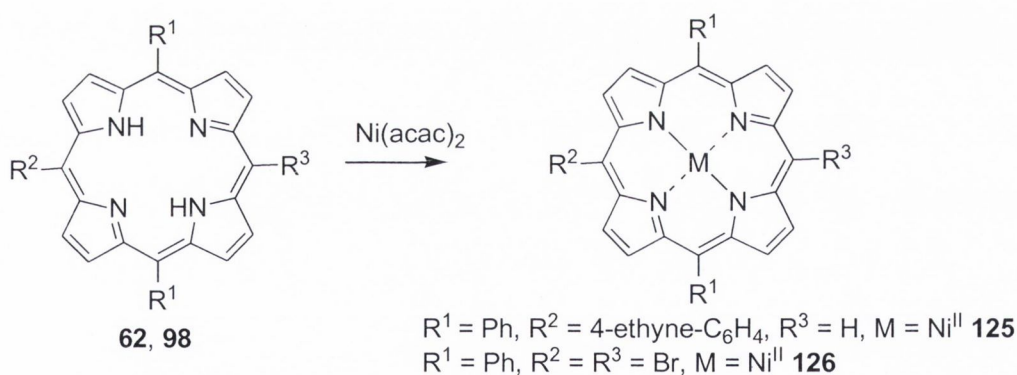
Where $R^3 = \text{H}$

R^1	R^2	#	%
Ph	Hexyl	115	89
Ph	Ph	116 ^[40]	93
		117 ^[202]	86
	H	118	90
4-MeO-C ₆ H ₄	4-MeO-C ₆ H ₄	119	87
3-MeO-C ₆ H ₄	<i>n</i> -Butyl	120	85
1-Ethylpropyl		121	81
Hexyl	H	122 ^[187]	77
Ar	Br	123 ^[228]	80
4-Me-C ₆ H ₄	butyl	124	92

where Ar = 3,5-Di-*tert*-butyl-C₆H₃

Scheme 2.4: Metallation of monomeric porphyrins with zinc(II). *Reagents and conditions:* Zn(OAc)₂ in MeOH, CHCl₃, 70 °C, 0.5 h.

The most predominant metal used was zinc, as not only has this metal been proven to improve efficacy in PDT,^[229] but also is easily inserted with short reaction time and is easily removed if so required as it is acid labile. Other metals, such as palladium, indium and nickel require more time for insertion and also are less labile so, if required, cannot be easily removed. Generally, the palladium, indium chloride and nickel complexes were synthesised for comparative purposes with zinc and free base counterparts, and will be discussed in Chapters 3 and 6. For zinc insertion, the acetate method, developed by Buchler,^[226, 230] was adopted and can be applied to all divalent metal ions, except those unstable in acetic acid as this is a by-product of the reaction. The method involves the addition of zinc(II)acetate dihydrate, the metal carrier, dissolved in methanol to a refluxing solution of the free-base porphyrin in chloroform yielding zinc metallated porphyrins **103-124** in yields ranging from 77-93 % (Scheme 2.4). Generally reaction times are short, with most completing in less than 30 minutes. The isolation of bromo porphyrins **108**, **110** and **111** proved problematic as such porphyrins were highly insoluble in organic solvents such as DCM and thus their isolation from the silica plug was difficult and impacted on yield.



Scheme 2.5: Metallation with nickel(II). *Reagents and conditions:* $\text{Ni}(\text{acac})_2$, toluene, 120 °C, 3.5 h.

For nickel insertion the acetylacetonate method was adopted,^[225] whereby the metal carrier used is acetylacetonate. Porphyrins **62** and **98** were metallated with nickel in excellent yields of 90 and 92 % forming porphyrins **125** and **126**^[44] respectively (Scheme 2.5).

2.2.5 Palladium catalysed coupling reactions

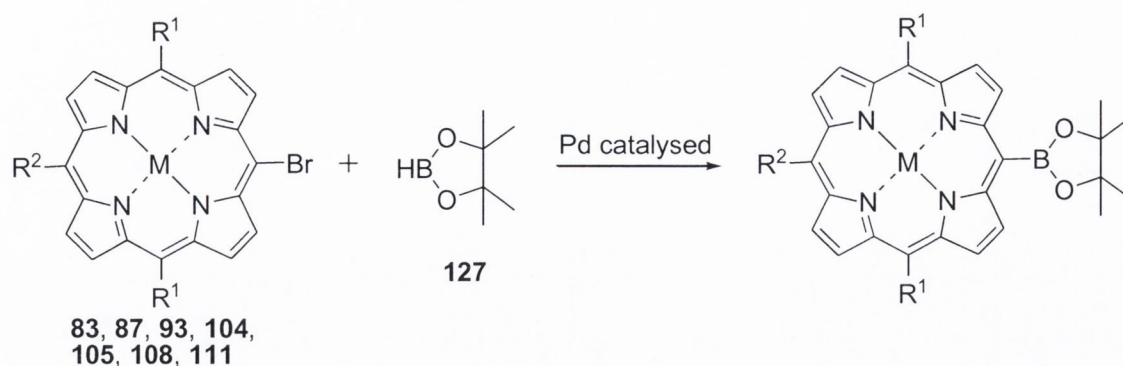
Transition metal mediated reactions enable the introduction of numerous functionalities onto organic substrates, via the generation of carbon-carbon (C-C) and carbon-

heteroatom (C-X, where X = O, N, B etc.) bonds and have a critical function in organic synthesis.^[231] Although numerous metal catalysts exist, the most extensively used transition metal for the catalysis of the generation of such bonds is palladium. Numerous palladium catalysed reactions, such as Stille, Heck, Sonogashira^[232] and Suzuki-Miyaura^[233] couplings are known, enabling the formation of new carbon bonds, with their mild reaction conditions allowing the tolerance of a versatile range of functionalities. Such palladium-catalysed reactions have been extensively applied to porphyrins, with generation of numerous novel moieties.^[41-42, 234]

Depending on the functionality desired, different Pd-catalysed couplings can be employed, the majority of which involve the derivatisation of a halo-porphyrin precursor. Sonogashira coupling^[235] allows for the introduction of alkynyl functionalities via the coupling of a halo porphyrin with a terminal alkyne. Suzuki-Miyaura couplings^[233, 236] allow for C-C bond generation via the coupling of an organoborate with a halo-porphyrin. These organoborate precursors can also be in the form of porphyrinyl borates, generated via an analogous Suzuki-Miyaura type coupling of haloporphyrins with a borane. Such Pd-mediated reactions were used extensively in our work for the construction of key monomeric porphyrin precursors and also in the production of multiporphyrin arrays. These palladium catalysed reactions proceed via a basic general mechanism involving three key steps: oxidative addition, transmetallation and reductive elimination.

Borylation

Organoboranes^[237] are key precursors for Suzuki coupling reactions and in many instances act as an alternative to haloporphyrins in these C-C coupling type reactions. Applying a procedure to generate aryl boronates developed by Murata *et al.*,^[238] the first reported synthesis of porphyrinyl borates was by Therien and co-workers and these so-called ‘Suzuki synthons’ were employed for numerous Suzuki type couplings.^[239] This Pd-catalysed reaction generates the desired porphyrin boranes from bromoporphyrin precursors and pinacolborane **127** in good to excellent yields and such synthons can be used as precursors, not only for the introduction of substituents to the porphyrin periphery, but also for the generation of directly-linked porphyrin dimers.



R ¹	R ²	M	#	Yield %
Ph	Ph	2H	128 ^[240]	54
Ph	Ph	Zn ^{II}	129 ^[219]	60
4-Me-C ₆ H ₄	H	Zn ^{II}	130 ^[241]	62
3-MeO-C ₆ H ₄	Ph	Zn ^{II}	131	62
4-Me-C ₆ H ₄	4-Me-C ₆ H ₄	2H	132 ^[242]	54
Ph	H	Zn ^{II}	133 ^[239]	69
Hexyl	Hexyl	2H	134	51

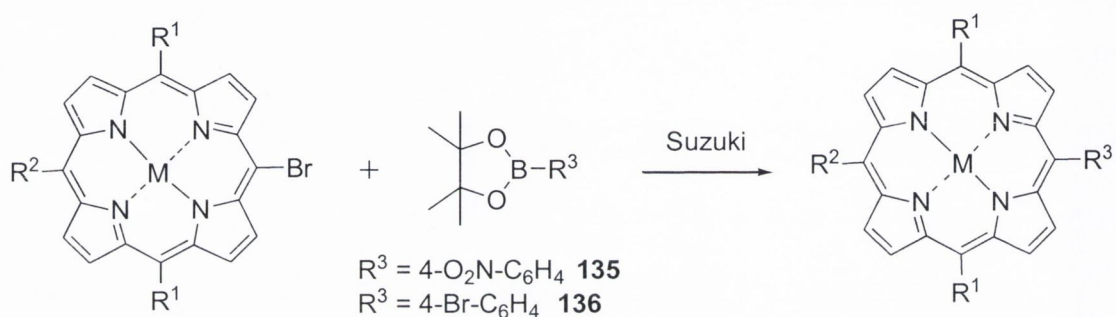
Scheme 2.6: Synthesis of borylated porphyrins **128-134**. *Reagents and conditions:* pinacolborane **127**, Pd(PPh₃)₄, DCE, TEA, 80 °C, 16 h.

Porphyrins **83, 85, 93, 104, 105, 108** and **111** were borylated to form the trisubstituted porphyrinyl boronates **128-134** in yields of 51-69 %. For aryl substituted porphyrins, the reactions proceeded quite well with higher yields than those observed for alkyl porphyrin **134**. Catalyst loading, reaction time and temperature have a substantial effect on the yields obtained. When more than 0.05 equivalents of palladium catalyst were used, the yields obtained were somewhat diminished due to the generation of a homo-coupled directly linked porphyrin dimer. These dimers, most likely, are generated from the borylated substrates which self-dimerise^[243] and thereby affect the yields of the desired borylated porphyrins.

The porphyrinyl boronates were subsequently used to form directly linked dimers via Suzuki coupling (Sections 3.2.1 and 4.2.3). A recent advancement in the synthesis of boronyl porphyrins was in the iridium-catalysed direct C-H activation, a method developed by Osuka and co-workers, although control over the number of boryl groups can be difficult. This method is advantageous as it does not require the halogen activation of the porphyrin,^[47] but it is not applicable for meso functionalisations.

Suzuki-Miyura coupling

For the introduction of 4-nitrophenyl and 4-bromophenyl substituents, Suzuki Pd⁰ mediated coupling, first applied to porphyrins by Therien and co-workers, was performed yielding porphyrins **63**, **136-140** in yields of 36-85%, from bromoporphyrins **83**, **94**, **98**, **105** and **123**, and aryl-boronic esters **135** and **136** (Scheme 2.7). It is interesting to note that for **63** and **137**, literature procedure states to use of 12 equivalents of boronic ester **135**^[209] but, on optimisation of reaction conditions, it proceeds in excellent yield with only 3.5 equivalents.



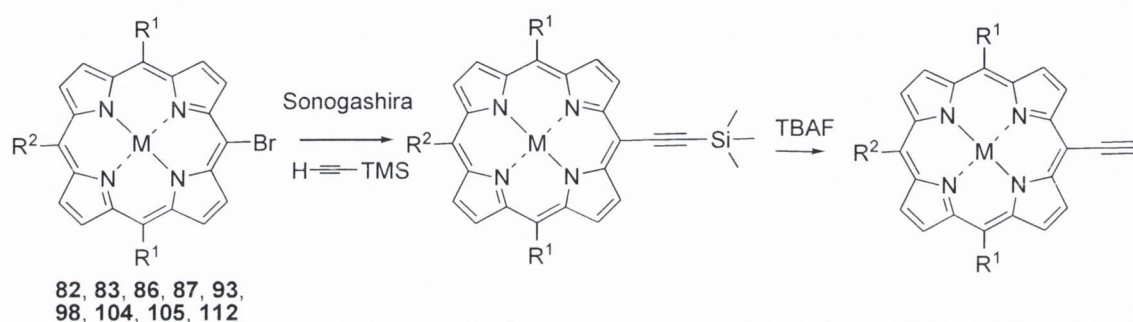
R ¹	R ²	R ³	M	#	Yield %
Ph	H	4-O ₂ N-C ₆ H ₄	Zn ^{II}	137	82
Ph	H	4-O ₂ N-C ₆ H ₄	2H	63 ^[209]	85
Ph	Br	4-O ₂ N-C ₆ H ₄	2H	138 ^[209]	36
Ph	4-O ₂ N-C ₆ H ₄	4-O ₂ N-C ₆ H ₄	2H	139 ^[244]	22
Ar	H	4-O ₂ N-C ₆ H ₄	Zn ^{II}	140 ^[245]	80
Ph	Ph	4-Br-C ₆ H ₄	2H	141 ^[246]	71

Scheme 2.7: Synthesis of Suzuki coupled porphyrins **63**, **137-141**. *Reagents and conditions:* a) **135** (3.5 equiv.), Pd(PPh₃)₄, THF, K₃PO₄, 67 °C, 16 h. b) **136**, AsPh₃, PdCl₂(PPh₃)₂, K₃PO₄, THF, 67 °C, 16 h.

For the synthesis of precursor **138**, as only 1 equivalent was employed, yields were diminished due to incomplete conversion and thus the presence of starting material **99** and disubstituted porphyrin **139**,^[244] recovered in yields of 28 and 22 %, respectively. The 4-bromophenyl substituted porphyrin **141** was generated in 71 % yield using modified conditions with Pd^{II} catalyst and phosphine ligand. Debrominated **141** or tetraphenylporphyrin was also formed as a side product in trace amounts. **141** was employed for the synthesis of phenylacetylene linked arrays (Section 3.2.3). The Suzuki-Miyaura coupling is a versatile method for the introduction of substituents to the

periphery and can also be used for the introduction of the phenylethynyl group in excellent yields. This, however, requires two additional steps when compared to the organolithium approach, as activation via halogenation and post-coupling deprotection is necessary. Borylated porphyrins can also react with aryl bromides under Suzuki conditions, although the competing homo-coupling forming directly linked porphyrin dimers can be problematic.^[243]

Sonogashira coupling



R ¹	R ²	M	TMS product #	Yield	Deprotected #	Yield
Ph	Ph	2H	142 ^[247]	58	151	91
Ph	Ph	Zn ^{II}	143 ^[247]	68	152 ^[248]	87
Ph	H	2H	144 ^[45]	55	153 ^[209]	92
Ph	H	Zn ^{II}	145 ^[119]	84	154 ^[119]	90
Ph	TMS-ethyne	2H	145 ^[249]	52	155 ^[228]	88
Ar	H	Zn ^{II}	146 ^[228]	65	-	-
Ar	Ph	2H	147	36	156	92
Ar	Ph	Zn ^{II}	148 ^[250]	46	157 ^[251]	94
Ar	Hexyl	2H	149	83	158	61
Ph	3-MeO-C ₆ H ₄	2H	150	48	159	90

where Ar = (3,5-Di-*tert*-butyl)C₆H₃

Scheme 2.8: Sonogashira coupling to give TMS-acetylene products **142-150** and TBAF deprotection to give alkynyl porphyrins **151-159**. *Reagents and conditions:* i) TMS-ethyne, PdCl₂(PPh₃)₂, CuI, TEA, THF, 40-60 °C, 16 h. ii) TBAF (1M in THF), CH₂Cl₂, 0.5 h, r.t.

The ethynyl group was introduced via Sonogashira coupling.^[235] It involves the coupling of bromoporphyrin derivatives with a protected acetylene under standard Sonogashira conditions of Pd^{II} catalyst, CuI as a co-catalyst and a base. The reaction mechanism

proceeds through the generation of an alkynyl cuprate *in situ*, and this species participates in the palladium coupling cycle to generate the desired alkynyl product.^[232]

Porphyrins **82**, **83**, **86**, **87**, **94**, **98**, **104**, **105** and **112** were subjected to Sonogashira coupling conditions (Scheme 2.8) with trimethylsilylacetylene to form the mono and disubstituted trimethylsilyl acetylenes **142-150** in yields of 36-88%. An alternative method for this synthesis is a one-step condensation reaction^[247] but this is not applicable for the unsymmetric targets and thus the stepwise approach was used. With free base porphyrins there was an inevitable insertion of copper into the core as a side product, thus leading to slightly lower yields of the desired materials. Metallated porphyrins are usually used under these conditions to avoid this formation, although for **148** this did not increase the yield significantly. Porphyrins **142-145** and **147-150** were subsequently deprotected using TBAF forming the free alkynyl porphyrins **151-159** in yields of 61-94%, the lowest yield being that for hexyl substituted porphyrin **158**.

2.3 Spectroscopic studies

2.3.1 ¹H NMR analysis

General considerations

The proton chemical shifts in porphyrins are quite distinct and can be divided into two categories: i) protons which lie above or inside the porphyrin ring and ii) protons which lie in the porphyrin plane. These protons are in the shielded and deshielded regions of the diamagnetic ring current effect, respectively, as the chemical shifts depend on the orientation and distance of the proton with respect to the delocalisation pathway of the π -electrons of the macrocycle. This can be seen in the free base porphyrins where the N-H protons inside the core are strongly shielded from the external magnetic field to upfield resonances (<0 ppm), whilst the meso and β -protons are strongly deshielded (~8-10 ppm). The meso protons are attached to more electron deficient carbons and hence are deshielded further downfield than β -protons.

¹H NMR of monomeric porphyrins

The substitution arrangement on the porphyrin periphery can easily be deduced by ¹H NMR spectra via the pattern of β -pyrrolic hydrogen signals, which depend on the overall symmetry of the molecule. Taking 1-ethylpropyl A₂, A₂B and A₂BC substituted

porphyrins **46**, **67** and **88** as examples (Figure 2.1), a clear pattern is observed on alteration of the symmetry of the porphyrin. 5,15- A_2 porphyrin **46**, having a two symmetry (D_2) axis, results in two AB systems for the non-equivalent β -protons at 9.4 and 9.7 ppm, for H2/H8/H12/H18 and H3/H7/H13/H17 respectively, the latter of which has a more low-fields shift due to the close proximity of the alkyl groups. The two meso protons exhibit a singlet at 10.2 ppm.

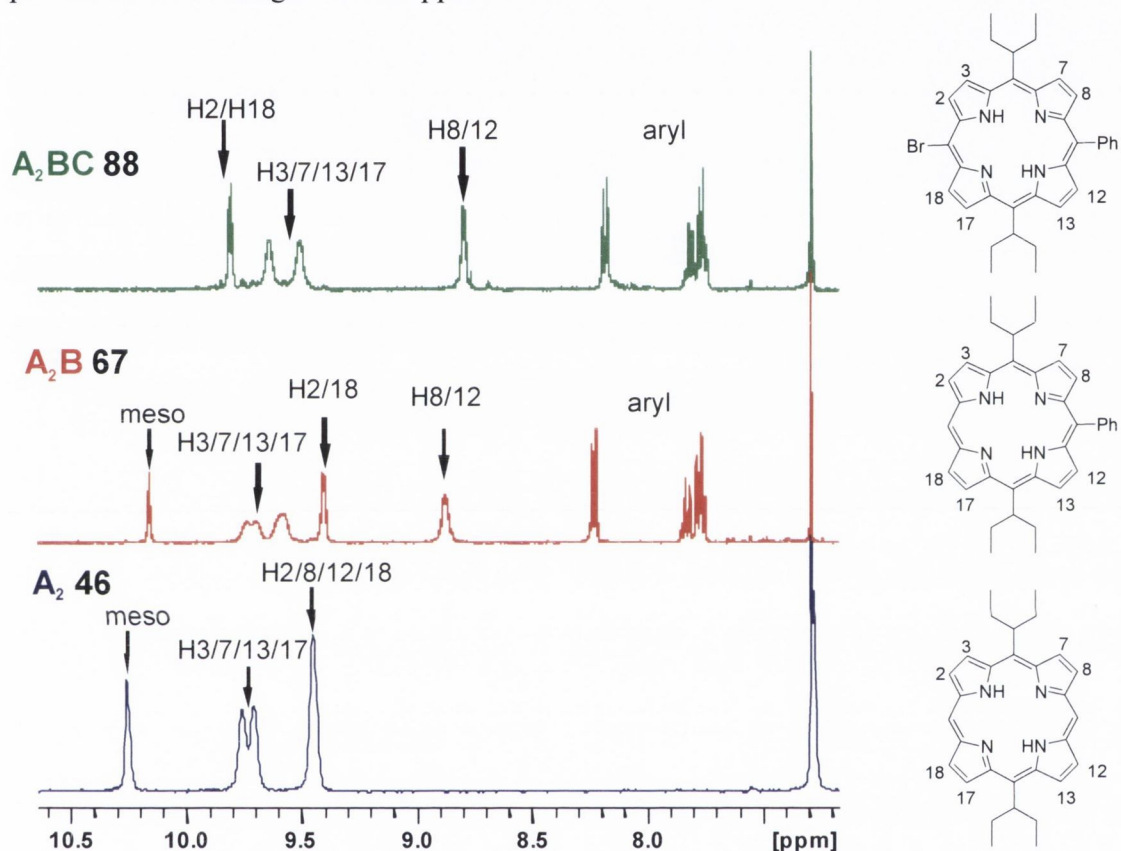


Figure 2.1: ^1H NMR spectra of 1-ethylpropyl substituted porphyrins **46**, **67** and **88** in CDCl_3 with porphyrin numbering system inset.

With phenyl substituted A_2B porphyrin **67**, there is reduced symmetry and a splitting of the AB signals for H2/H18, H3/H17, H7/H13 and H8/H12 is seen, with the highest field shift at 8.8 ppm occurring for H8/H12, as these protons lie in closest proximity to the phenyl ring and are thus affected by the ring current effect of this substituent. The meso proton resonates at 10.1 ppm as a singlet. The A_2BC substituted porphyrin **88**, exerts a different pattern. Again, four β -signals are seen but a substantial deshielding effect is observed for the H2/H18 AB system as these protons lie adjacent to the electronegative bromo substituent, resulting in a low field resonance for these protons. With **67** and **88**, the phenyl protons are seen at higher fields between 7.7 and 8.2 ppm and the alkyl substituents occur in typical regions, from 1.0 to 4.5 ppm, depending on the distance

from the macrocyclic ring. The strongly shielded inner N-H protons lie in the low field – 2 to 3 ppm region. Although it was impossible to detail the effects that all the substituents incorporated have on the porphyrin ^1H NMR resonances, the spectra shown in Figure 2.1 exhibit the typical regions for substituted monomers and these are vital for comparison when analysing oligomeric porphyrin arrays. Differences will arise depending on the substituents attached but the general region values can be useful as a guideline when assigning structures.

2.3.2 UV/vis spectroscopy

Porphyrins have very characteristic UV-vis absorbance spectra and much information regarding the structure can be obtained from such. Figure 2.2 shows typical free-base and metalloporphyrin UV/vis spectra of porphyrins **82** and **159**, and **121** and **125**, respectively. The intense Soret band lies in the 400 nm region whilst the Q bands, four for free-base and two for metalloporphyrins, lie between 500 and 650 nm, depending on the substituents attached.

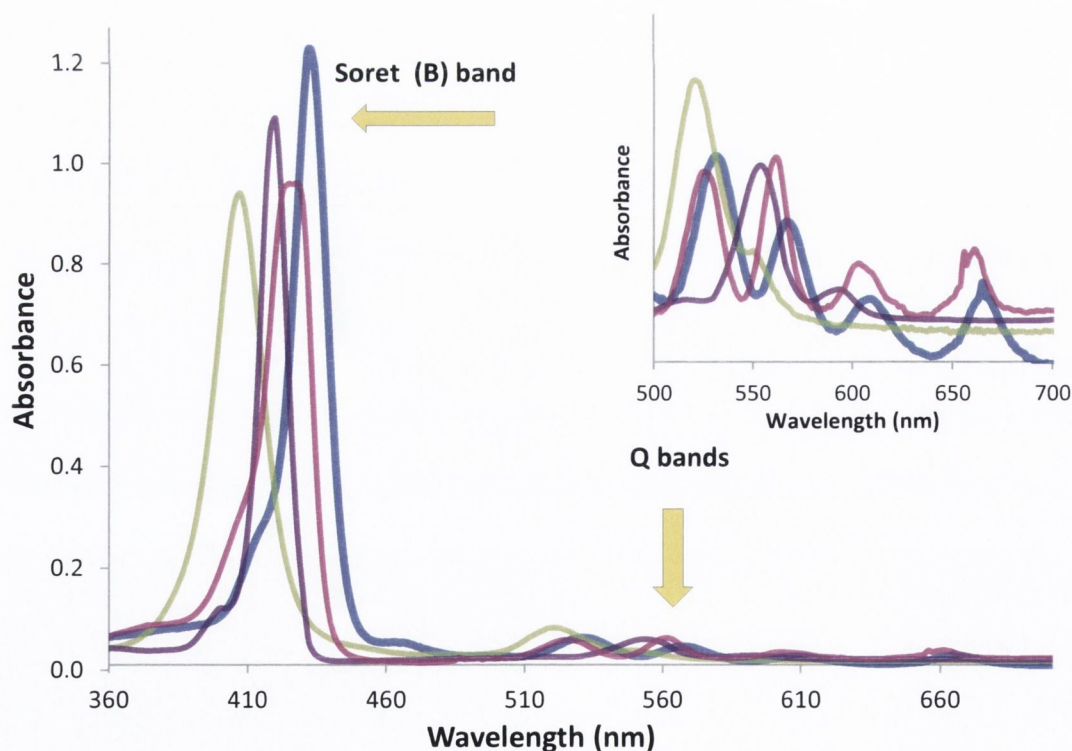


Figure 2.2: UV-vis absorption spectra of free base porphyrins **159** and **82** (pink and blue lines) and metalloporphyrins **121** (purple) and **125** (green) in CH_2Cl_2 .

The most pronounced bathochromic shift for monomeric porphyrins was observed with trimethylsilylalkynyl and alkynyl substituted porphyrins **142-159** whereby a λ_{max} in the region of 660-670 nm was observed for free base porphyrins, an enhancement of 15-20 nm with respect to their unsubstituted precursor. This can be attributed to the enhanced conjugation and the UV spectra of such precursors will be important in the analysis of porphyrin arrays. Nickel porphyrin **125** exhibited a hypsochromic shift in its profile, typical of d-block elements with unfilled d-orbitals. Electrons may be donated to the porphyrin's LUMO, thereby raising its energy and thus the π - π^* transition which causes the hypsochromic shift in the absorption spectrum, with respect to its free-base counterpart. These spectra show an example of the typical absorption profiles for porphyrin monomers and will be used for comparative purposes against porphyrin arrays.

2.4 Conclusions

Numerous synthetic strategies were employed for the synthesis of the monomeric porphyrin precursors. A library of compounds was synthesised, all of which were used in further coupling reactions for the synthesis of porphyrin arrays, as will be described in the subsequent chapters. The activation of the periphery via halogenation, the introduction of conjugated linkers and borylation of the macrocycle will all enable the construction of conjugated porphyrin arrays, along with directly linked and triply fused porphyrin oligomers. It is evident that, via the methods explored, almost any substituent can be incorporated into the porphyrin, an important trait for the design of multiporphyrin arrays. In most cases, reaction conditions were optimised but there is some scope to further develop the parameters to further enhance yields, particularly in the case of borylations and Sonogahsira coupling reactions.

CHAPTER 3:

Conjugated Porphyrin Arrays

3.1 Introduction

Multiporphyrin arrays have a wide range of potential applications in areas such as light-harvesting, non-linear optics (NLO), organic light emitting diodes (OLEDs), optoelectronics and photodynamic therapy (PDT). Hence, these systems have been studied widely.^[9, 58, 60-61, 70, 86, 252-253] Despite the vast knowledge about and investigations of such arrays, the majority of work involved studies of symmetric multiporphyrin systems. Whilst these are also of interest to our area of research, the main focus here was on unsymmetric arrays, through which amphiphilicity for PDT could be introduced or, with respect to NLO, push-pull systems could be arranged via arrays with different substituent and/or porphyrin subtypes.

We are interested in nonlinear optical materials and Prof. Senge's group has initiated a programme aimed at the development of new photosensitisers for PDT.^[202, 208, 223] Currently commercially available photosensitisers show absorption in the 530 to 630 nm range, which limits the penetration of tissue by light.^[73-74] Increasing the absorption wavelength of the photosensitiser may enable a deeper penetration and therefore the targeting of deeper tumours. Here conjugated dimers and trimers are ideal potential photosensitiser candidates as their absorption maximum should exhibit a bathochromic shift to this region. The type of linkage in the porphyrin arrays will influence the structure and the properties of the system. So by extending the conjugation of the porphyrin π -system, and hence increasing the wavelength absorption, these oligomers could be used as potential photosensitisers for PDT or for other optical applications. Recent work by Anderson *et al.* exemplifies this concept, whereby butadiyne linked dimers were synthesised and tested for *in vitro* PDT.^[81, 196] Our aim was to synthesise novel alkyne and phenylacetylene linked arrays and further develop the synthetic chemistry for unsymmetrical array systems. As the delocalisation of electrons extends into the alkyne spacer group, these arrays are linear and sterically non-demanding.^[254] Hence, the communication between the chromophores should be efficient making them attractive for not only for PDT but also for NLO, OLED and other optical applications.

Our approach incorporated two strands: the first was the synthesis of unsymmetric dimers, namely alkyne linked arrays. These unsymmetric dimers can contain both hydrophilic and hydrophobic entities at the various meso positions (Figure 3.1), whereby the amphiphilicity is enhanced and thus, in theory, assisting with the entry of the

photosensitiser into the cell target.^[255] The second approach was to synthesise symmetric conjugated porphyrin dimers and trimers with free meso positions. Linear trimeric arrays with such linkers, in particular the phenylacetylene linker, have not been investigated to a great extent, with only two such free meso trimers previously synthesised.^[64, 256] Once appropriate lead structures are identified further modifications, e.g., the introduction of water solubilising groups, are possible at the free meso positions to further optimise their biological utility. Here, the basic chemistry of this approach using model compounds is outlined.

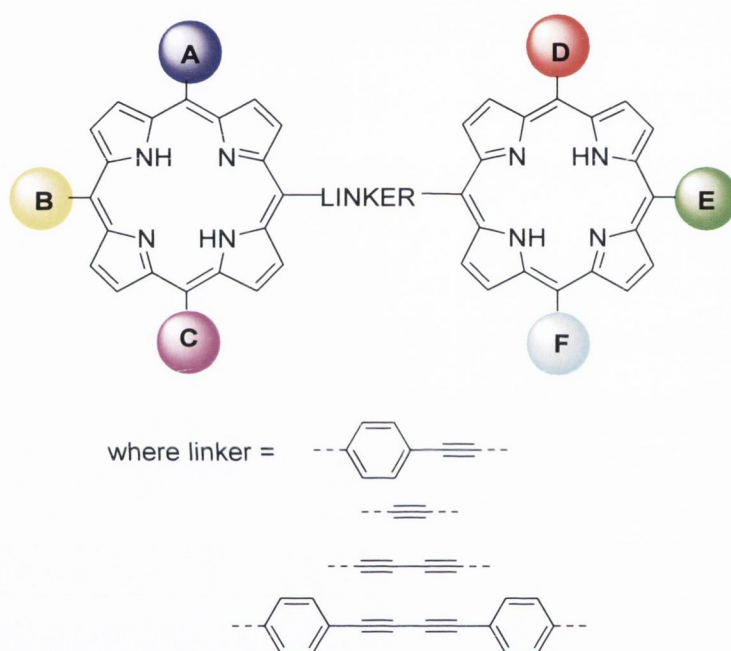


Figure 3.1: Model for conjugated unsymmetric dimers

3.2 Synthesis

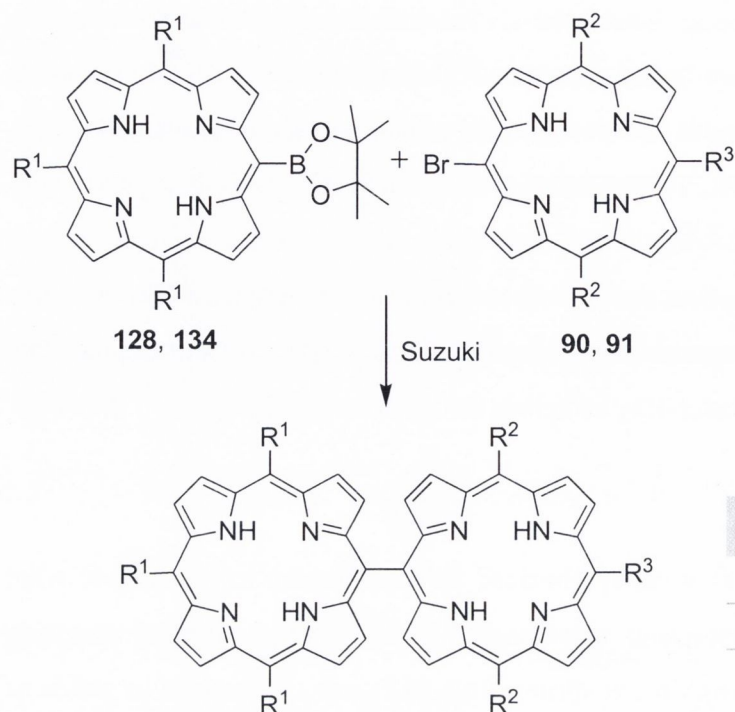
The synthetic strategy for the synthesis of conjugated porphyrin oligomers was two-fold, incorporating both the synthesis of symmetric dimers and trimers with free meso positions and also the synthesis of unsymmetric arrays. Both strategies utilised Pd-catalysed cross-coupling reactions and the free meso positions on the symmetric arrays allow subsequent chemical modifications to be carried out. Also, for a mass spectrometric comparative study, some diphenylbutadiyne and butadiyne symmetric dimers were synthesised using a Pd-mediated Glaser coupling method. Both of these approaches utilise the organolithium methods, developed by Kalisch and Senge,^[39, 116, 257] to introduce the phenylacetylene linker and the substituents on the porphyrin core.

Sonogashira coupling was used to introduce the alkyne linker and also for the coupling reactions.^[119, 130, 258] Some directly linked dimers were synthesised via Suzuki coupling^[155, 239] to compare their properties to those oligomers which contain conjugated linkers. Depending on the type of oligomer/linker desired, different well established palladium-catalysed coupling methods were adopted for their synthesis. The most utilised method was copper-free Sonogashira coupling and the others were Suzuki-Miyaura coupling (for the directly linked dimers), Sonogashira coupling (as a comparative to the copper free method) and also Pd-mediated Glaser-Hay coupling for homocoupled dimers.

3.2.1 Directly linked dimers

Directly meso-meso linked dimers were synthesised for comparison to investigate what effect the linker has on the absorption wavelength. Using Suzuki-Miyaura coupling methods,^[239, 259] directly linked amphiphilic dimers **160-162** were synthesised in yields of 29-51% (Scheme 3.1). The porphyrinyl boronates **128** and **134** provided the hydrophobic entity whilst bromoporphyrins **90** and **91** provided the hydrophilic entity. Yields for the 3-methoxyphenyl substituted dimers **160** and **162** were lower than those for 4-methoxyphenyl substituted dimers **3**, most likely due to the stronger electron donating effects of the *para* methoxy group over the *meta* group on the porphyrin macrocycle.

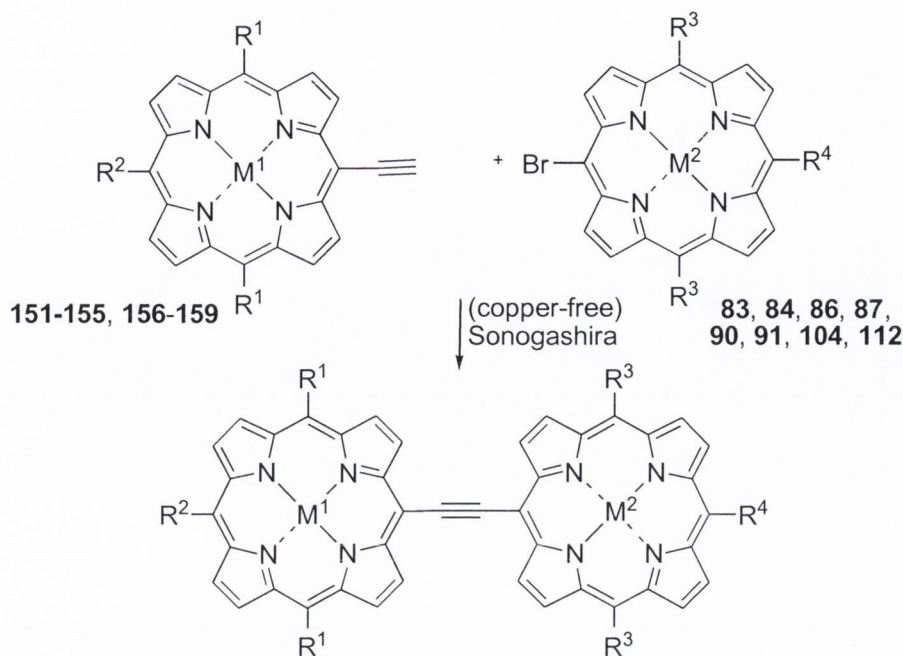
Easier purification of hexyl substituted dimers **161** and **162** was observed due to larger differences in polarity. Whilst these arrays do not show much promise as candidates for PDT due to the lack of a bathochromic shift in their absorption profile (Section 3.4), they were of interest for comparison with the conjugated linked arrays, i.e., to observe the linker effect on the photophysical properties of the array. These directly linked dimers will also be discussed in Chapter 4 as they can act as precursors to triply fused systems.



Scheme 3.1: Synthesis of directly linked porphyrins via Suzuki coupling. *Reagents and conditions:* Pd(PPh₃)₄, Cs₂CO₃, toluene, DMF, 80 °C.

3.2.2 Alkyne linked dimers

To synthesise unsymmetric dimers, without any free meso positions, the introduction of all substituents prior to the coupling reaction to form the oligomer was implemented. These unsymmetric alkyne linked dimers were initially synthesised via original Sonogashira coupling conditions,^[119, 235, 260] using Pd^{II} and CuCl as a co-catalyst. However, formation of the homocoupled product **182** as an undesirable side product (see Scheme 3.3) was observed. This homocoupling takes place during the reduction of Pd^{II} to Pd⁰, thus it was decided to use a copper-free/Pd⁰ Sonogashira approach.^[126, 261-262] This coupling protocol yielded the unsymmetric dimers **163-176** in moderate to good yields ranging from 25-68% (Scheme 3.2). Generally these dimers exhibited good solubility in most organic solvents. However, depending on substituents and in some cases, upon metallation with zinc, this solubility was somewhat diminished. This was particularly noticeable for the phenyl substituted dimers **171** and **176**.



R ¹	R ²	M ¹	R ³	R ⁴	M ²	Yield %	#
Ph	Ph	2H	4-MeO-C ₆ H ₄	<i>n</i> -Butyl	2H	29	163
Ph	Ph	2H	3-MeO-C ₆ H ₄	3-MeO-C ₆ H ₄	2H	29	164
Ar	Ph	2H	4-MeO-C ₆ H ₄	4-MeO-C ₆ H ₄	2H	64	165
Ar	Ph	2H	Hexyl	Hexyl	2H	45	166
Ar	Ph	2H	Ph	Ph	2H	45	167
Ar	Ph	2H	Ar	hexyl	2H	34	168
Ar	Ph	2H	Ar	Ph	2H	43	169
Ar	Ph	2H	Ph	Ph	Zn ^{II}	54	170
Ar	Ph	Zn ^{II}	Ph	Ph	Zn ^{II}	52	171
Ar	Ph	Zn ^{II}	Hexyl	Hexyl	Zn ^{II}	68	172
Ph	Ph	2H	Ph	3-MeO-C ₆ H ₄	2H	38	173
Ph	Ph	2H	Ph	Hexyl	2H	39	174
Ph	Ph	2H	Ph	Ph	2H	48	175
Ph	Ph	Zn ^{II}	Ph	Ph	Zn ^{II}	47	176

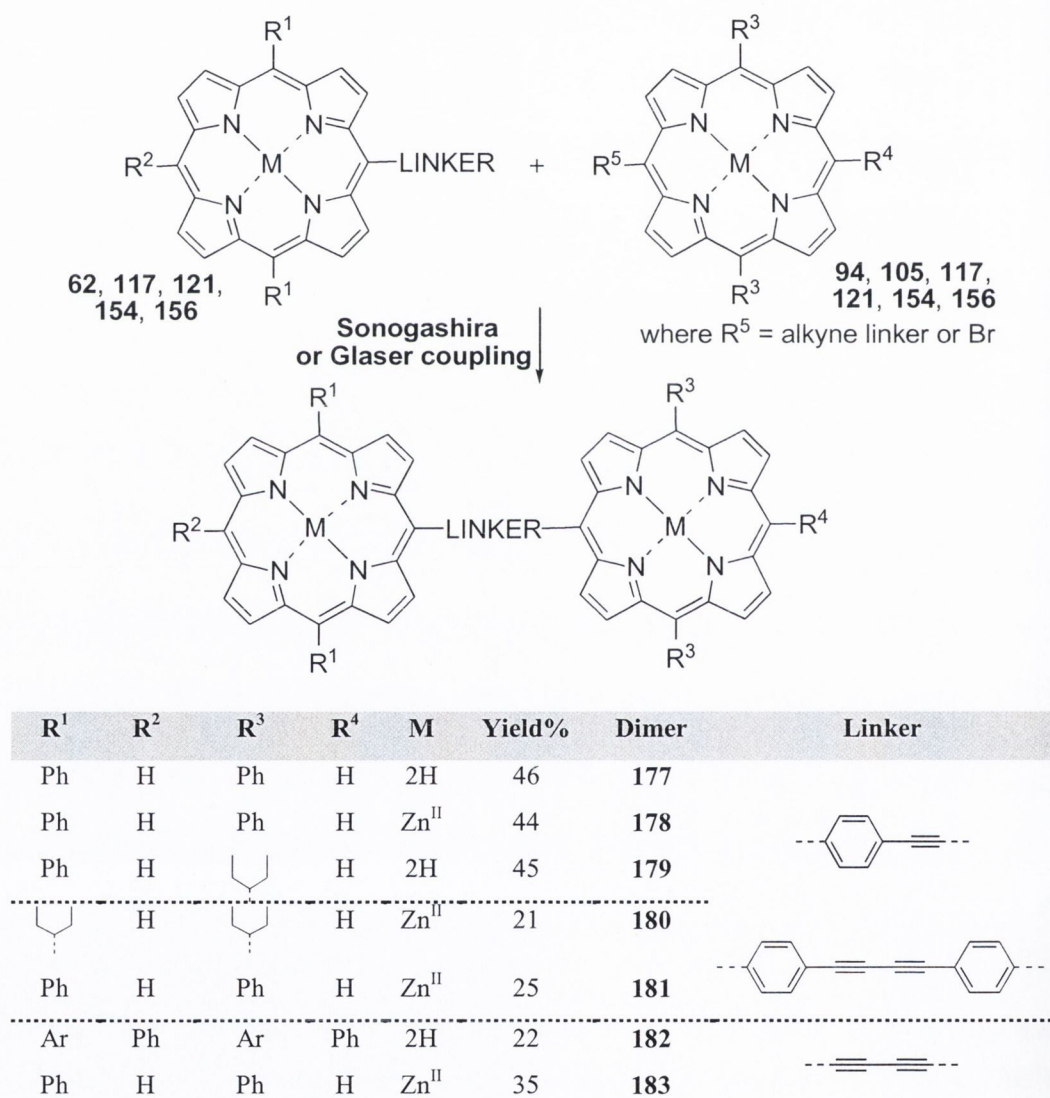
where Ar = 3,5-Di-*tert*-butyl-C₆H₃

Scheme 3.2: Synthesis of alkyne linked dimers. *Reagents and conditions:* Sonogashira - PdCl₂(PPh₃)₂, CuI, TEA, THF, 40-60 °C, 16 h; copper-free Sonogashira - Pd₂(dba)₃, AsPh₃, THF, TEA, 60 °C, 16 h.

Although yields of some dimers were moderate, this can be attributed to difficulties in separations, particularly with alkoxy substituted dimers **163** and **164**. The introduction of bulky aryl substituents (e.g., 3,5-di-*tert*-butylphenyl) greatly enhanced the solubilities of the arrays, as aggregation was minimised due to the presence of the bulky *tert*-butyl

groups, thus improving the yields. Phenyl substituted symmetric dimers **175** and **176** were synthesised for the determination of structural and optoelectronic properties of these oligomers as thin films via spectroscopic ellipsometry, in collaboration with Dr. Simona Pop (Leibniz-Institut für Analytische Wissenschaften ISAS, Berlin, Germany). These porphyrin oligomer thin films have potential applications as organic field effect transistors (OFETs) and in organic solar cells.

3.2.3 Phenylacetylene and butadiyne linked dimers



where Ar = (3,5-di-*tert*-butyl)C₆H₃

Scheme 3.3: Synthesis of phenylacetylene and butadiyne linked dimers. *Reagents and conditions:* copper-free Sonogashira coupling - Pd₂(dba)₃, THF, TEA, 60 °C, 16 h. Pd-Glaser coupling - toluene, Pd(PPh₃)₂Cl₂ (0.01 eq.), CuI (0.05 eq.), I₂ (0.5 eq.).

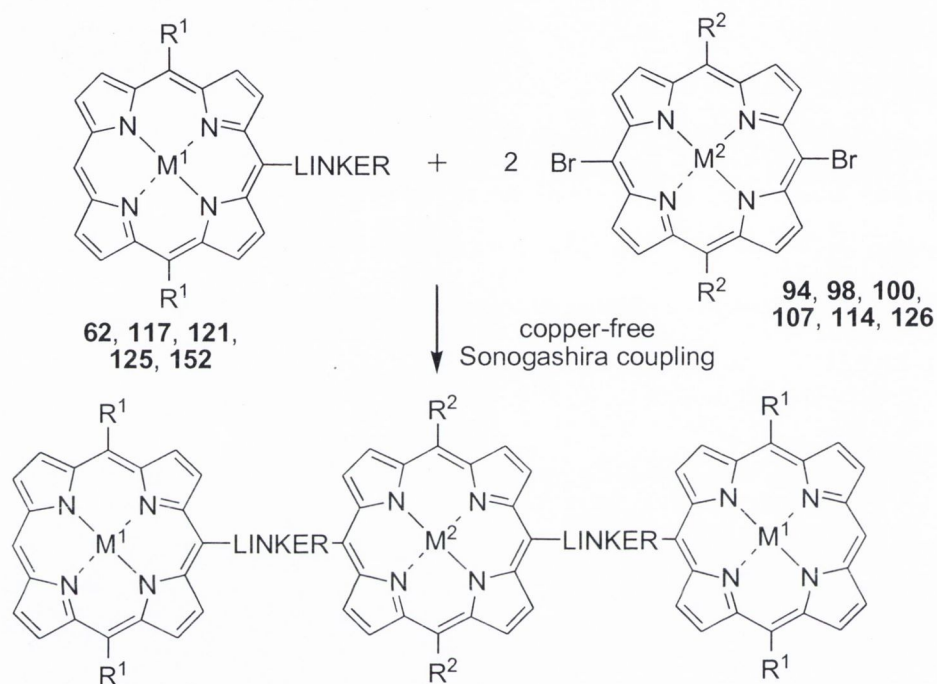
The phenylacetylene linked dimers were prepared in a similar manner to dimers **163-176**. In general, the copper-free method^[126] worked quite well giving porphyrins **177-179** in yields of 44-46 % (Scheme 3.3). In these cases the desired dimer was the main product and they exhibited good solubility in organic solvents. For the diphenylbutadiyne and butadiyne homocoupled arrays, a Pd-mediated Glaser homo-coupling, developed by Liu *et al.*, was used.^[263] However, this method proved less successful with yields of 25 and 35% for dimers **181**,^[202] and **183**,^[264] the latter of which was synthesised for a mass spectrometry comparison. Reactions were carried out under dry air and reported results for these conditions show good yields.^[134, 265] A more oxidative environment is most likely needed to improve yields but as these dimers were only used for a mass spectrometry study, further reaction optimisation was not carried out. The other homocoupled dimers **180** and **182** resulted as side product from the synthesis of trimer **189** and dimer **169**, respectively.

3.2.4 Porphyrin oligomers

In order to synthesise the targeted porphyrin trimers, a dibrominated porphyrin was reacted with a mono-‘linker’-substituted porphyrin to form the desired trimer via the previously described copper-free Sonogashira coupling. This method was initially developed by Lindsey and coworkers.^[126] The free base phenyl substituted trimers **184** and **185** proved to be quite insoluble in most organic solvents, although this made their purification easy via filtration using DCM as solvent. Any remaining monomer or other side products were removed via column chromatography and pure trimers **184** and **185** were obtained in yields of 40 and 32%, respectively (Scheme 3.4).

In order to improve solubility to enable full characterisations to be carried out and to minimise possible palladium insertion, zinc(II) was introduced into the monomer porphyrin core, yielding trimer **186** (26%), with dimer **181** being isolated as a side product in a yield of 23%. In addition, to improve solubility, 5,15-dibromo-10,20-bis(3,5-di-*t*-butyl-C₆H₃)porphyrin **100** was coupled to **117**, producing trimer **188** in a 28% yield. Whilst these efforts improved the solubility of the desired product, the column chromatographic purification remained problematic. Much streaking was observed as the trimers were only partially soluble in DCM/*n*-hexane and hence there was an inevitable loss of desired product. Increasing the number of equivalents of palladium(0) catalyst had no positive effect on yields as palladium insertion into the porphyrin core was observed

and these Pd(II) products appeared as very slow moving fractions, whose presence was detected by mass spectrometry but these were not isolated. In some cases palladium actually caused a displacement of zinc but only in trace quantities and at elevated catalyst loading and reaction temperature. Nickel trimer **187** was synthesised from monomers **125** and **126** for a mass spectrometry comparative study and was not isolated.



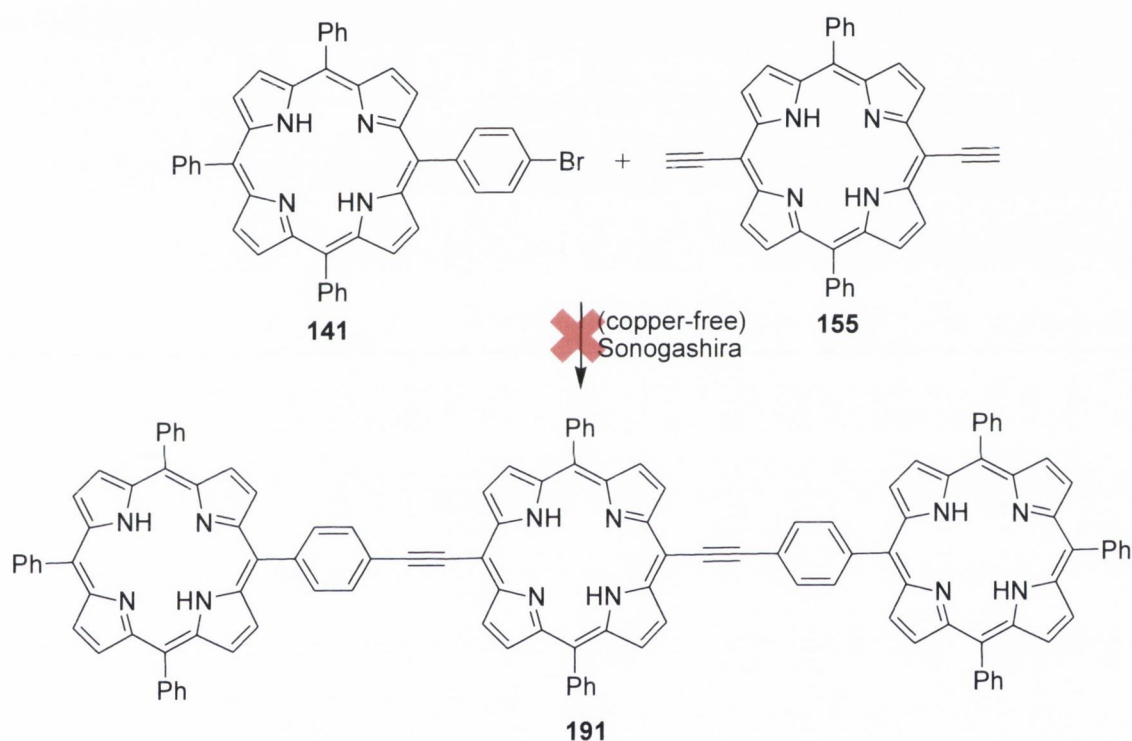
R ¹	R ²	M ¹	M ²	Yield %	#	Linker
Ph	Ph	2H	2H	40	184	---≡---
Ph	Ph	2H	2H	38	185	
Ph	Ph	Zn ^{II}	Zn ^{II}	45	186	
Ph	Ph	Ni ^{II}	Ni ^{II}	n/d	187	
Ph	Ar	Zn ^{II}	2H	28	188	
		Zn ^{II}	Zn ^{II}	46	189	
Ph		Zn ^{II}	Zn ^{II}	21	190	

where Ar = (3,5-Di-*tert*-butyl)C₆H₃

Scheme 3.4: Synthesis of linear trimers. *Reagents and conditions:* Copper-free Sonogashira coupling - Pd₂(dba)₃, AsPh₃, THF, TEA, 60 °C, 16 h.

Another approach to improve yields was to introduce different substituents on the porphyrin periphery. Initially dihexylporphyrin monomers were used but as dibromodihexylporphyrin **99** is highly insoluble in THF, it was therefore not appropriate for the

copper-free Sonogashira coupling. Hence, 1-ethylpropyl disubstituted porphyrins **101** and **114** were chosen as starting materials. At first, reactions with these porphyrins gave many side products and their absorption profiles indicated the formation of directly linked oligomers (Section 3.4). However, on repeating the reaction using the zinc monomers **121** and **114**, followed by purification *via* preparative TLC, the desired trimer **189** was isolated in a 46% yield as the main fraction. For the synthesis of **190**, the desired trimer was obtained in a yield of 21 %, with similar problems on purification as seen with trimer **189**.



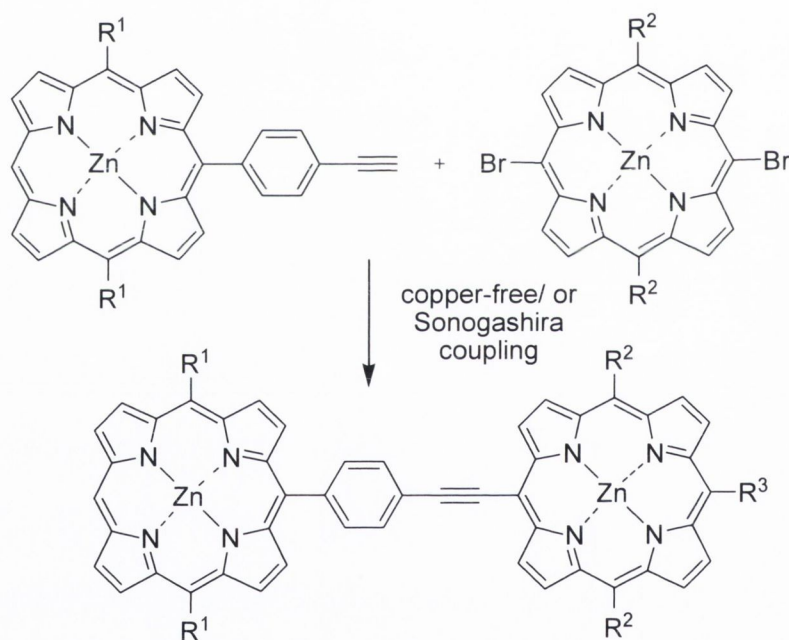
Scheme 3.5: Attempted synthesis of linear trimer **191**. *Reagents and conditions:* Copper-free Sonogashira coupling - $\text{Pd}_2(\text{dba})_3$, AsPh_3 , THF, TEA, 65 °C, 16 h.

The reverse strategy, i.e. having a diethynyl central unit and reacting it with 4-bromophenyl sides was also endeavoured (Scheme 3.5) for the synthesis of fully meso substituted trimer **191**. However, this method proved unsuccessful as **191** could not be isolated. It may have formed as a dark residue that could not be removed from the column and UV-vis analysis of the crude material indicated that an oligomeric product had been synthesised. The main product isolated was debrominated **141** (TPP) and the failure of this reaction can be attributed to the poor solubility of the desired target, observed with trimers **184** and **185**. Previous syntheses of such arrays utilised the more reactive 4-iodophenyl derivatives of **141**, along with phenyl acetylene, to yield

diphenylacetylene linked arrays.^[126] Such a substituent here may be beneficial, but the solubility issue with the target most likely would outweigh this benefit. Osuka and co-workers reported the synthesis of such trimers using diiodo porphyrins and original Sonogashira conditions, with yields of 57 %, along with the expected homocoupled products.^[130] In this case, the substituents on the periphery are (3,5-di-*tert*-butyl)phenyl, which would assist with the solubility and thus the isolation of the array, in comparison to phenyl substituted trimer **191**.

3.2.5 Side products

A number of side products were isolated during the trimer syntheses (Scheme 3.6). For the synthesis of **186**, the Glaser coupled dimer **181** was a side product of this reaction, and also the dimer side product **178**, due to incomplete reaction.



R ¹	R ²	R ³	#	Yield %
1-Ethylpropyl	1-Ethylpropyl	Br	192	40
Ph	1-Ethylpropyl	Br	193	42

Scheme 3.6: Side product formation during the synthesis of trimers. *Reagents and conditions:* Sonogashira coupling - PdCl₂(PPh₃)₂, CuI, TEA, THF, 40-60 °C, 16 h. Copper-free Sonogashira coupling - Pd₂(dba)₃, AsPh₃ THF, TEA, 60 °C, 16 h.

For the synthesis of trimers **189** and **190** using Sonogashira conditions, the bromo dimer "side products" **192** and **193** proved to be the main products isolated in yields of 40 and

42 % respectively, showing an incomplete reaction with no trimer formation. This suggests that the reaction conditions are not ‘forceful’ enough for the trimer to form. The Glaser coupled product **180** was also a side product here due to the presence of CuI. Addition of more copper/Pd, increasing the temperature and reaction time gave no improvement on the outcome as the trimers were not formed, only more side products.

3.3 NMR studies

3.3.1 ^1H and ^{13}C NMR spectroscopy

Noteworthy NMR spectra resulted from the analysis of the oligomers synthesised. Depending on the linker between the porphyrin units, quite distinct chemical shift patterns were observed (Figure 3.2).

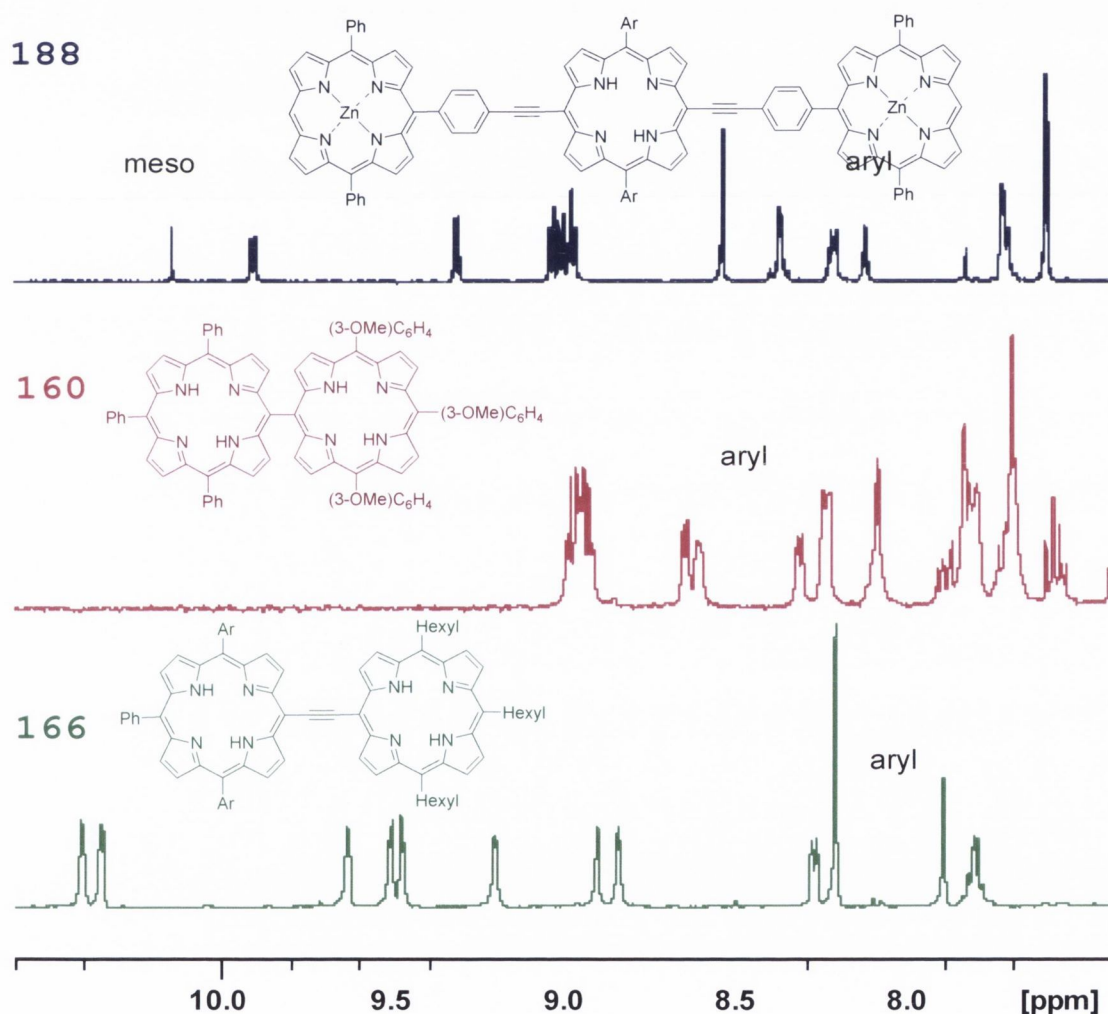


Figure 3.2: ^1H -NMR spectra (400 MHz) of oligomers **160**, **166** and **188** in CDCl_3 showing β and aryl regions.

With the directly linked dimer **160**, a large shift of approximately 0.9 ppm of the β protons to higher fields was observed, in comparison with the monomeric porphyrins, where the last set of β signals was observed at approximately 9.8 ppm. This is due to the strong shielding effect of the neighbouring porphyrin ring current, as observed with aryl substituted monomers (Section 2.3.1). In contrast, the alkyne linked oligomers exhibited a different pattern with the β protons deshielded to lower field resonances. Some of these shifts occur at around 10.4 ppm, a shift of approximately 0.7 ppm with respect to monomeric components, as shown for dimers **166-168** in Figure 3.2.

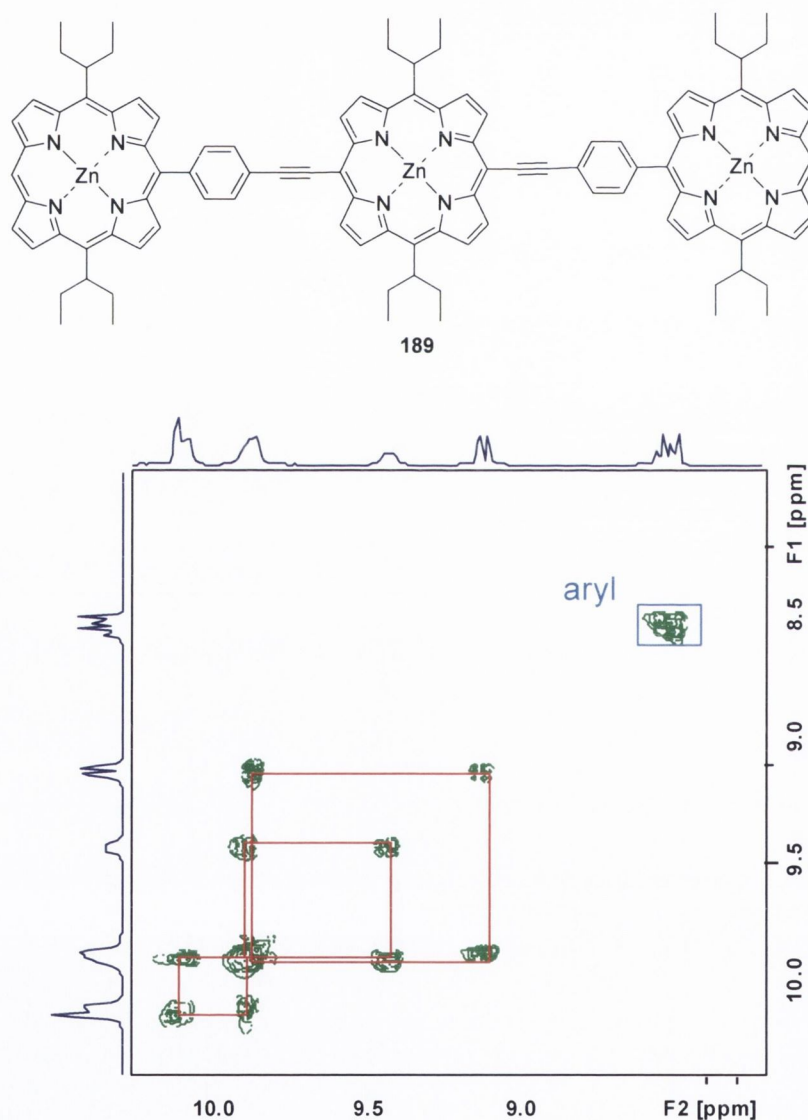


Figure 3.3: ^1H - ^1H COSY NMR (600 MHz) spectra of trimer **189** in d_8 -THF showing aryl and porphyrin regions.

The highest field signals are observed for the ‘inner’ β protons due to the close proximity of the alkynyl group. Also, these β protons exhibit signals over a wider range than those of the directly linked dimers. With the phenylacetylene linked trimers, a deshielding effect was also observed for the meso and β protons, being more pronounced for the inner β protons of the central porphyrin unit than the β protons of the outer porphyrins. This is evident from the ^1H NMR spectrum of **188** (Figure 3.2).

Using ^1H - ^1H COSY NMR analysis (Figure 3.3), β -region and aryl-region correlations on trimer **189**. It is interesting to note that with **189**, the meso proton signal overlaps with that of the β signals. Furthermore, the signals are quite broad for this alkyl substituted trimer, most likely due to aggregation. The overlap was also seen for the alkyl substituted monomers **114** and **112**, indicating that it is a result of the substitution pattern on the array and independent of the linker.

3.4 UV/vis spectroscopy

The extension of the porphyrin π -conjugation results in the decrease in the HOMO-LUMO gap and this is due to the change in the electron density distribution on the porphyrin.^[121, 130] The absorption spectra of the porphyrin oligomers depend on the type of linker used and the substituents on the porphyrin macrocycle. With the porphyrin oligomers, most showed a significant split in the Soret band,^[58, 132, 266] indicating strong conjugation between the porphyrin units, except for the diphenylbutadiyne linked dimers where a slight split was seen, indicating here that the communication between porphyrin subunits is not very efficient.

Likewise, in the case of directly linked dimers **160-162**, a split in the Soret band was observed due to excitonic coupling,^[58] but no bathochromic shift was observed as there is no conjugation between the units. The dimer behaves like its monomeric component and thus these systems are not of interest with respect to PDT and NLO but useful as a comparative against the conjugated systems.

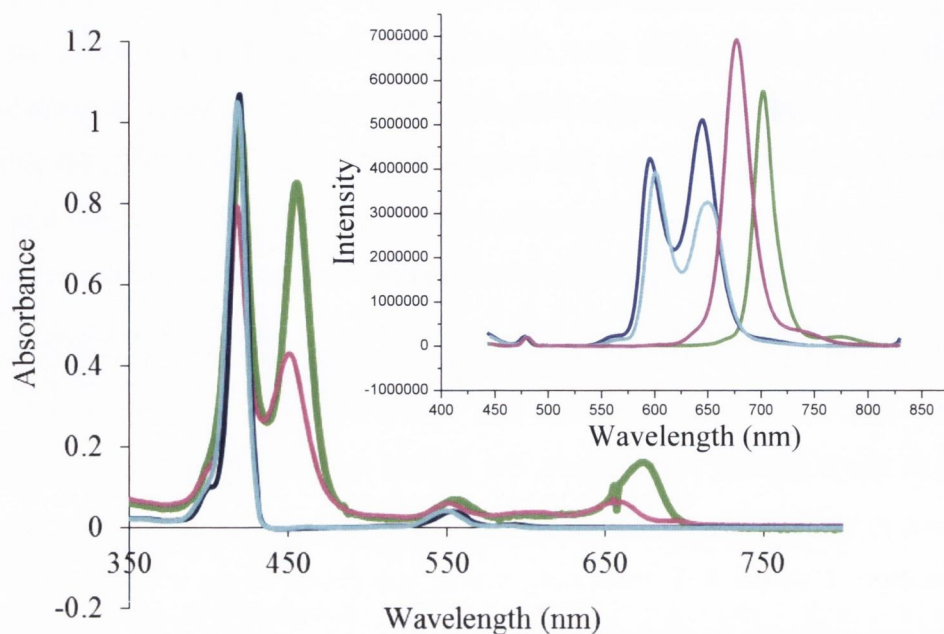


Figure 3.4: UV/vis absorbance spectrum of trimers **187** and **189** versus monomers **116** and **121** in CH_2Cl_2 . Inset: Emission spectrum of trimer **187** versus monomer **116** excited at 443 nm and trimer **189** versus monomer **121**, excited at 445 nm in THF. Concentration: 1.7×10^{-7} M in THF.

On the other hand, the phenylacetylene linked dimers and trimers showed a significant split, in particular with trimer **189** (Figure 3.4). This shows that there is efficient interaction between all porphyrin units in the array. Additionally, in comparison to monomer Q-band values, there is a large bathochromic shift due to increase in conjugation, into the 700-800 nm region for some trimers. A strong broad Q-band absorbance intensity was also observed with these arrays, especially for alkyl trimer **189**. Emission studies also showed a bathochromic shift for these oligomers when compared against their monomeric components. This is expected due to the increase in π -conjugation, thus these oligomers are possible leads for applications in NLO and PDT.

With the unsymmetric alkyne linked dimers, again there was a Soret band split and also a significant bathochromic shift to approximately 730 nm (Figure 3.5). The split differs from that of the phenylacetylene linked arrays due to the less rigid geometry of the alkyne linker, thus allowing the dimer to adopt many different conformations. As seen with the trimeric arrays, the Q-band absorbance of these dimers was more intense in comparison to their monomeric porphyrins. Emission spectra exhibited a significant bathochromic shift, again due to the increase in π -conjugation.

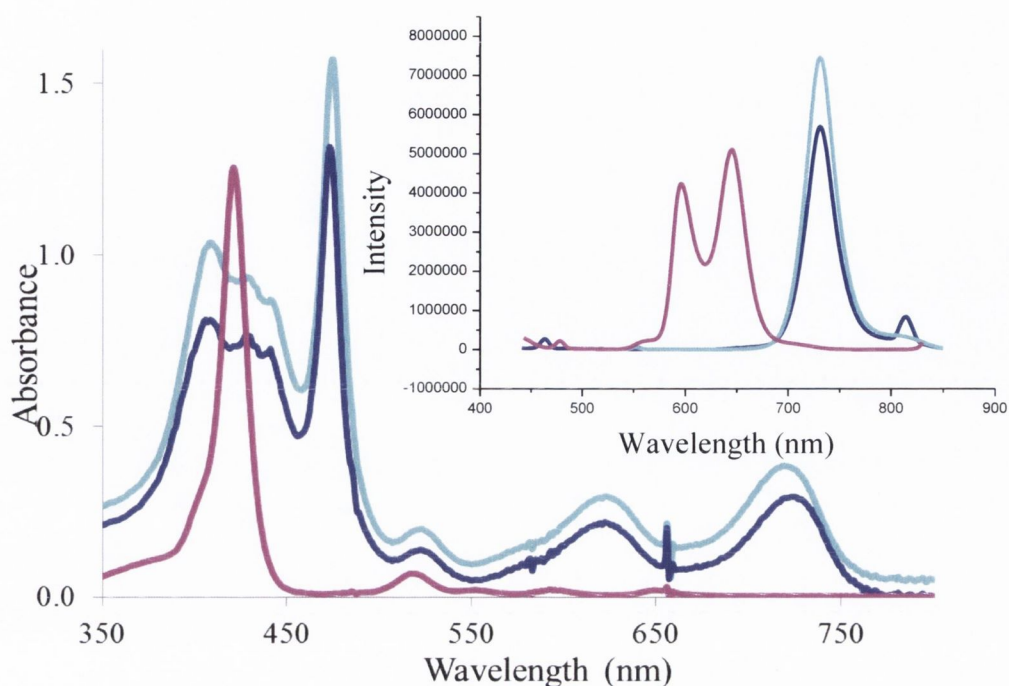


Figure 3.5: a) Absorbance spectrum of unsymmetric dimers **165** and **166** versus monomer **156** in CH_2Cl_2 . Inset: Emission spectrum of **165** and **166** excited at Soret bands 410 nm and 470 nm versus monomer **156** in THF. Concentration: 1.7×10^{-7} M in THF.

3.5 Mass spectrometry

Mass spectrometry provides a useful tool for the structural elucidation of porphyrins.^[267] The mass spectrometric analysis of compounds **178**, **181**, **186**, **190**, **192** and **193** gave unusual results. The spectra for dimer **181** and trimer **186** contained signals due to the parent ions of the compounds at m/z 1250 and 1773 respectively, confirming the elemental composition (Figure 3.6). However, the spectra also showed peaks due to the demetallated species which is not usually observed. Signals at 1187 and 1124 for dimer **181** and at 1711, 1647 and 1584 for trimer **186** correspond to sequential loss of zinc from the oligomers. Fragmentation of metalloporphyrins typically proceeds without loss of the metal ion, except in rare cases.^[268] Studies utilising MALDI-tof mass spectrometry only showed loss of metal for magnesium porphyrins which are considered the most labile metalloporphyrins. Studies on zinc porphyrin arrays, in particular, also show that there is no significant demetallation of the compounds.^[269-270]

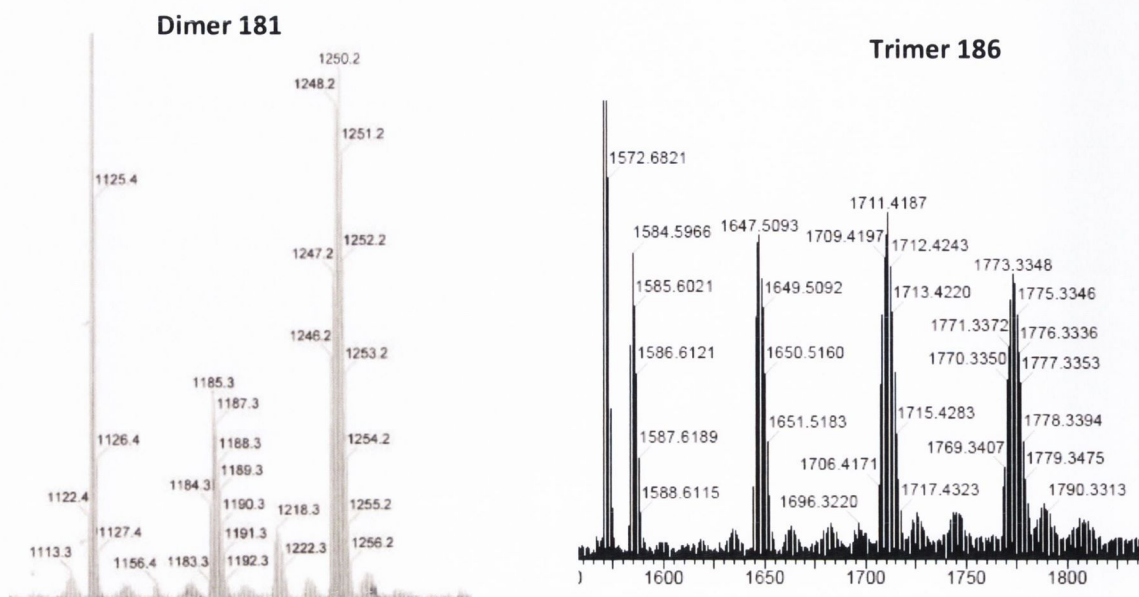


Figure 3.6: Mass spectra of **181** and **186** showing the loss of zinc from the porphyrin core.

A similar fragmentation was observed with dimers **178**, **192** and **193** and trimer **190**. Note, that this demetallation was not observed in the mass spectra of the butadiyne linked dimer **183**,^[264] in metallated alkynyl dimers **171**, **172** and **176**, nor in the case of trimer **189**. This indicates that demetallation is affected both by the linker and the substituents on the porphyrin rings. Likewise, the nickel(II) trimer **187** did not exhibit any loss of nickel from its core, thereby illustrating that this fragmentation process is also metal dependent. The purity of all arrays was confirmed by ¹H-NMR analysis which shows that there is no demetallation in the analytes as no inner N-H signals were observed. This eliminates any possibility that losses in zinc were due to the presence of partially demetallated products.

3.6 Conclusions

Porphyrin dimers and trimers were synthesised in moderate to good yields using Pd-mediated Glaser coupling reactions and copper-free Sonogashira coupling reactions. These provide a useful route towards the synthesis of such oligomers. Introduction of alkyl substituents into the periphery greatly enhanced the solubility and hence the yields. The uncapped oligomers with free meso positions allow for subsequent chemical modifications of the free meso positions. All dimers and trimers exhibited a bathochromic shift in their UV-vis absorption spectra compared to the monomers. In

particular, the alkyne linked dimers showed strong absorption around 720 nm, making them good candidates for use as, e.g., possible photosensitisers in PDT and in other optical applications. With unsymmetrical dimers and trimers, amphiphilicity can be enhanced through the alteration of substitution patterns, and they also allow for the fine-tuning of optical properties which would enhance either their PDT or NLO effect. Unsymmetrical arrays are advantageous in that they may be constructed with both hydrophilic and lipophilic components for applications in PDT, or electron withdrawing and electron donating groups may be introduced to enhance NLO effects. In addition, the mass spectrometry of the phenylacetylene linked and diphenylbutadiyne linked oligomers exhibited an unusual demetallation pattern for the zinc(II) compounds. This novel fragmentation process is metal and substituent dependent and may be of importance to bioinorganic studies. Further tandem mass spectrometry studies of the behaviour of zinc in linked porphyrin arrays could be executed to provide additional insight in the exact nature of the demetallation process. Also, future work will involve the screening of amphiphilic dimers as photosensitisers for PDT via liposomal formulations and the construction of more water soluble arrays via the introduction of long-chain alkoxy, glycol and bile-acid groups to the peripheries.

CHAPTER 4:

Fused Porphyrin Arrays

4.1 Introduction

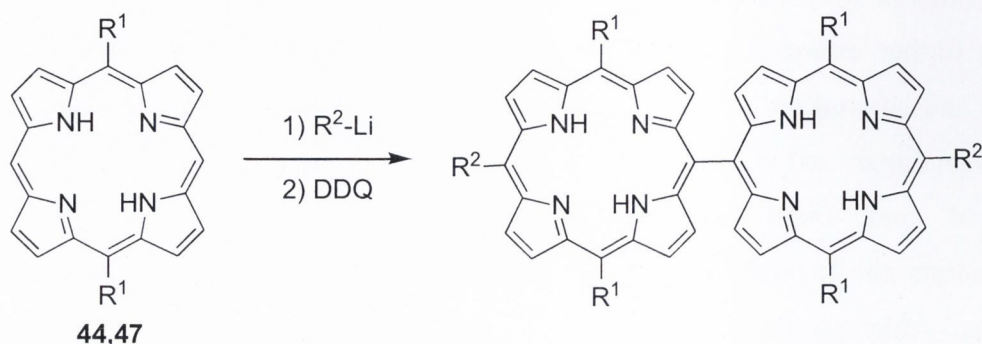
Long wavelength absorption of porphyrins is desired for a wide range of applications and one way to extend the absorption profile of porphyrins is via the construction of alkynyl linked arrays, whereby a λ_{max} of greater than 700 nm can be reached (Chapter 3). To further extend the absorption into the near-IR region, methods developed by Osuka and co-workers^[173] can be adopted for the generation of so-called triply fused porphyrin dimers and higher arrays. By doing so, a λ_{max} of 1050 nm and beyond may be achieved and these covalently linked multiporphyrin arrays can act as multichromophoric model systems for the study of electron transfer in light-harvesting systems. Although the Osuka group,^[169] amongst others,^[174, 271] have extensively researched this area, their work primarily deals with symmetric arrays and photophysical studies of such porphyrins.^[57] Only limited research has been carried out on so-called unsymmetrical fused dimers^[272] and post-modifications of fused arrays.^[182-183, 273] We envisaged developing both novel symmetric fused dimers and unsymmetric arrays, for the purpose of applying them to the area of PDT, which has not previously been undertaken. By the introduction of various substituents to the porphyrin periphery and subsequent post-fusing modifications, the arrays can be fine-tuned for PDT, via the introduction of water solubilising groups, and other optical applications such as NLO via the introduction of donor/acceptor groups to generate push-pull systems. Thus, synthetic strategies for the development of such arrays will be described in this chapter.

4.2 Synthesis of meso-meso directly linked dimers

Following the synthesis of meso-meso directly linked porphyrins by Susumu *et al.* in 1996 via a condensation reaction,^[142] there has been extensive development of the synthesis of such arrays. These include total synthesis,^[143] Ulmann coupling,^[144] oxidative fusing of free meso porphyrins with oxidants such as hypervalent iodine (PIFA),^[145] silver salts (AgPF_6)^[147, 150] and DDQ/ $\text{Sc}(\text{OTf})_3$, along with electrochemical oxidation.^[152] A method developed by Senge *et al.*^[257] involving the oxidative dimerisation of porphyrin anions can also be employed and, additionally, a stepwise synthetic strategy involving the activation of the porphyrin and subsequent Suzuki coupling.^[155] These meso-meso directly linked porphyrin dimers are important precursors for the synthesis of triply fused bis-porphyrins and thus we adopted various

known strategies to synthesise such arrays, depending on the substitution pattern on the periphery required, i.e. it being symmetric or unsymmetric.

4.2.1 Dimerisation via organolithium method



R ¹	R ²	Dimer	Yield %
Ph	Ph	194	68
Ph	<i>n</i> -Butyl	195	59
Ar	Ph	196	63
Ph	4-H ₂ N-C ₆ H ₄	197	n/d
Ph	4-O ₂ N-C ₆ H ₄	198	n/d

where Ar = 3,5-Di-*tert*-butyl-C₆H₃

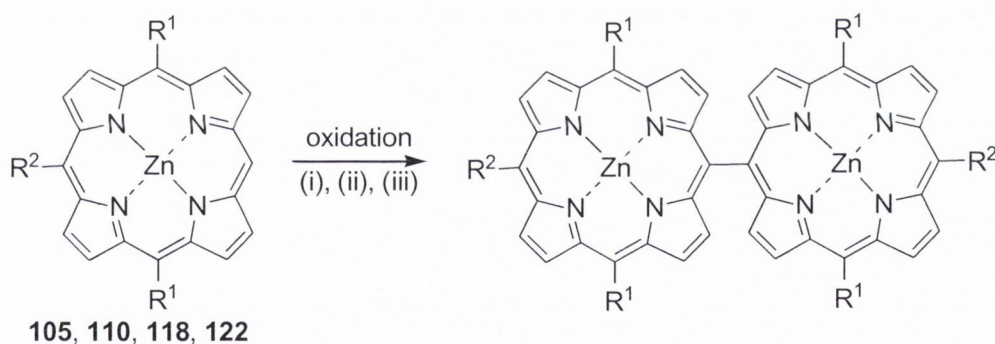
Scheme 4.1: Synthesis of directly linked bisporphyrins **194-198** via organolithium approach. *Reagents and conditions:* i) RLi, -78 to 0 °C, THF, 1 h ii) DDQ, 1 h.

Using a method developed by Senge and co-workers, directly linked symmetric dimers can be generated in excellent yields using organolithium reagents. The introduction of meso substituents via organolithium reactions has been investigated by the Senge group and is a versatile method of introducing aryl and alkyl substituents to the porphyrin periphery. Utilising this method, the 5,10,15-trisubstituted porphyrin anion can be trapped by skipping the hydrolysis step and oxidised to a π -stabilised radical. Subsequent radical dimerisation yields the substituted dimer in good yields.^[257, 274] This method is particularly useful for obtaining free base porphyrin dimers in one step, and advantageous over most other oxidative methods which require metallated porphyrins, namely zinc and nickel. Taking 5,15 disubstituted porphyrins **44** and **47**, and reacting these with phenyllithium **52** or *n*-butyllithium **53**, free base dimers **194**^[207], **195**^[207] and **196** were obtained in good yields of 59-68 %. Minor products which can arise from the reaction are the tri- and tetrasubstituted monomers which may have an effect on yield. Syntheses of zinc derivatives of **194**^[146, 160] and **196**^[174, 275] have been performed

previously by DDQ and PIFA oxidation methods in similar yields but from tri-substituted precursors. This technique thus has an added advantage as 5,15-disubstituted-porphyrins are employed as starting materials.

Attempts to introduce the 4-aminophenyl and 4-nitrophenyl substituent via this organolithium approach and subsequent dimerisation to form dimer **197** and **198** were unsuccessful. For their synthesis, the organolithium reagent must be generated *in situ* prior to the reaction with the porphyrin (Section 2.2). The generation of the aryllithium reagents proved difficult, with only **44** and butylated starting material being recovered from the attempted synthesis of **197** and **198**. As the attachment of *para*-nitro and -amino substituted phenyl groups proved challenging, the organolithium approach for the synthesis of **197** and **198** is not very practical and thus alternative strategies were investigated.

4.2.2 PIFA oxidation



R ¹	R ²	Dimer	Yield %
Hexyl	H	199	n/d
Ph	H	200	n/d
Ph	Br	201	58
3-MeO-C ₆ H ₄	Br	202	81

Scheme 4.2: Synthesis of directly linked porphyrin dimers via PIFA oxidation. *Reagents and conditions:* i) PIFA, CH₂Cl₂, -78 °C ii) rt, 0.75 h. iii) NaBH₄, MeOH.

Hypervalent iodine reagents can be applied for the synthesis of directly linked porphyrin arrays. These reagents possess many advantages over powerful oxidants such as AgPF₆ and DDQ/Sc(OTf)₃ in that they are safer but have a similar reactivity to those of metal oxidisers.^[166, 168, 276] Bis(trifluoroacetoxy)iodobenzene (PIFA) is one such reagent and

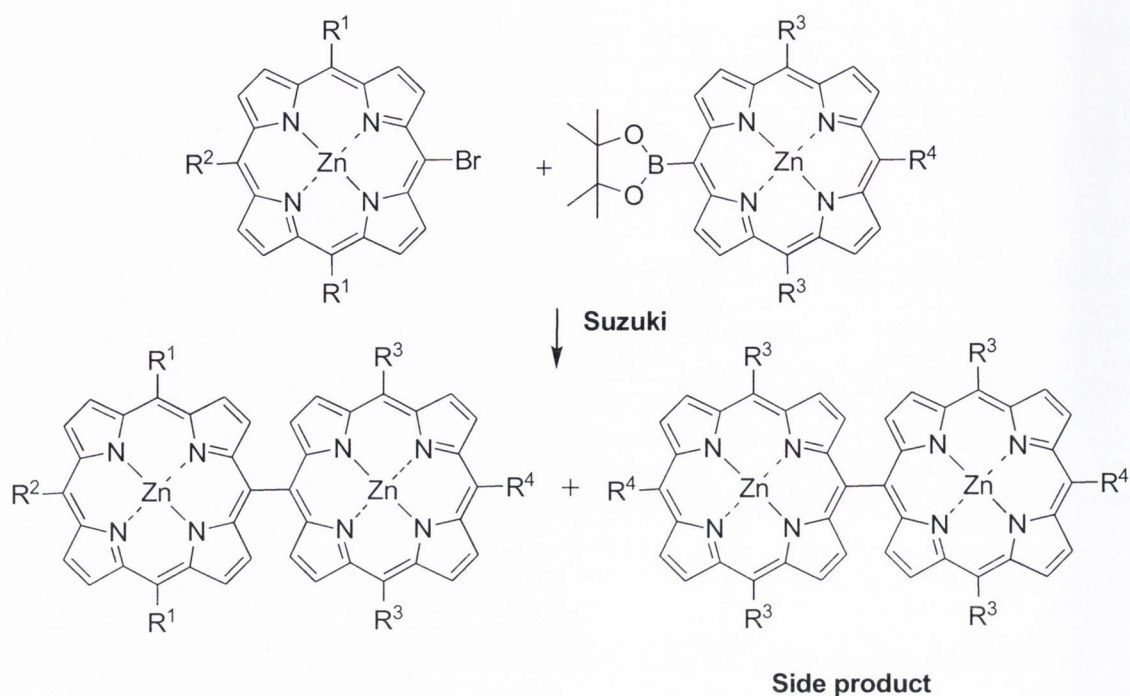
contains a highly electrophilic iodine centre which can promote diverse coupling reactions, including the synthesis of meso-meso directly-linked bisporphyrins in excellent yields.^[146] Interestingly, high yields were obtained for electronegative substituents such as trifluoroalkyl groups and thus bromo-substituted monomers were chosen as starting materials. Dimers of such compounds would enable further chemistry to be carried out at these positions as the bromo-substituent activates the meso carbon to which it is attached. Also, 5,15-disubstituted porphyrins were employed for the synthesis of bisporphyrins incorporating two free meso positions, with the same objective in mind, as post-modifications at these positions could be implemented. 5,15-Disubstituted porphyrins **118** and **122** and 5,10,15-trisubstituted porphyrins **105** and **110** were used as the starting materials for such oxidative couplings to form singly linked dimers. Using 0.8 equivalents of PIFA, bromo-substituted symmetric dimers **201**^[160, 277] and **202** were synthesised in good to excellent yields of 58 and 81 %, respectively. The reaction mechanism involves the oxidative generation of a porphyrin radical cation, which dimerises to form the bisporphyrin product. For the reaction to proceed well, a non-coordinating solvent is required. If a coordinating solvent is used, PIFA no longer will be able to co-ordinate to the central metal ion and little oxidative product will form.^[146]

Attempts to synthesise dimers **199** and **200**, bearing free meso positions, in acceptable yields proved unsuccessful. Taking 5,15-disubstituted porphyrins **118** and **122**, the desired dimers were only synthesised in very low yields, identified by mass spectrometry and UV-vis analysis. Due to the inevitable formation of oligomerised products, dimers **199** and **200** were not isolated and this method of synthesising bisporphyrins with unsubstituted meso positions was not feasible. Also, it must be noted that this PIFA oxidation method can also be used for the synthesis of triply fused β - β , meso-meso, β - β linked bis-porphyrins, using an excess of PIFA oxidant (Section 4.3). Other oxidants, such as DDQ/Sc(OTf)₃, can be employed for the synthesis of symmetric dimers via this mechanism, although for singly linked dimers these oxidants were not attempted. Moreover, for most cases in the literature, bromo-substituted directly linked dimers were synthesised via stepwise strategies^[278] or by using stronger oxidants such as AgPF₆ and I₂.^[160] This hypervalent iodine synthesis is therefore advantageous for the synthesis of such activated directly linked dimers.

4.2.3 Stepwise synthesis involving palladium catalysed coupling reactions

To overcome the challenge of synthesising directly-linked porphyrin dimers bearing free meso positions, a new synthetic strategy was implemented involving a stepwise approach. This approach culminates in a final C-C bond forming palladium catalysed coupling reaction, namely Suzuki-Miyaura coupling, between a bromo-porphyrin and borylated porphyrin to give singly linked bisporphyrins (Section 3.2.1).^[155] This strategy was adopted to synthesise unsymmetric hexasubstituted dimers and dimers with one or two free meso positions which would enable post ‘fusing’ modifications. For the incorporation of an alkyne linker and the construction of a tetramer encompassing both directly linked and ethynyl linked porphyrins, another palladium catalysed coupling was utilised, specifically copper-free Sonogashira coupling. This stepwise strategy concludes with the coupling of a bromo-porphyrin with an alkynyl porphyrin (see Section 3.2.2).

The synthesis of hexasubstituted unsymmetric dimers and pentasubstituted dimers with one free meso position involved a stepwise strategy. This strategy involved the final step of Suzuki coupling of a borylated porphyrin **129**, **130**, **131** or **133** with a bromoporphyrin **103**, **110**, **111** or **113**, to give the desired dimers **203-209** in yields ranging from 43-66 % (Scheme 4.3). Although the yields for these Suzuki couplings were good, they were hindered by the competing homocouplings of the borylated porphyrins **129** and **130**, giving the homocoupled dimers **210** and **211** in yields of 18 and 22 %, respectively.^[243] Such directly-linked dimers were used in subsequent fusing reactions to form triply-linked dimers and also, in the cases of free meso dimers **206-208**, in functionalisation reactions. Pentasubstituted dimers were chosen as targets as it was hoped that dimers possessing only one meso position free would limit the possibility of higher oligomer formation when these were subjected to oxidative fusing (Section 4.3).

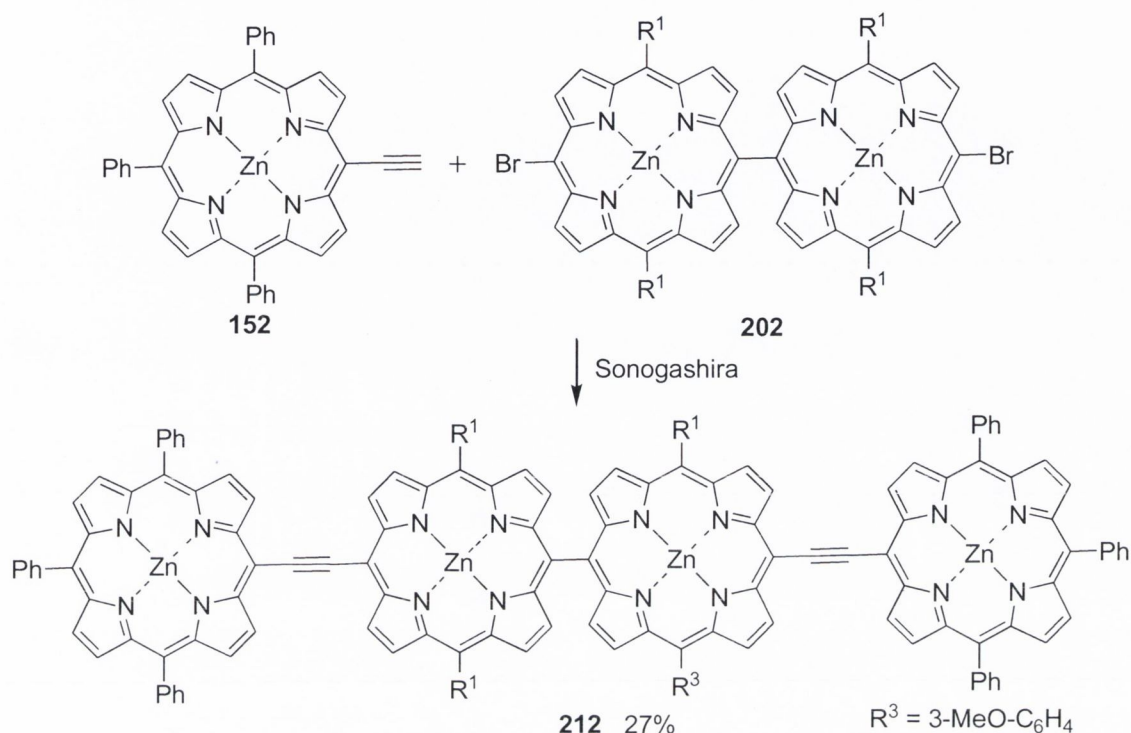


R ¹	R ²	R ³	R ⁴	Dimer	Yield %
Hexyl	Hexyl	Ph	H	203	43
Ph	Ph	4-Me-C ₆ H ₄	H	204	58
Ph	Ph	3-MeO-C ₆ H ₄	H	205	53
3-MeO-C ₆ H ₄	Ph	3-MeO-C ₆ H ₄	H	206	60
1-ethylpropyl	Ph	4-Me-C ₆ H ₄	H	207	63
3-MeO-C ₆ H ₄	Ph	4-Me-C ₆ H ₄	H	208	60
Ph	Ph	3-MeO-C ₆ H ₄	Ph	209	66
		R ³	R ⁴	Side product	Yield %
		Ph	Ph	210	18
		4-Me-C ₆ H ₄	H	211	22

Scheme 4.3: Synthesis of directly linked porphyrin dimers via Suzuki coupling. *Reagents and conditions:* Pd(PPh₃)₄, Cs₂CO₃, toluene, DMF, 80 °C, 18 h.

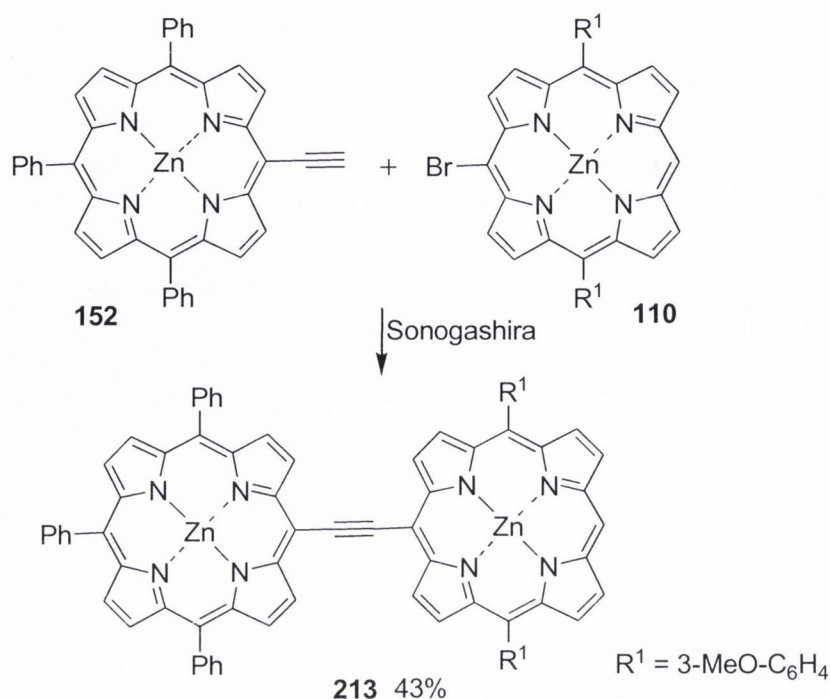
For the synthesis of tetrameric arrays incorporating an alkyne linker two strategies were undertaken. The first involved the copper-free Sonogashira coupling^[126] of directly linked bromo bisporphyrin **202** with alkynyl porphyrin **152**, which gave the desired tetramer **212** in 27% yield. Yields for **212** were low due to difficulties in separation and the formation of other oligomeric, namely trimeric and dimeric, derivatives of **212** as side-products. These undesirable oligomers were not characterised but their formation was evident from mass spectrometry and UV-vis analysis. Tetramer **212** incorporates

mixed connectivity's, i.e. alkynyl and directly linked porphyrins, the effects of which will be analysed on triply fusing the central porphyrin units at the free β -positions.



Scheme 4.4: Synthesis of tetramer **212** via Sonogashira coupling. *Reagents and conditions:* $\text{Pd}_2(\text{dba})_3$, AsPh_3 , THF, TEA, 60 °C, 24 h.

The second strategy involved the synthesis of alkynyl linked dimer **213** via copper-free Sonogashira coupling of monobromo porphyrin **110** with alkynyl porphyrin **152** to produce dimer **213** in a yield of 44%. This yield was moderate due to separation difficulties as the desired dimer was shown to streak during column chromatography and some product was lost through contamination and co-elution with other fractions. Also, a side product of this reaction was a Glaser homocoupled dimer,^[279] although copper-free Sonogashira conditions were used. This Glaser coupling took place most likely due to a palladium catalysed homocoupling.^[126] This alkynyl dimer contains one free meso position whereby oxidative fusing can be carried out to generate the fused tetramer as an alternative to using oligomer **212**.



Scheme 4.5: Synthesis of alkynyl dimer **213** via copper-free Sonogashira coupling. *Reagents and conditions:* $\text{Pd}_2(\text{dba})_3$, AsPh_3 , THF, TEA, 60 °C, 16 h.

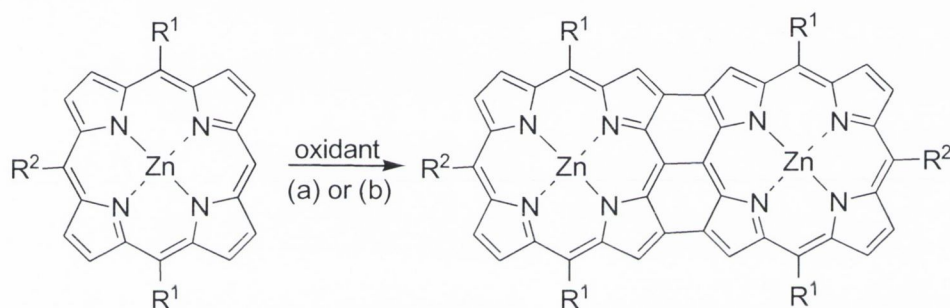
4.3 Synthesis of β - β , meso-meso, β' - β' triply fused arrays

Triply fused porphyrin dimers have a large extended π -conjugated system, with absorption profiles extending into the near infrared region, making them attractive for a wide range of optical applications. As with singly linked bisporphyrins, there are various synthetic strategies^[173-174, 280] which have been developed for their generation since their first synthesis via electrochemical oxidation by Osuka and co-workers.^[169] Chemical oxidations of zinc free meso monomeric porphyrins is the most attractive route for the synthesis of symmetric triply-fused porphyrin dimers and a variety of oxidants can be utilised. The most efficient are the powerful metal oxidants of $\text{Sc}(\text{OTf})_3/\text{DDQ}$ and hypervalent iodine (PIFA), although other oxidants such as gold derivatives^[176] can be used and give similar yields. We primarily focussed on the synthesis of novel symmetric triply-fused bisporphyrins and higher arrays via the above strategies and also the synthesis of unsymmetric fused dimers by similar principles.

4.3.1 Symmetric β - β , meso-meso, β' - β' triply fused arrays

We aimed to synthesise a variety of A_3 and A_2B symmetric bisporphyrins with a range of substituents, some enabling follow-up chemistry or so-called post-fusing

modifications to be carried out. The central metal ion is of great importance to the oxidative process and thus zinc porphyrins were employed for the synthesis, as it has a lower first oxidation potential and therefore is more easily oxidised than Ni or Pd counterparts.^[158] Similarly to singly-fused arrays, the reaction mechanism involves oxidative double ring closure via generation of a porphyrin radical cation,^[173, 280] which couples with another radical cation to form the dimeric product. It has been shown that electron withdrawing substituents on the porphyrin periphery can affect yields for oxidative fusing.^[176, 281] In spite of this, a series of symmetric dimers were synthesised and yields compared in relation to substituents, shown in Scheme 4.6. Similar yields were obtained with both DDQ/Sc(OTf)₃ and PIFA oxidants, exhibiting the versatility of the oxidative fusing process and the reagents which can be employed.

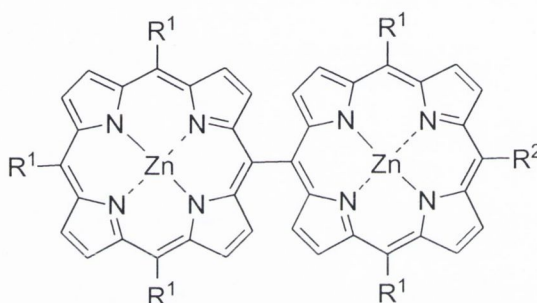


R ¹	R ²	Oxidant	#	Yield %
Ph	Ph	DDQ/Sc(OTf) ₃	214	67
Ph	4-O ₂ N-C ₆ H ₄		215	54
Ar	4-O ₂ N-C ₆ H ₄		216	56
3-MeO-C ₆ H ₄	<i>n</i> -Butyl		217	60
4-MeO-C ₆ H ₄	4-MeO-C ₆ H ₄		218	73
Ph	4-Ethynyl-C ₆ H ₄		219	67
Ph	Hexyl		220	42
4-Me-C ₆ H ₄	<i>n</i> -Butyl		221	58
Ph	H	DDQ/Sc(OTf) ₃ or PIFA	222	n/d
Hexyl	H		223	n/d
Ph	Br		224	12
3-MeO-C ₆ H ₄	Br		225	15

where Ar = 3,5-Di-*tert*-butyl-C₆H₃

Scheme 4.6: Synthesis of fused symmetric dimers *Reagents and conditions:* a) DDQ, Sc(OTf)₃, toluene, 50 °C, 3 h. b) i) PIFA, CH₂Cl₂, -78 °C – rt, 3 h. ii) NaBH₄, MeOH, 0.5 h.

The novel triply fused bis-porphyrins **214-221** could thus be prepared from 5,10,15 trisubstituted zinc(II)porphyrin precursors in moderate to excellent yields of 42-73 %, following the Osuka oxidation method and this strategy can be applied for the synthesis of other fused arrays. For some oxidations with DDQ/Sc(OTf)₃, two products were observed: the desired triply fused dimer and also the directly linked bisporphyrins **226-228** as a side product, which can be separated via column chromatography on aluminium oxide, thereby affecting yields for dimers **217**, **220** and **221**. Through optimisation of conditions via raising reaction temperature and increasing reaction duration, these side products were minimised and full conversion to the triply fused dimer was achieved.



R ¹	R ²	Dimer	Yield %
3-MeO-C ₆ H ₄	<i>n</i> -Butyl	226	23
Ph	Hexyl	227	30
4-Me-C ₆ H ₄	<i>n</i> -Butyl	228	29

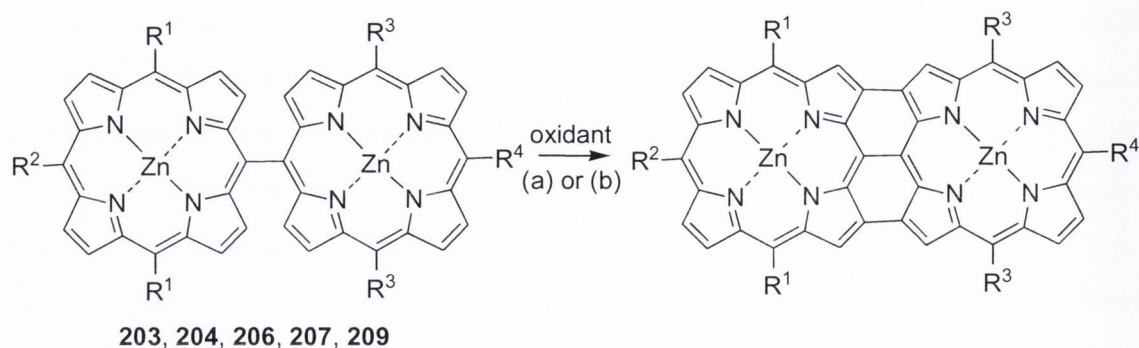
For the meso free dimers, **222** and **223**, and the bromo dimers **224** and **225** both the DDQ and PIFA method were employed. Unfortunately, due to the inherent extensive polymerisations of monomers **118** and **122**, dimers **222** and **223** were not isolated. Similar to the singly linked bisporphyrin counterparts, this strategy for obtaining free meso dimers is not attractive. For **224** and **225** best results were acquired using PIFA as oxidant, although yields were much lower than for alkyl and aryl substituted dimers **214-221**. Previous syntheses of fused bromodimers using these oxidants also gave poor results, with Anderson and co-workers reporting only 9 % yield for the (3,5-di-*tert*-butyl)phenyl derivative of **222** using DDQ.^[281] This is due to the electron-withdrawing nature of the bromo substituent which lowers the oxidation potential of the porphyrin and thereby reducing the yields of such arrays.^[176] Using DDQ, directly linked dimer **201** was isolated in approximately 10 % yield, but the desired fused dimer was not

detected, presumably due to the poor solubility of the dimer. It has been shown that the use of gold(III) salts for the oxidative coupling of meso-meso directly linked bisporphyrins is more powerful than DDQ and can be applied for the synthesis of fused dibromo dimers in excellent yields. This technique is not compatible with zinc porphyrins as extensive demetallation is observed, thus nickel(II) porphyrins are preferred using this oxidant.^[176]

4.3.2 Unsymmetric arrays

Adopting a synthetic strategy similar to that for the symmetric arrays, directly-linked unsymmetric bisporphyrins were fused oxidatively using DDQ/Sc(OTf)₃ or PIFA (Scheme 4.7). With dimers **203**, **204**, **206**, **207** and **209**, attempts at triply fusing had both positive and negative results. For the meso free arrays, as seen with bisporphyrins **119**, **200**, **222** and **223** (Section 4.2.2 and 4.3.1), free meso dimers **229-232** were not isolated. Although all exhibited typical triply-fused near-infrared absorption profiles, the desired dimers were not detected via mass spectrometry and purification was not possible. It had been anticipated that employing only one free meso position for oxidation might minimise polymerisation but this was not the case. Again, there is preferential fusing at this ‘free-meso’ side of the directly linked bisporphyrin resulting in a mixture of dimeric and tetrameric products. Due to the poor solubility of these arrays, isolation of such was not achieved via chromatographic methods.

Trace quantities of hexyl substituted dimer **229** were detected but NMR analysis was not achieved due to the low yields obtained. The fact that this dimer was detected with respect to the aryl substituted targets **230-232**, was most likely due to the influence of the hexyl substituents on the solubility. It was hoped that by using the milder PIFA oxidant that oligomerisation could be minimised, but this was not the case, with similar results for dimers **231** and **232**. Control over the oxidation for the generation of triply fused systems cannot be achieved in acceptable yields for free-meso dimers and therefore this strategy is not appropriate. For the hexasubstituted dimer **233**, this problem was not encountered as there was no unsubstituted meso position for oligomerisation to occur. The triply-fused dimer **233** was obtained in a good yield of 56 % following oxidation of **209**, indicating that the method can be applied to unsymmetric directly linked dimers bearing six meso substituents.

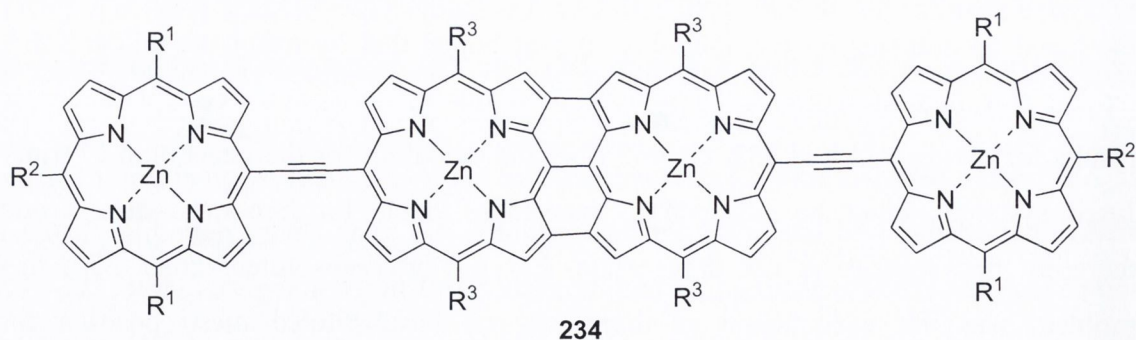


R ¹	R ²	R ³	R ⁴	Dimer	Yield
Hexyl	Hexyl	Ph	H	229	<5
Ph	Ph	4-Me-C ₆ H ₄	H	230	n/d
3-MeO-C ₆ H ₄	Ph	3-MeO-C ₆ H ₄	H	231	n/d
3-MeO-C ₆ H ₄	Ph	4-Me-C ₆ H ₄	H	232	n/d
Ph	Ph	3-MeO-C ₆ H ₄	Ph	233	56

Scheme 4.7: Synthesis of triply fused unsymmetric dimers. *Reagents and conditions:* a) DDQ, Sc(OTf)₃, toluene, 50 °C, 3 h. b) i) PIFA, CH₂Cl₂, -78 °C – rt, 3 h. ii) NaBH₄, MeOH, 0.5 h.

4.3.3 Tetrameric Arrays

To develop a novel tetrameric porphyrin incorporating both a fused moiety and a conjugated alkynyl linker, a twofold synthetic strategy was attempted. The first involved the synthesis of directly-linked tetramer **212**, via Sonogashira coupling, and subsequent oxidation to give the triply-fused tetramer **234**. The second was the synthesis of alkynyl dimer **213** and successive fusing to yield **234**.



The oxidation reactions proved quite cumbersome, with both the DDQ/Sc(OTf)₃ and the PIFA methods being utilised. After many attempts, the desired tetramer **234** was obtained from both strategies via either oxidation methods in moderate to good yields,

the highest of 58 % obtained with PIFA oxidation of dimer **213**. With **213** there was less steric hindrance than **212** for oxidative fusing to occur at the free meso side. Furthermore, the dimer exhibited better solubility in CH₂Cl₂ than tetramer **212** and this affected the yield. The formation of **234** was confirmed by mass spectrometry, UV and NMR analysis. This is the first example of an alkynyl-linked array incorporating a triply fused bisporphyrin moiety and **234** exhibited unusual photophysical characteristics (Section 4.5).

4.4 NMR Analysis

The proton NMR spectra of fused arrays are very distinctive, having remarkably different resonances with respect to their monomeric and dimeric precursors. As the arrays have extensive delocalised π -electron systems through the entire molecule, a profound effect on the ring current of the array is observed. The aromaticity of these arrays is decreased, thereby causing a substantial shift of the porphyrin signals to higher fields.^[156]

Taking trisubstituted monomer **119** and fused dimer **218** as examples, the change in the spectrum upon fusing is substantial, with a drastic shift in signals to higher fields observed for dimer **218** (Figure 4.1). The inner β -protons, H3/H17, resonate around 7.0 ppm, occurring as a singlet. This singlet is characteristic for symmetric fused dimers and is a good indicator that fusing took place. There is a loss of meso-H20 and β -H2/H18 low-field signals on fusing. The other eight β -protons exhibit a signal as two doublets at 7.5 ppm, the most deshielded of which reflects H8/H12, furthest from the effect of the fusing although all significantly different from those of **119**. All remaining resonances correspond to the *para*-methoxy-phenyl protons, with a similar substitution pattern as seen for the monomer **119**, but observed at a higher field. Two singlets at 3.9 ppm reflect the methoxy-CH₃ signals, at slightly higher field strength with regard to the monomer.

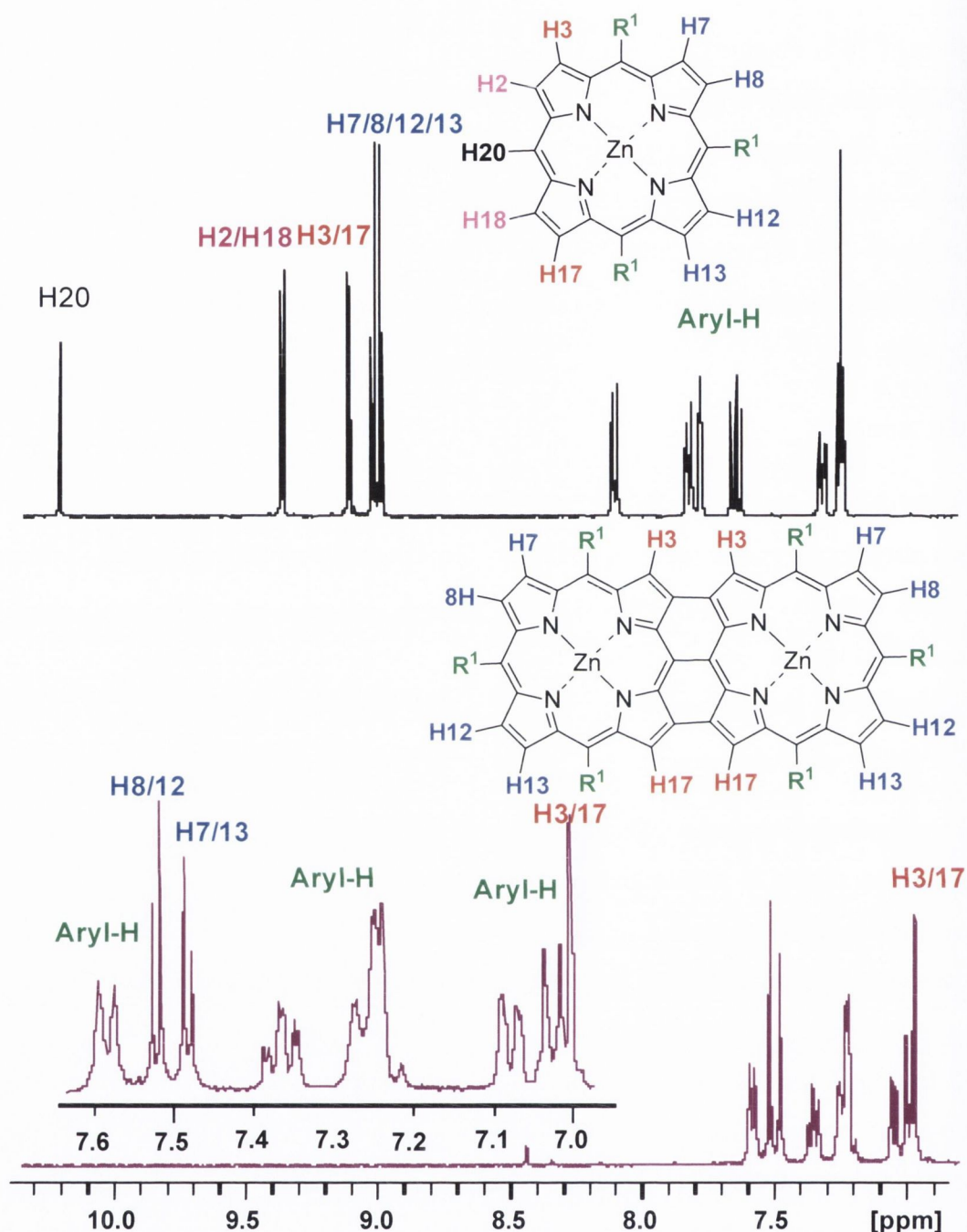


Figure 4.1: ^1H NMR spectrum (600 MHz) of monomer **119** (black) and fused dimer **218** (purple) showing the aryl and porphyrin regions in CDCl_3 . ($\text{R}^1 = 4\text{-MeO-C}_6\text{H}_4$)

These resonances are further confirmed via 2-dimensional ^1H - ^1H NMR total correlation analysis (TOCSY) of **218**, showing the β and aryl regions (Figure 4.2). The singlet at 7.0 ppm is evidently not correlating to any other protons and thus can be assigned to the inner β -protons, with the doublets at 7.5 ppm signifying the resonances for the other eight β -protons. Although specific to dimer **218**, the general pattern of signals can be applied for the deduction of structures of symmetrically fused arrays.

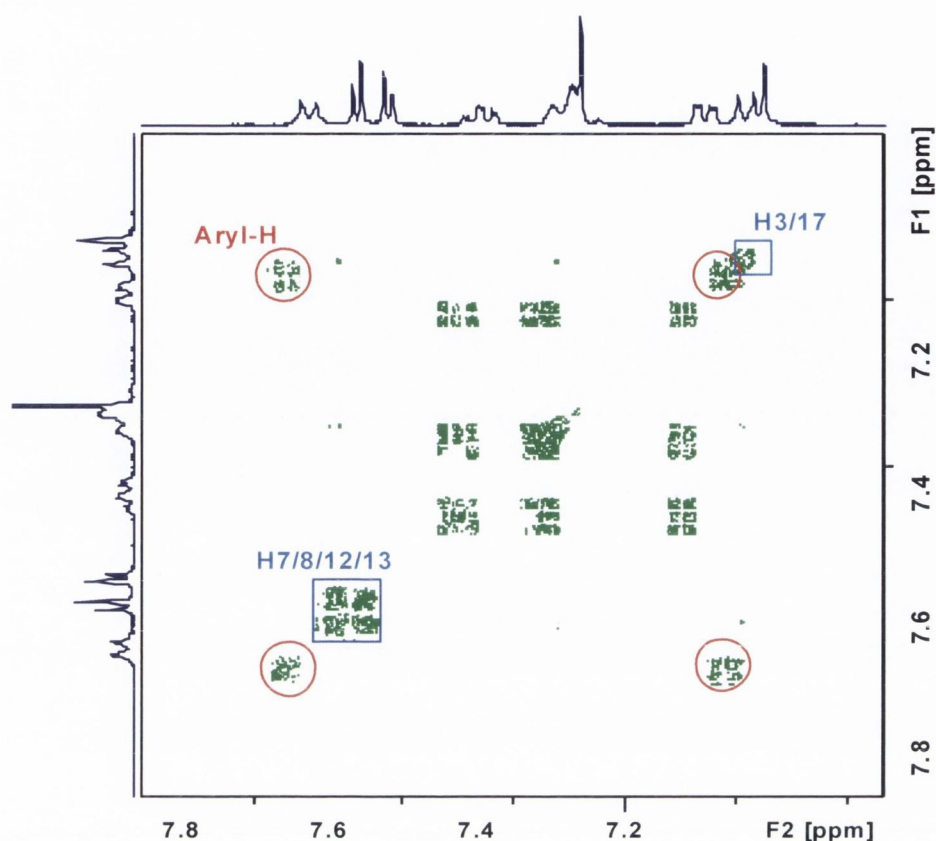


Figure 4.2: ^1H - ^1H TOCSY NMR of the aryl region of **218** in CDCl_3 .

A similar pattern was observed for all symmetric dimers **214-221** and unsymmetric dimer **233**, the resolution of peaks depending on the solubility of the array in CDCl_3 . In some cases, using pyridine- D_5 in CDCl_3 minimised aggregation enabling the generation of sharper and more distinguished peaks in proton NMR spectra. However, in spite of this, broad signals were still observed for the majority of fused arrays. The attainment of carbon spectra was not as straightforward and for dimers **215**, **217**, **220** and bromo-dimers **224** and **225**, the addition of pyridine- D_5 had a negative effect on the ^{13}C -NMR spectra as this solvent can overshadow the spectrum, (Section 3.3.1). Therefore for these dimers, carbon assignments were impossible to achieve and this may be a common trait for fused porphyrin arrays.

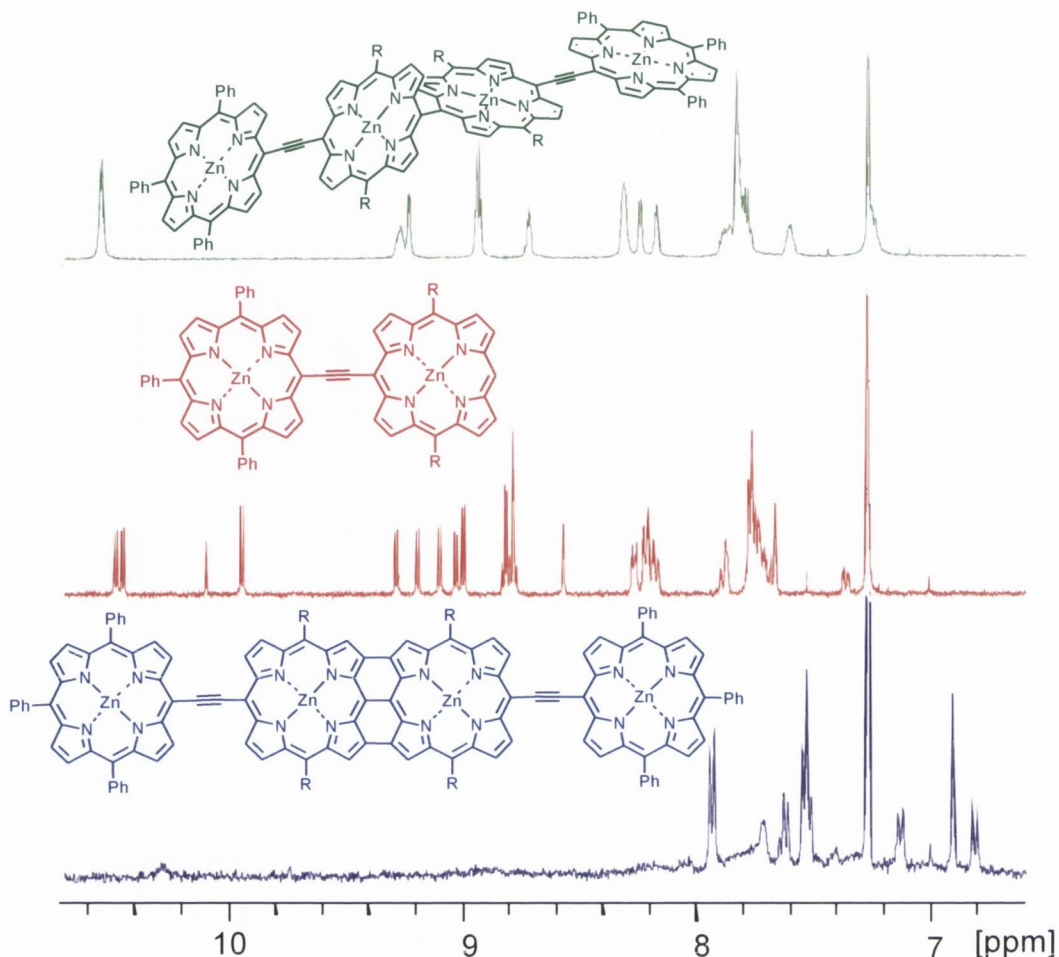


Figure 4.3: ^1H NMR spectrum (400 MHz) of aryl regions of tetramer **212** (green), dimer **213** (red) and fused tetramer **234** (blue) in CDCl_3 . ($\text{R} = 3\text{-OMe-C}_6\text{H}_4$)

For fused tetramer **234**, a similar effect was observed, with a significant shift of signals to higher fields on oxidative fusing of the central porphyrin units (Figure 4.3). Here, in comparison with tetramer **212** and dimer **213**, low field signals reflect the β -protons of the outer porphyrin units, at higher resonances than those seen with dimer **218** due to the distance which these protons are from the fused central bisporphyrin. The characteristic singlet at 6.9 ppm signifies the inner β -protons of the central porphyrin units. These are substantial shifts from starting materials **212** and **213**, whereby the β -protons are observed between 9 and 10.5 ppm.

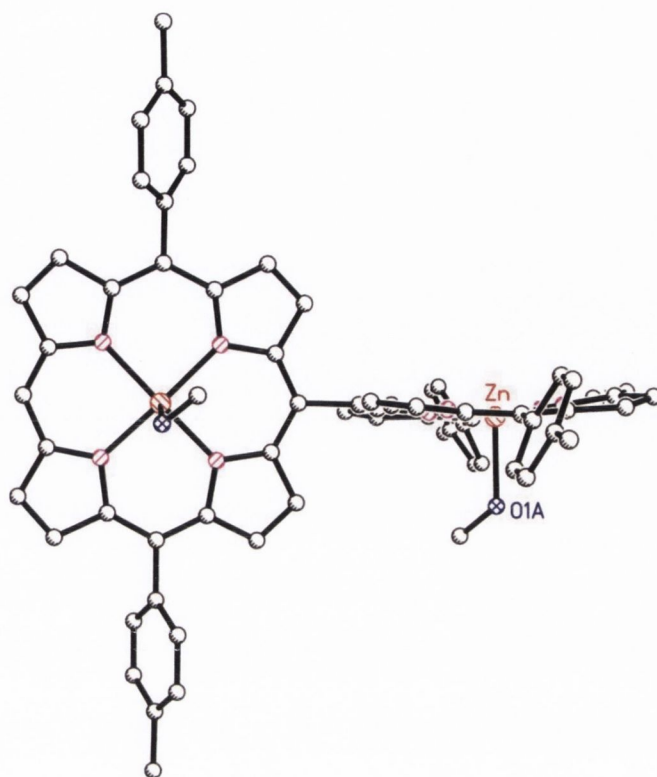


Figure 4.4: X-ray crystal structure of **211**.

Preliminary X-ray data of **211** indicate a structure as shown in Figure 4.4. The molecular structure is characterised by slightly distorted macrocycles with pentacoordinated zinc centers each carrying an axial methanol molecule. The two macrocycles are almost orthogonal to each other, typical of directly linked dimers. The compound crystallised as a CH_2Cl_2 -MeOH solvate. As the present crystal quality was insufficient to give a high resolution a recollection of diffraction data with better crystals is necessary for these compounds.

4.5 UV/vis/NIR Spectroscopic Analysis

Probably the most interesting characteristic of triply fused arrays is their absorption profiles and these can be a key and convenient indication as to their formation. The extension of conjugation results in a substantial bathochromic shift in the absorption profile due to lowering of HOMO-LUMO energy gaps, causing a considerable shift into the near-infrared region. ^[57, 282]

Comparing fused dimer **221** it with its directly-linked dimeric counterpart **228** and monomer **124**, there was a significant difference in their profiles (Figure 4.5). Monomer **124** exhibited a characteristic metallated porphyrin absorption profile with a λ_{max} of 578

nm. Directly-linked dimer **228** exhibited a splitting of the Soret band due to excitonic coupling between the porphyrin units and had a λ_{max} of 598 nm. However, with triply-fused dimer **221**, a substantial shift was observed. There was a broad splitting of the Soret band, at 414 and 576 nm, again due to excitonic coupling between porphyrin units and a λ_{max} well into the near-IR region of 1080 nm. Additionally, strong visible region absorbances were observed at 803 and 945 nm.

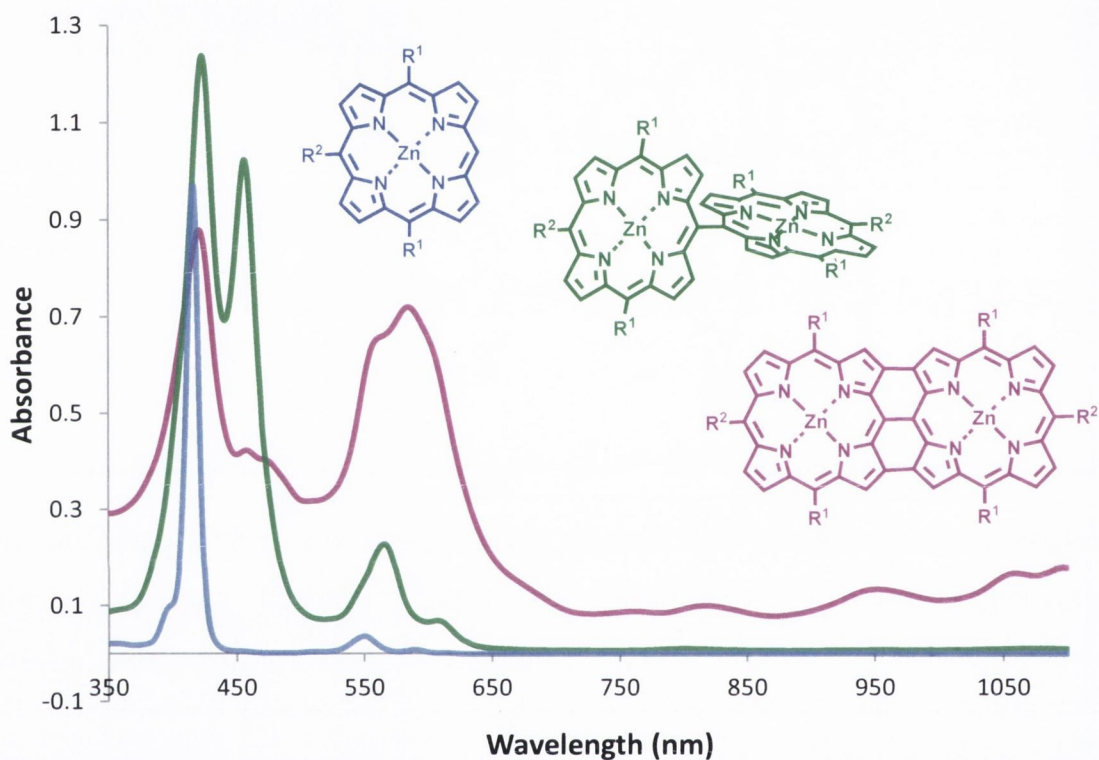


Figure 4.5: UV/vis/NIR absorption spectra of monomer **124** (blue), direct dimer **228** (green) and fused dimer **221** (pink) in ethylacetate.

A similar absorption profile was observed for dimers **214-221** and such characteristic spectra provide a useful analytical tool as to the formation of the fused array. These absorption patterns were also observed for the crude mixtures of free meso dimers **222** and **223**, and their higher oligomers, demonstrating that fusing took place.

For tetramer **234**, there was a substantial change in absorption, the profile of which was identical from both synthetic strategies i.e. the oxidative fusing of tetramer **212** and dimer **213**. Compared to the starting materials tetramer **212** and dimer **213**, a significant difference in absorption can be seen for **234** (Figure 4.6). With tetramer **212** and dimer **213**, there is a split in the Soret band, similar to the alkynyl-linked dimers and both oligomers have a maximum absorption wavelength of 688 and 692 nm, respectively.

Upon fusing, a completely different profile was observed, exhibiting a broad spectrum with few distinguishable peaks. This could be attributed to aggregation effects of the fused tetramer, but it is clear there is absorbance in the near-IR region. Despite the inability to distinguish peaks, the presence of a triply-fused porphyrin moiety was confirmed via the shift in absorption.

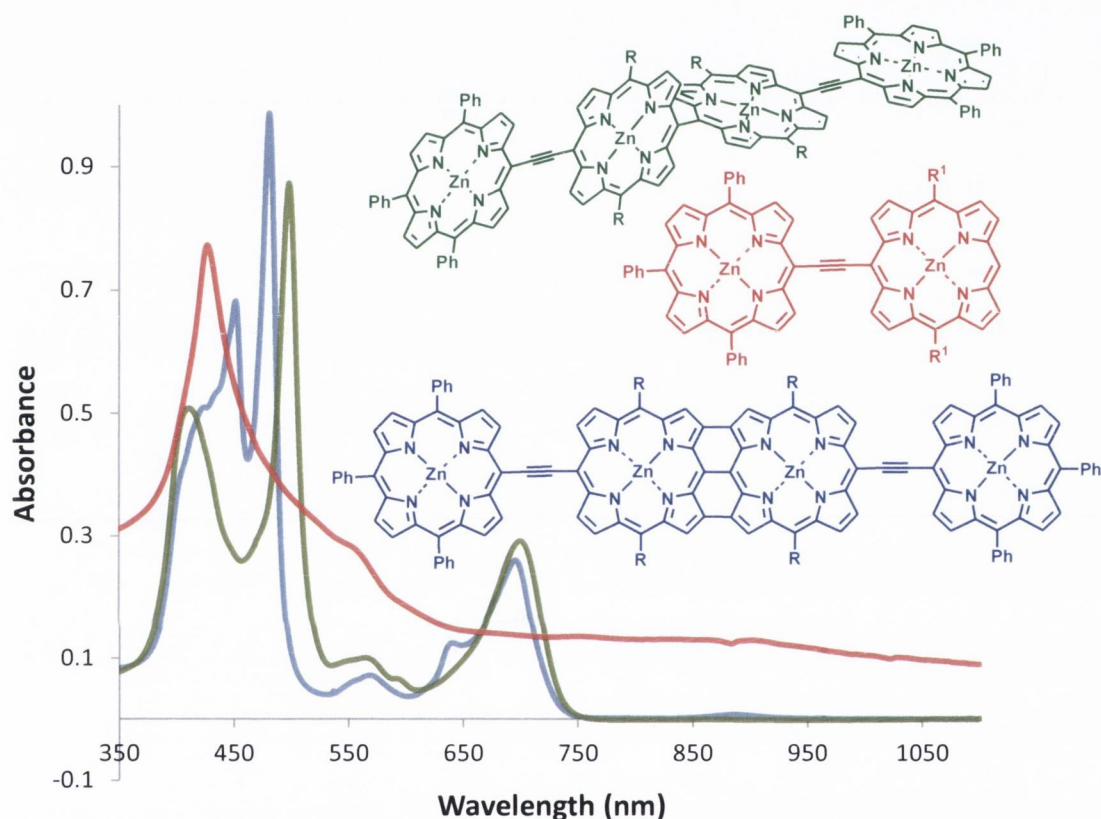


Figure 4.6: UV/vis/NIR spectra of dimer **213** (blue), tetramer **212** (green) and fused tetramer **234** (red) in ethyl acetate. (where R = 3-OMe-C₆H₄)

An interesting effect was seen when employing a co-ordinating solvent for the UV/vis/NIR analysis of fused dimers. As noted by Osuka and co-workers,^[187] there is a red-shift in absorption on addition of a co-ordinating solvent. With dimers **214** and **218**, on comparing their profiles in CH₂Cl₂ against those in CH₂Cl₂ with 2 % triethylamine, a significant bathochromic shift was observed (Figure 4.7). With dimer **214**, there was a red shift of 38 nm, from 1067 nm to 1105 nm, whilst with dimer **218**, this effect is less pronounced with a shift of 13 nm observed. Many studies have been carried out on solvent effects on the absorption profiles in monomeric porphyrins. The spectral shifts are generally attributed to displacement of the metal ion resulting in a distortion of the macrocycle, or, from a charge transfer to the macrocycle from the co-ordinating solvent

resulting in an increase in the HOMO energy level, thereby reducing the energy gap.^[283] However, studies on solvent dependent spectral shifts in fused arrays are limited and further investigations are thus required to determine the precise nature of this bathochromic shift.

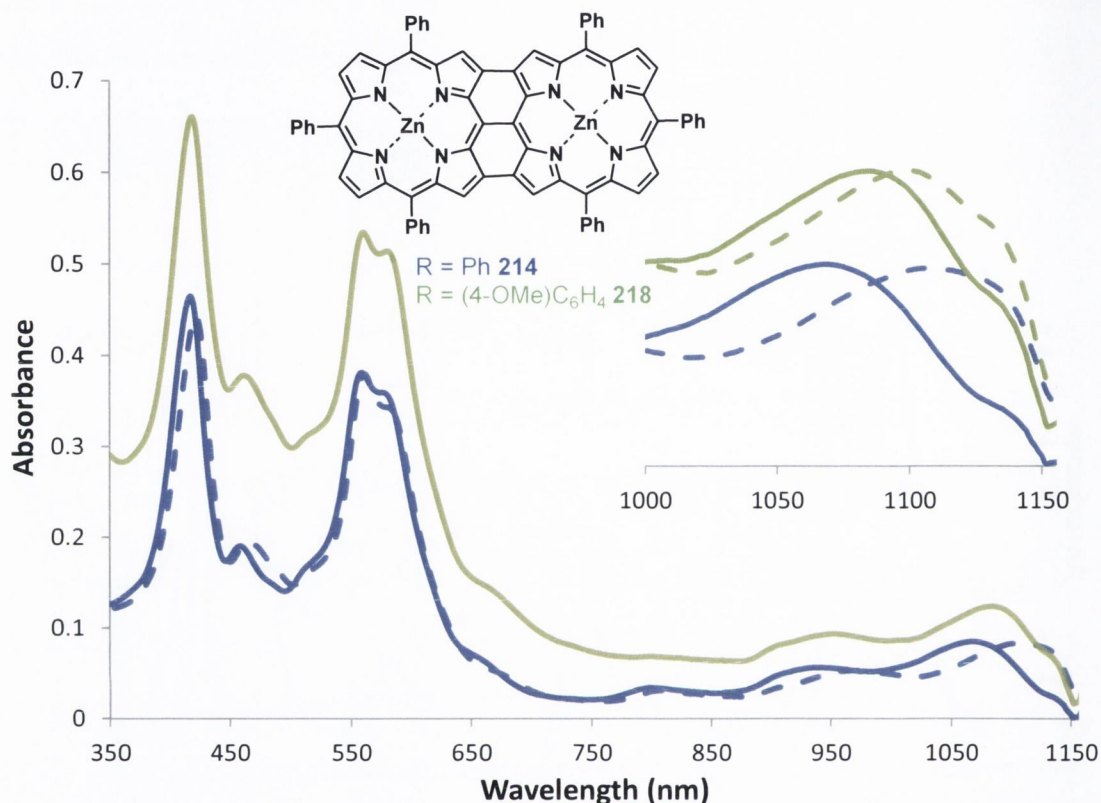


Figure 4.7: UV/vis/NIR spectrum of dimers **214** (blue) and **218** (green) in a) CH₂Cl₂ (solid line) and b) CH₂Cl₂ with 1% TEA (dashed line).

4.6 Conclusions

A library of symmetric directly singly- and triply-linked dimers were synthesised in moderate to good yields via oxidative fusing, tolerating a wide range of functionalities on the porphyrin periphery. Attempts to triply fuse monomers and dimers bearing one or two free meso positions proved, in most cases, unsuccessful due to the inevitable formation of oligomerised products. Although having limited success with alkyl substituted dimers, this route is not viable as yields were low. A series of unsymmetric directly-linked dimers were synthesised in good yields via a stepwise strategy. However, the oxidative double ring closing of meso free dimers proved again unsuccessful. As a result, a change in strategy was needed for post-functionalisation of triply-fused arrays. All triply linked dimers isolated exhibited a substantial

bathochromic shift in their absorption profile into the near-infrared region, thus making these arrays potential candidates for optical applications such as PDT and NLO. Through the introduction of water solubilising moieties the dimers could be applied to PDT or by the introduction of electron donating and withdrawing substituents to the field of NLO. There are considerable possibilities to develop a library of unsymmetrically fused dimers and fine-tune these for optical applications. The fused tetramer synthesised is the first example of a fused array incorporating alkynyl-linked porphyrins and other linkages could also be explored.

CHAPTER 5:

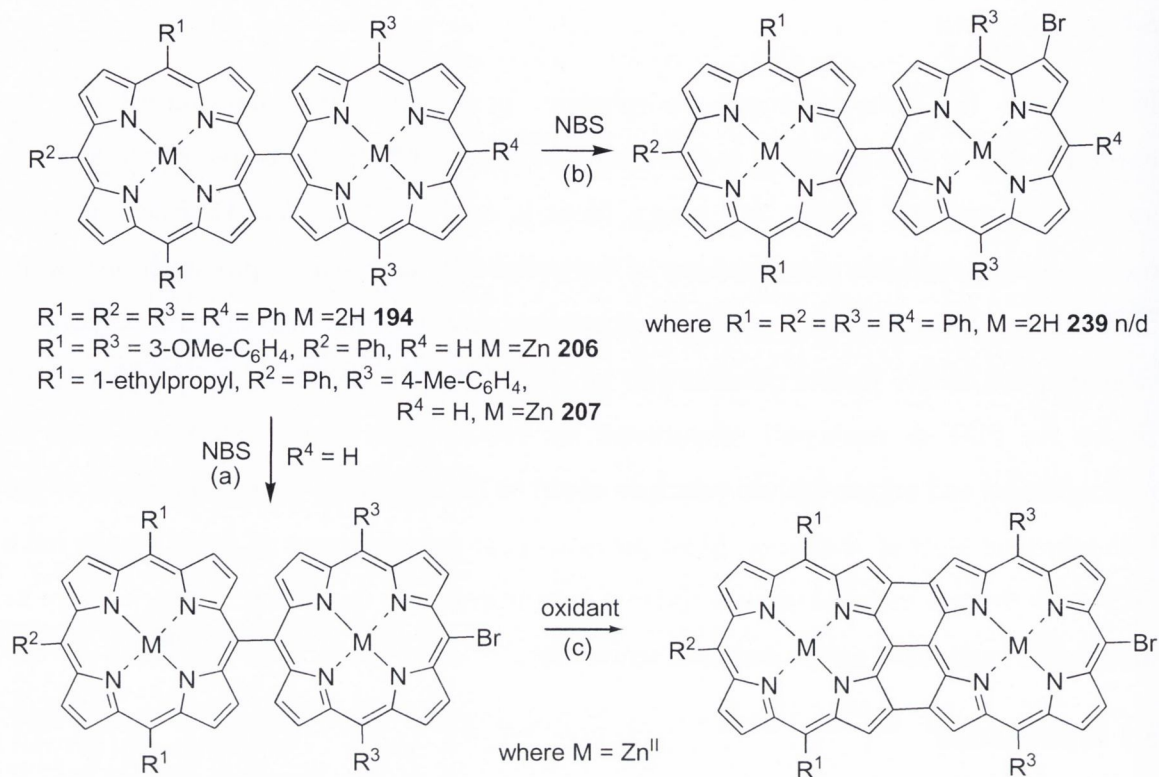
Reactivity of Porphyrin Arrays

5.1 Introduction

In order to fine tune oligomeric porphyrins, post-fusing functionalisations can be executed. These derivatisations enable fused dimers to be more attractive candidates for application purposes. Within our group, focus is on PDT, NLO and OLEDs and with these in mind, synthetic modifications of the peripheries of fused porphyrin dimers were undertaken. These included activation reactions such as brominations and nitrations, which would enable further chemistry to be carried out, for example, the attachment of sugars for PDT or push-pull substituents for NLO. Also, functionalisations such as cycloaddition and organolithium reactions could be beneficial for the enhancement of the bathochromic shift of the array. Most previous post-modifications of fused arrays have dealt with the pre-installation of activating substituents and thus, there is much scope to investigate such fused arrays and their reactivity.

5.2 Bromination

Bromoporphyrins are vital precursors for modification reactions as they enable a range of palladium catalysed reactions to be carried out. As the fusing of porphyrins with free meso positions, both singly and triply, did not deliver adequate results, an activating substituent such as bromine needs to be introduced prior to the oxidative fusing step to enable direct meso post-fusing modifications. Brominations at the meso positions of porphyrins have been extensively investigated (Section 2.2.3), and using standard bromination conditions of NBS and chloroform, directly-linked dimers **206** and **207** could be brominated at their free meso position, yielding dimers **235** and **236** in excellent yields of 85 and 90 %, respectively (Scheme 5.1). These bromo porphyrins were subsequently oxidatively fused using DDQ/Sc(OTf)₃ to form the triply fused dimers **237** and **238**, approximate yields of 25-35 %. The fused bromo dimers were difficult to purify due to their poor solubility and required large volumes of co-ordinating solvent for their removal from silica. As a result of their poor solubilities and also due to overshadowing pyridine-D⁵ peaks, NMR spectroscopic analysis was difficult, similar to those discussed in Section 4.4. Both dimers exhibited UV/vis/NIR spectra characteristic for fused systems and this was confirmed via HRMS. In spite of this poor solubility, **237** and **238** were used for post-fusing modification reactions.



R^1	R^2	R^3	#	Yield %
3-MeO-C ₆ H ₄	Ph	3-MeO-C ₆ H ₄	235	85
1-Ethylpropyl	Ph	4-Me-C ₆ H ₄	236	90

Fused #	Yield %
237	25
238	30

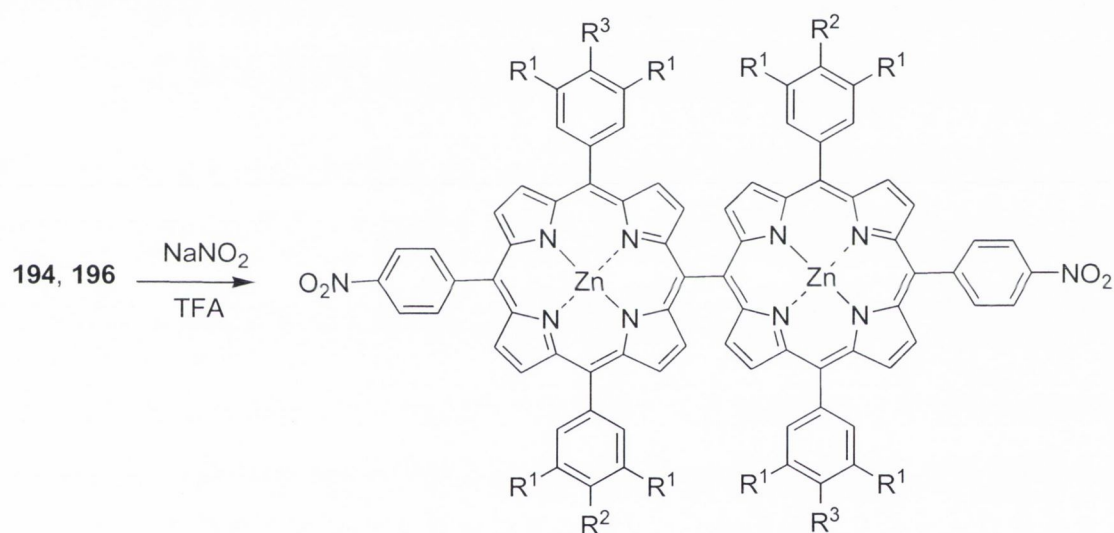
Scheme 5.1: Bromination of directly linked dimers. *Reagents and conditions:* a) NBS, CHCl₃, 0 °C, 3 h. b) NBS, CHCl₃, 70 °C, 3 h. c) DDQ, Sc(OTf)₃, toluene, 50 °C, 3.5 h.

To investigate the possibility of brominating dimers at the β -position, meso phenyl substituted directly linked dimer **194** was used and it was envisaged that β -bromination would enable β post-fusing modifications to be possible, yielding β -substituted fused arrays, few of which are in existence.^[273] Test reactions on **194**, however, were not very successful in that multiple brominations occurred. It was hoped that the dimer would act in a similar fashion to that of tetraphenylporphyrin,^[284] whereby the mono-bromination can be controlled and is very high yielding,^[285] to produce monobrominated dimer **239**. Conversely, this was not the case and numerous brominated products were formed, none of which were isolated due to multiplicity of brominated products involved. Control over this bromination seems unmanageable and therefore this route for β functionalisations of

dimers was abandoned. Hence, other strategies for β functionalisations of dimers were necessary.

5.3 Nitration

Nitrophenyl porphyrins are intermediates for the attachment of sugars via ‘Click’ chemistry. From these, reduction and azido formation yields azido-phenyl porphyrins which can undergo Click reactions with alkynyl sugars/bile acid to form porphyrin-sugar conjugates.^[83] These conjugates are beneficial to the area of PDT as the sugar moiety enhances both the solubility of the porphyrin and also its selectivity. There has been considerable research into such monomeric conjugates but thus far, little investigation has gone into dimeric porphyrin-sugar or bile acid conjugates.^[84, 86]



R^1	R^2	R^3	#	Yield %
H	NO_2	H	240	38
H	NO_2	NO_2	241	trace
3,5-di- <i>tert</i> -butyl	H	H	242	n/d

Scheme 5.2: Synthesis of nitro dimers **240-242**. *Reagents and conditions:* NaNO_2 , TFA, 24 h.

It was hoped that via nitration of dimers **194** and **196**, the desired nitrophenyl porphyrins **241** and **242** could be synthesised. Using standard nitration conditions, developed by Smith and co-workers,^[206] dimer **194** was nitrated via electrophilic aromatic substitution, using sodium nitrite in TFA. This generates the NO_2^+ electrophile which nitrates specifically at the *para* position of the phenyl ring, the number of nitrations depending on quantity of sodium nitrite and TFA used. It had been shown that nitration of TPP gives

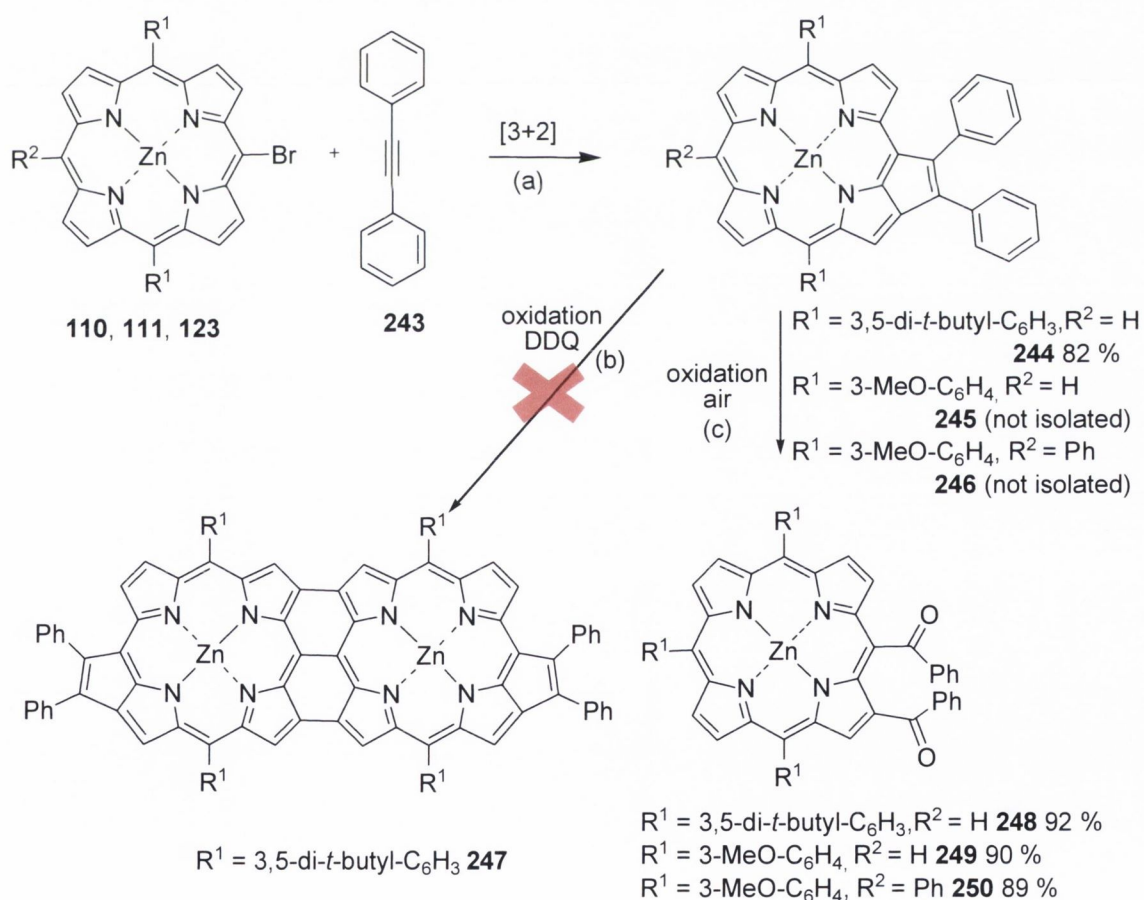
predominantly the di- and trisubstituted products, only when a substantial nitrating excess is used was the tetrasubstituted product formed.^[206] However, a recent study has contradicted this and tetra-nitro phenyl porphyrin can be obtained in yields of up to 90 % using a more efficient work-up and chromatographic procedure.^[286] Xue *et al.* noted that during the nitration process, the trinitrated product is least favoured due to the *ortho*-effect of mononitration. This is useful to our studies as difficulties arose on nitrating dimer **194**, with the main product formed was the tetra-nitrated product **240** in a yield of 38 % (Scheme 5.2). Increasing both reaction time and equivalents of NaNO₂ did not enhance the reaction, only when more than 200 equivalents of NaNO₂ was used was the desired hexanitrated product **241** detected. Only trace quantities of **241** were formed, with the main product again being tetranitro dimer **240**. The formation of **241** was confirmed by mass spectrometry analysis. Other attempts to nitrate all six positions involved the use of fuming nitric acid,^[244, 287] the original method which is harsher than that developed by Smith and co-workers, but this had similar results. Using TPP as the ‘base’ structure, full nitration of dimer **194** would be the equivalent of tri-nitrated TPP, which is not favoured, and this may be a reason for dimer **240** being the predominant product.^[286]

Attempts to generate nitro-dimer **242** via nitration of **196** were also unsuccessful. Here, it was hoped that the bulky *tert*-butyl groups would block the aryl ring from nitration, thus generating a bis-nitrophenyl product **242**, i.e. allowing regioselective control over nitration. This was not the case and only starting material was recovered. Thus, the approach of nitrating porphyrin dimers is not very efficient and nitro-incorporation is more successful when introduced at the monomeric stage, i.e. via condensation and Suzuki coupling reactions (Chapter 2). It was also shown in Chapter 4 that *para*-nitrophenyl substituted dimers can be generated from oxidative fusing methods in good yields, thus this method is preferred.

5.4 Cycloaddition reactions - [3+2] Annulation

Cycloaddition reactions on monomeric porphyrins are widely known, generating perturbed macrocycles with enhanced photophysical properties.^[42, 288] To investigate the reactivity of the brominated dimers **237** and **238**, we decided to adopt a [3+2] annulation strategy developed by Osuka and co-workers.^[289-292] This involves a palladium catalysed C-C bond forming reaction via carbopalladation of a bromo-porphyrin with internal

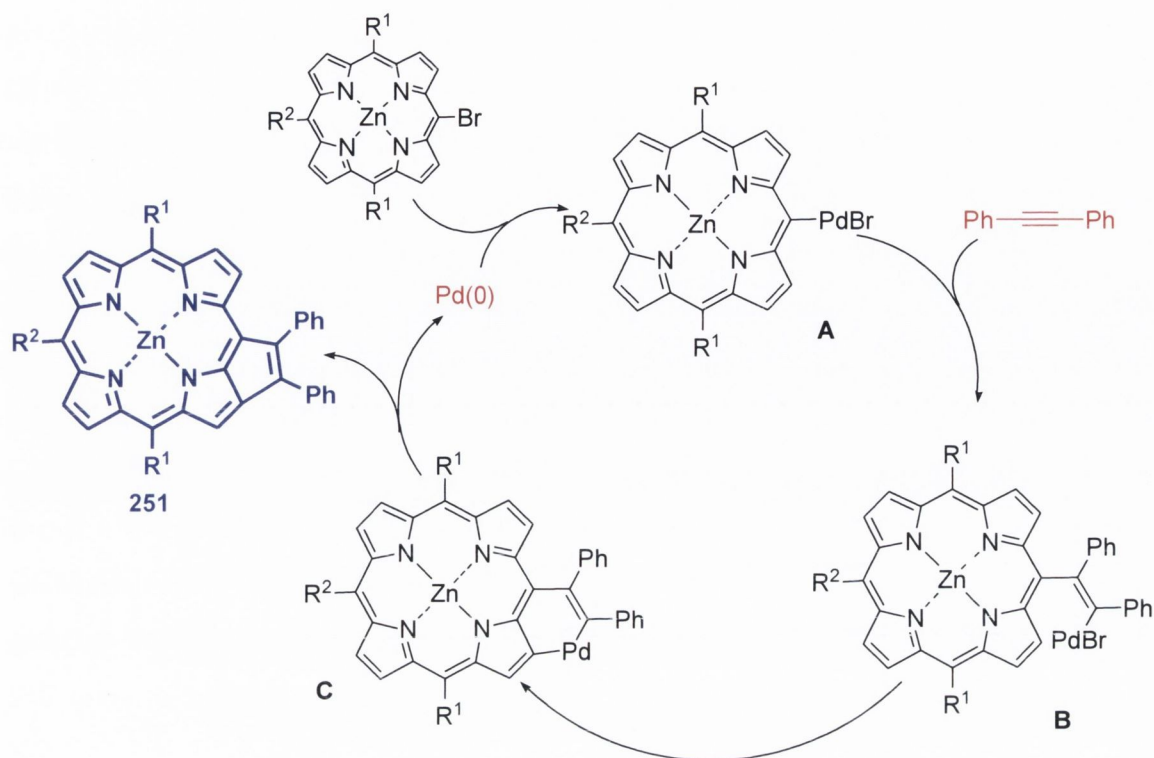
alkynes.^[293-294] The resulting product is a 7,8-dehydropurpurin incorporating a fused cyclopentadiene ring which causes a significant distortion of the porphyrin macrocycle. Tetrapyrroles with exocyclic 5-membered rings have biological significance but in spite of this synthetic derivatives of such are not that common.^[295] Resulting from the perturbation of the macrocycle, these species have interesting photophysical properties and exhibit a bathochromic shift in their absorption profile.^[296] We sought to apply this chemistry to dimeric porphyrins and develop a novel ‘fused on fused’ system which we hoped would further enhance the properties of the triply-fused array. This type of macrocycle was first discovered following the attempted oxidation of a free meso porphyrin with an internal alkynyl substituent. Instead of fusing directly at the free meso position as anticipated, a dehydropurpurin-porphyrin dyad formed.^[297] Other than this initial investigation, further attempts to incorporate the cyclopentadiene moiety into dimeric porphyrins have not been explored.



Scheme 5.3: Synthesis of dehydropurpurin porphyrins **244-246** and ring-opening products **248-250**. *Reagents and conditions:* a) Pd₂(dba)₃, (*o*-Tol)₃P, toluene, *N,N*-dicyclohexylamine, 120 °C, 24 h. b) DDQ, Sc(OTf)₃, toluene, rt, 3 h. c) CHCl₃, air, light, 24 h.

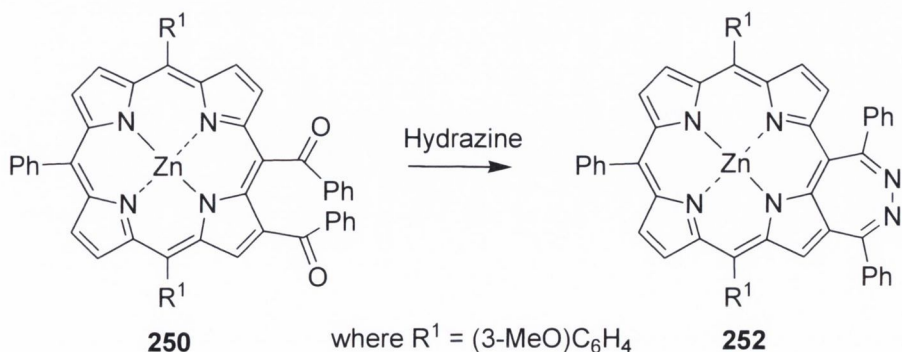
The initial strategy involved the synthesis of a dehydropurpurin macrocycle with a free meso position and subsequent fusing with standard oxidative conditions which we anticipated would yield the desired triply-fused dimeric dehydropurpurin. To test reaction conditions, the [3+2] annulation was carried out on bromoporphyrins **110**, **111** and **123** with diphenylacetylene **243** (Scheme 5.3). All reactions were carried out using zinc porphyrins, as this metal is a prerequisite for the next step of oxidative fusing. For the generation of dehydropurpurins **244-246**, the reaction proceeded well in excellent yields of up to 82 % debrominated starting material detected as the only side product from the reaction. Unfortunately, as discovered by Osuka and co-workers, the zinc-dehydropurpurins are unstable in dilute solution and on exposure to air and light. The cyclopentadiene ring-opens, most likely following a singlet oxygen oxidation mechanism, to give the 1,5-diketones **248-250** in almost quantitative yields. This is not seen with nickel(II) or palladium(II) porphyrins and it is thus presumed to occur from singlet oxygen generation. For **245** and **246**, the ring-opened products **249** and **250** were forced to form via dilution with CHCl_3 and stirring open to the air overnight. Initial attempts using smaller volumes of CHCl_3 exhibited minimal decomposition of the dehydropurpurin, reflecting a somewhat more stable adduct than that described in the literature.^[289] Attempts to triply-fuse **244** employing standard oxidative conditions using DDQ/ $\text{Sc}(\text{OTf})_3$ for the generation of dimer **247** were ineffective, with the main product isolated being the ring-opened adduct **248** (Scheme 4.3). As the outer C-C double bond in the cyclopentadiene ring is prone to oxidation in zinc porphyrins, it does not survive these strong oxidative conditions and thus a different strategy for the development of a ‘fused on fused’ dimer was required.

The proposed mechanism for this palladium catalysed coupling reactions involves the oxidative addition of Pd^0 to the C-Br bond (A) and subsequent carbopalladation with the internal alkynyl bond to give an alkenyl-palladium species (B). There is an intramolecular activation of the C-H bond and loss of HBr, forming a palladcycle (C) and following this, reductive elimination to give the cyclised porphyrin (dehydropurpurin) **251** and regenerated Pd^0 (Scheme 5.4).^[289, 294]



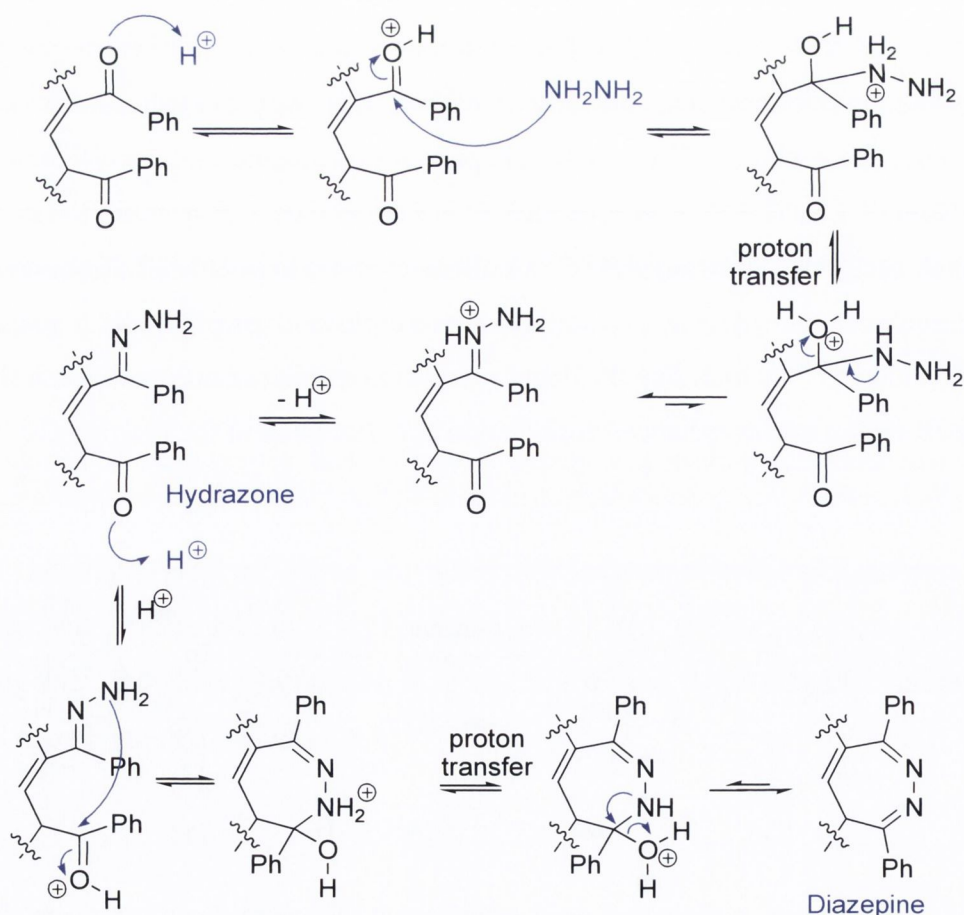
Scheme 5.4. Mechanism for the formation of dehydropurpurin **251**.

In order to provide a utility for the ring-opened products, further chemistry was investigated. 1,5-diketones are widely known to undergo various cyclisation reactions to give 5, 6 and 7-membered ring products, depending on reagent and conditions used.^[298] The reaction of 1,5-diketones with various amino derivatives can result in the generation of nitrogen containing heterocycles.^[299] Osuka and co-workers utilised this methodology with ammonia to generate a novel pyridine-fused porphyrinoid, namely an oxopyridochlorin,^[300] which like the dehydropurpurins, exhibits a substantial red shift into the near-IR region due to enhanced conjugation and distortion of the macrocycle.



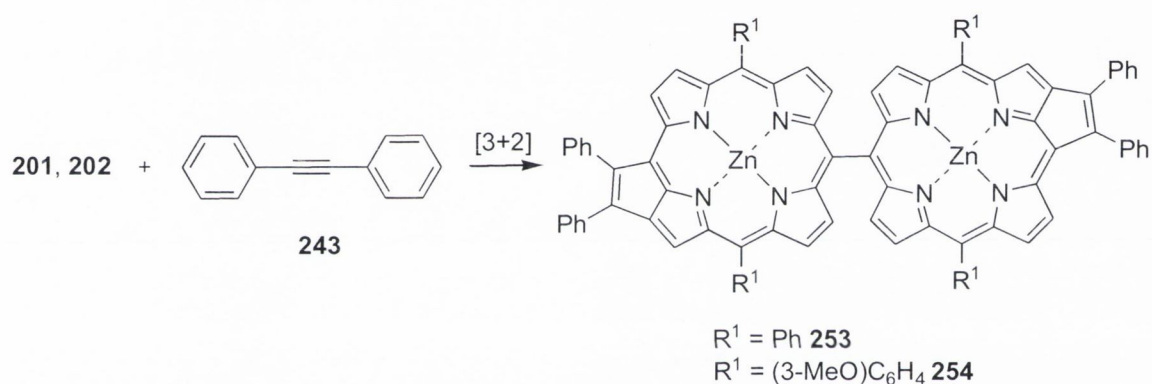
Scheme 5.5: Synthesis of a diazepine fused porphyrinoid **252**. *Reagents and conditions:* hydrazine hydrate, toluene, acetic acid, MW, 7 min.

We decided to use hydrazine as a substrate to develop a novel diazepine-fused porphyrin, to explore the reactivity of the porphyrin 1,5-diketones generated and the effect that the fused diazepine moiety would have on the macrocycle. Taking 1,5-diketone **250** and employing microwave conditions,^[301] the desired product **252** can be obtained in a good yield of 80 % (Scheme 5.5). Hence, if only the 1,5-diketone can be isolated, further chemistry is possible to generate novel fused systems, although the macrocycle here is not perturbed as the ring generated is not conjugated. Scheme 5.6 shows the most likely mechanism for the synthesis of the diazepine-porphyrinoid **252**. The condensation mechanism initiates with the protonation of the carbonyl oxygen under acidic conditions and subsequent nucleophilic attack of hydrazine at the electrophilic carbon. A series of proton transfer and elimination of water yields the indicated hydrazone intermediate. Another attack by the hydrazine moiety, this time intramolecularly, closes the ring. Subsequent proton transfer and loss of water yields the 1,2-diazepine porphyrin **252**. Attack by the other nitrogen would generate a 6-membered ring derivative but this, however, was not detected.



Scheme 5.6: Mechanism for diazepine ring formation.

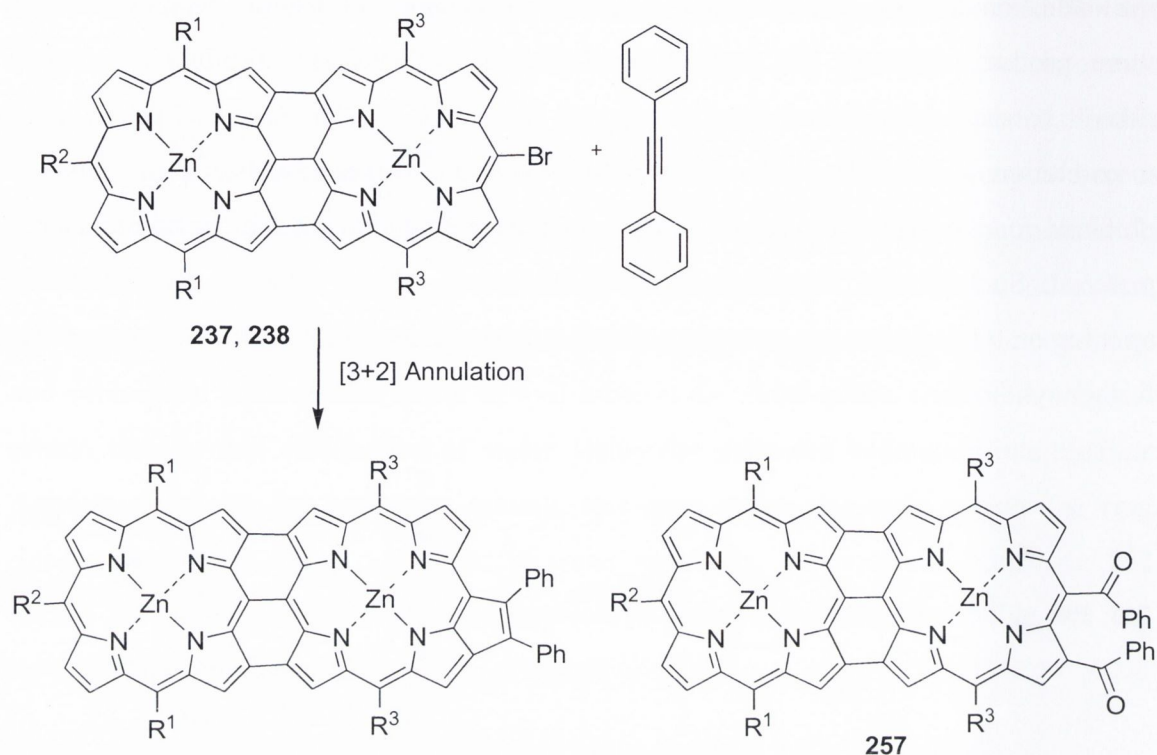
In parallel to cycloaddition reactions of monomers and subsequent oxidative fusing, the [3+2] annulation was also attempted with the bromodimers **201** and **202**, resulting in cycloaddition products **253** and **254**, respectively (Scheme 5.7). For the synthesis of **253**, three products formed, the desired disubstituted cycloaddition product, the mono derivative and debrominated starting material, separation of which was not possible due to co-elution on both silica gel and aluminium oxide. For dimer **254**, a yield of 72 % was obtained for the bisdehydropurpurin, with only trace detection of debrominated starting material. Such dimers have interesting UV spectra, although due to inevitable ring opening on oxidation to generate triply-fused systems, these compounds were not used in further synthesis.



Scheme 5.7. Synthesis of directly linked bis-dehydropurpurins **253** and **254**. *Reagents and conditions:* $\text{Pd}_2(\text{dba})_3$, (*o*-Tol) $_3\text{P}$, toluene, *N,N*-dicyclohexylamine, 120 °C, 24 h.

As the initial strategy of fusing monomeric dehydropurpurin **244** was unsuccessful, it was decided to attempt the cycloaddition on fused bromo-dimers so that no further oxidation would be necessary. This would, in theory, avoid any decomposition of the cyclopentadiene ring to the 1,5-diketone. Employing bromo-dimer **237**, the palladium catalysed [3+2] annulation reaction was attempted, but with no success. The main fraction isolated was unreacted starting material, with no detection of annulated dimer **255**. This may be attributed to the insolubility of the starting material but further investigations are needed. Trying to overcome the solubility issues, dimer **238** was used, with alkyl and tolyl substituents. The reactivity was enhanced but the desired product **256** was only obtained in a yield of less than 5% and it co-eluted with debrominated starting material. Also observed was the ring-opened product **257**, which may have decomposed during purification when open to the air or due to trace presence of oxidants in the starting material. Due to time constraints, optimisations of these reactions were not

possible and the products formed were only characterised by HRMS with **256** showing a parent ion peak at m/z 1342.3580, calculated for $[C_{84}H_{62}N_8O_2Zn_2]$ 1342.3579.



R ¹	R ²	R ³	#	Yield %
(3-MeO)C ₆ H ₄	Ph	(3-OMe)C ₆ H ₄	255	n/d
1-ethylpropyl	Ph	Tolyl	256	< 5 %

Scheme 5.8. [3+2] Annulation of fused dimers with diphenylacetylene showing side products. *Reagents and conditions:* Pd₂(dba)₃, (*o*-Tol)₃P, toluene, *N,N*-dicyclohexylamine, 120 °C, 24 h.

Although having limited success with fused dimers, the [3+2] annulation strategy is an efficient method of enhancing the bathochromic shift. Recently, nickel(II) triply-fused dimers have been synthesised via gold-mediated oxidation^[176] and these could be applied for this cycloaddition, thus minimising the possibility of ring-opening. Further investigations into such arrays are needed.

NMR analysis

[3+2] cycloaddition with the porphyrin macrocycle to generate dehydropurpurins, which disrupts the aromaticity, causes significant shifts in ¹H NMR resonances to a higher field

with respect to typical porphyrins. This aromaticity is restored upon ring-opening to the 1,5-diketone and thus resonances return to lower fields.

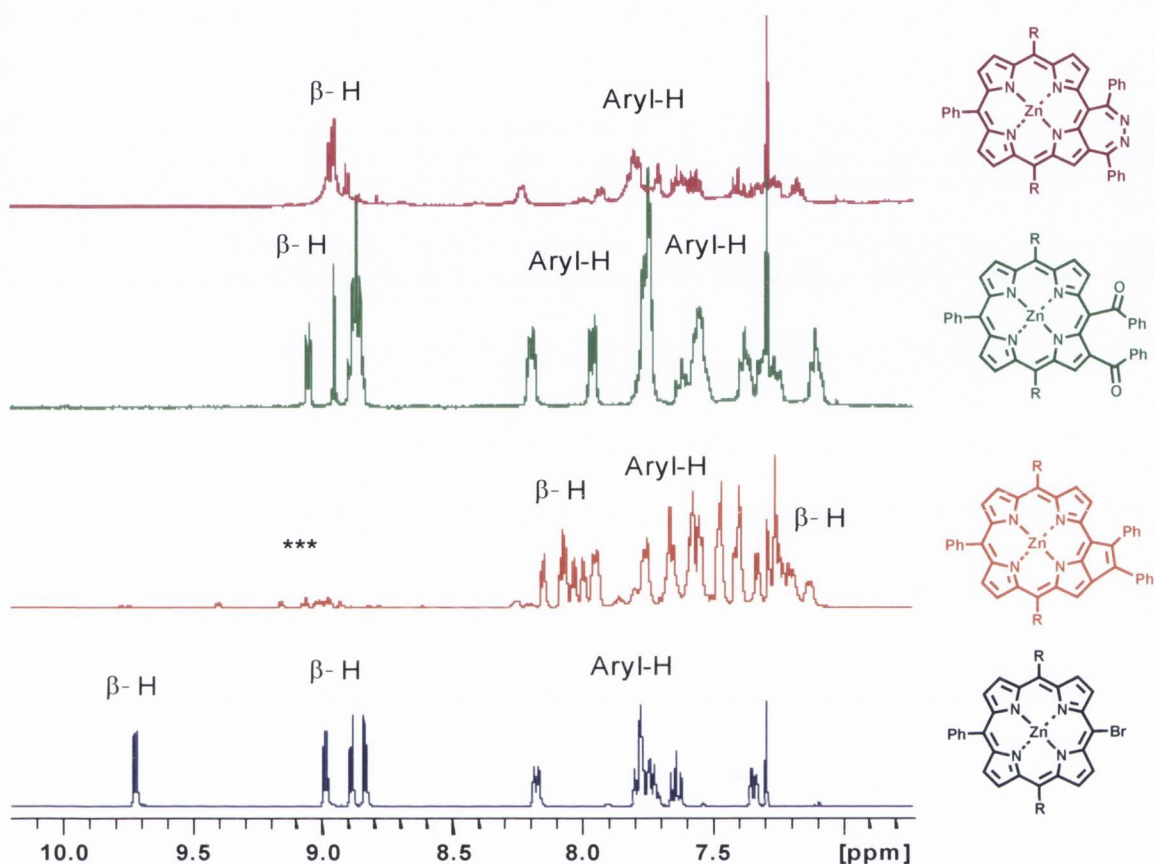


Figure 5.3: ¹H NMR (400 MHz) spectra the porphyrin/aryl regions of bromoporphyrin **111** (blue), dehydropurpurin **245** (orange), 1,5-diketone porphyrin **250** (green) and diazepine-fused porphyrin **252** (purple) in CDCl₃. (where R = 3-OMe-C₆H₄)

Figure 5.3 shows a comparison of bromo-porphyrin **111**, dehydropurpurin **245**, 1,5-diketone porphyrin **250** and diazepine fused porphyrin **252**. On generation of **245** from bromo porphyrin **111**, there was a substantial shielding of β-signals from between 8.8 and 9.8 ppm to 7.2 to 8.2 ppm. Also, with **111** there are four β-proton signals, with six signals for the β-protons in **245**, due to the distortion of the macrocycle. This most evident for the β-protons closest to the cyclopentadiene ring which occur as two singlets. The methoxy CH₃ for **111** occurs as a 6H singlet but with **245**, two 3H singlets are observed due to the asymmetry of the macrocycle. Some impurities are present in the spectrum of **245** as here the ring opening was promoted to generate diketone **250**. The spectrum for **250** returns to that for a porphyrin with the β-signals resonating in the region of 8.6–9.1 ppm. The ketone functional groups were also confirmed via ¹³C NMR analysis with low field resonances of 194.5 and 199.3 ppm for the carbonyl carbons attached to the β and

meso carbons respectively. Diazepine-fused porphyrin **252** exhibits a slight difference in chemical shifts for the β -protons, typical of fused moieties, with the two closest to the fused ring occurring as singlets of highest field strength in the β -region. The structure was confirmed by HRMS, with a parent ion of m/z 864.2222, calculated for $[C_{54}H_{36}N_6O_2Zn]$ 864.2191, and also the loss of signals at 194 and 198 ppm in ^{13}C NMR analysis for the carbonyl carbons.

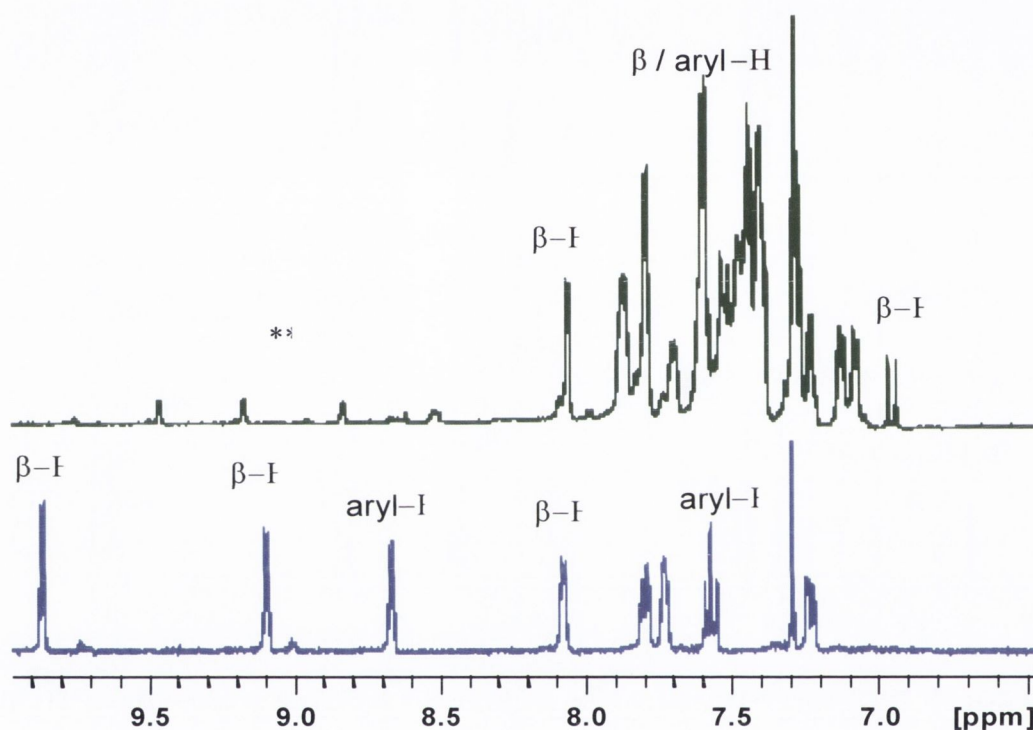


Figure 5.4: Low frequency region of 1H NMR (400 MHz) spectrum of fused directly linked dimer **254** (green) versus bromo dimer **202** (blue) in $CDCl_3$. ** = impurities

With respect to dimer **254**, shown in comparison to bromodimer **202** in Figure 5.4, there is a substantial shift of resonances on [3+2] annulation. The two singlets at the highest frequency of 6.9 ppm reflect the protons closest to the cyclopentadiene ring. All the other protons lie within the 7–8.2 ppm region and, unfortunately due to multiplicities, are not very distinguishable. From 2-D NMR analysis, the doublet at 8.1 ppm signifies the β -protons furthest from the fusing, with the other β -protons resonating in the aromatic region. The small peaks above this value are impurities, due to trace debrominated starting material as no detection of carbonyl signals from the possible ring opened product in ^{13}C NMR was seen. The high field methoxy signals split on fusing from one 12H singlet to two 6H singlets, expected due to the different environments for the methoxy group nearest and furthest away from the cyclopentadiene ring. HRMS analysis

confirmed the structure, with parent ion peak at m/z 1518.3505, calculated for $[\text{C}_{96}\text{H}_{62}\text{N}_8\text{O}_4\text{Zn}_2]$ 1517.3477.

UV-vis and NIR analysis

The [3+2] adducts synthesised provide interesting absorption profiles due to the perturbation of the porphyrin macrocycle. Taking monomer **244** and the ring-opened form **248**, as shown in Figure 5.5, there is a significant split of the Soret band into a blue shifted band at 408 nm and a bathochromically shifted band at 481 nm, with a broad absorbance, similar to those in the literature.^[289, 295] Comparing this dehydropurpurin to the ring-opened form **248**, the spectrum returns to that of a typical monomeric porphyrin, thus the progress of both reactions can be monitored via UV-vis analysis. Also, it demonstrates the effect of the cycloaddition on the photophysical properties of porphyrin and how this could be used to enhance or fine-tune compounds for optical applications.

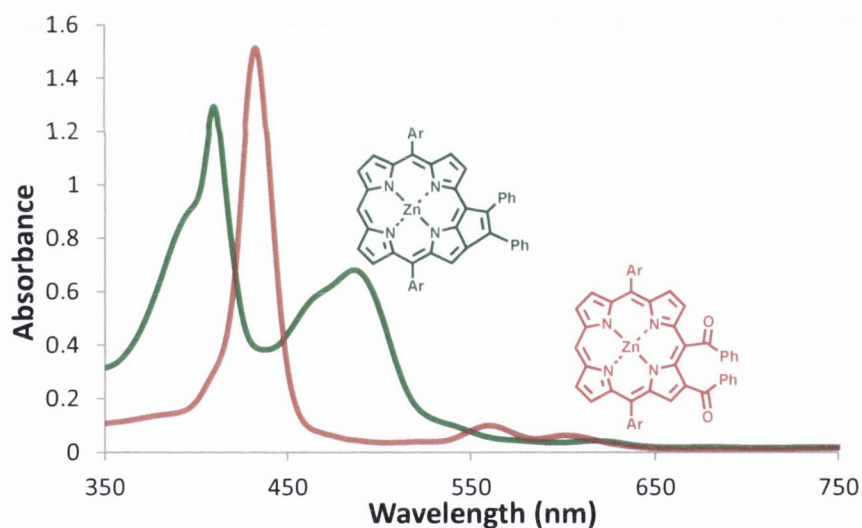


Figure 5.5: UV-vis absorption of **244** (green) and **248** (red) in CH_2Cl_2 . (where Ar = (3,5-di-*t*-butyl) C_6H_3)

With dimers **202** and **254**, a similar trend was observed (Figure 5.6). The bromo-dimer **202** shows a typical absorption profile for a directly linked dimer, a sharp split in the Soret band due to excitonic coupling between the porphyrin units. With annulated dimer **254**, there was a significant broadening and shift of the Soret band, similar to monomer **244**, with the red-shifted band absorbing at 508 nm. Also, there is a red shift of Q bands, with a λ_{max} of 687 nm, compared to 608 nm for **202**. This is indicative of the extent of distortion of the porphyrin macrocycles within the dimer as a result of [3+2] annulation.

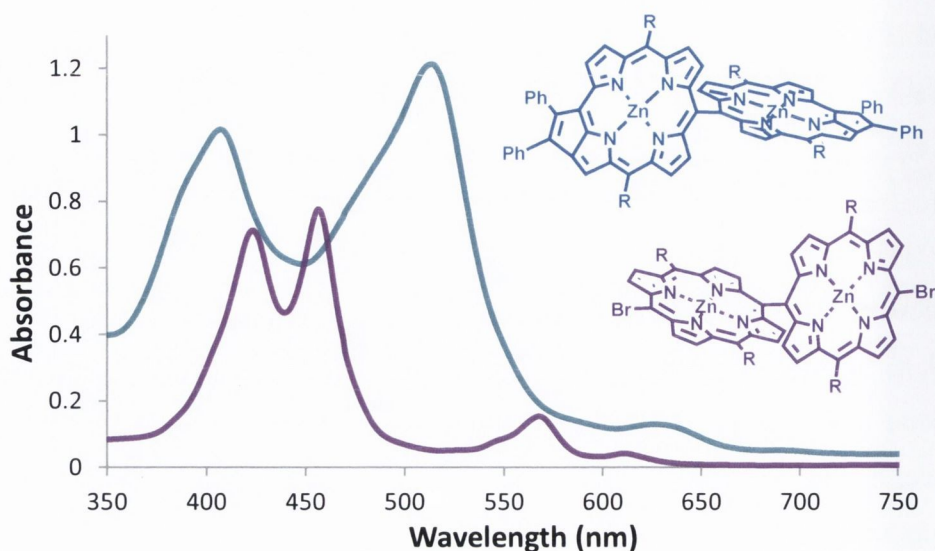


Figure 5.6: UV-vis absorption spectrum of **202** (purple) and **254** (blue) in CH_2Cl_2 . (where $\text{R} = 3\text{-OMe-C}_6\text{H}_4$)

For fused dimer **256**, identifying whether the cycloaddition took place was more difficult due the characteristic broad and red-shifted absorption profiles of fused arrays. There was an increase in intensity of the second Soret band, i.e. a more pronounced split with respect to bromo-dimer **238** and also in intensity of the last Q band (Figure 5.7). Such differences in absorbances imply that the annulation took place, generating a novel ‘fused on fused’ dimer, but unfortunately in too low a yield to obtain good NMR data.

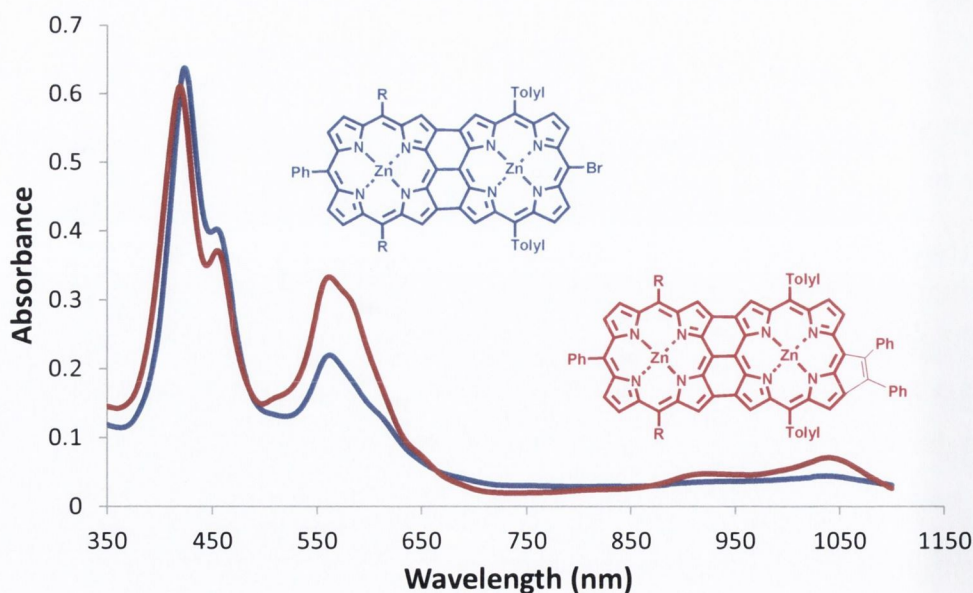
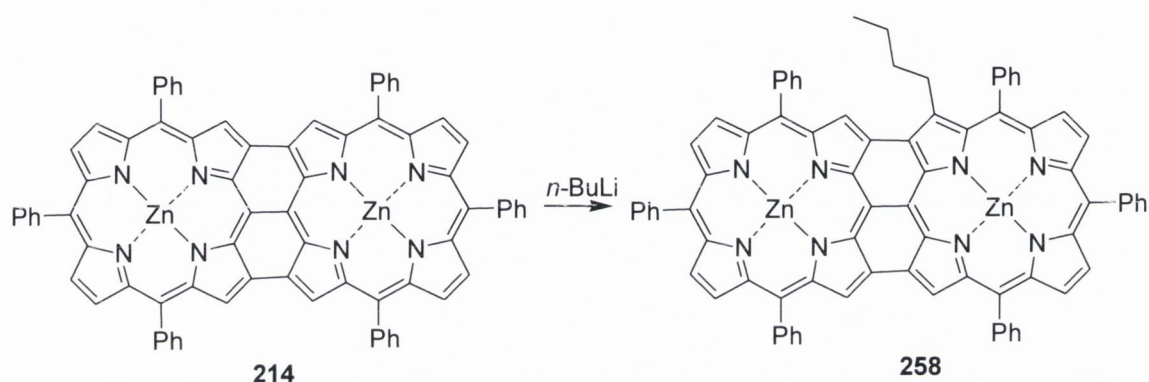


Figure 5.7: UV-vis and NIR spectra of **238** (blue) and **256** (red) in CH_2Cl_2 . ($\text{R} = 1\text{-ethylpropyl}$)

5.5 Organolithium reactions

In further attempts to functionalise the β positions of dimers, a chlorin formation, using organolithium reagents was investigated. Although high yielding for the introduction of meso substituents, the introduction of β substituents via organolithium methods can be quite challenging and low yielding and can result in the formation of chlorins, bacteriochlorins and porphodimethenes, depending on reaction conditions and substrates.^[198, 302]



Scheme 5.9. Synthesis of β -butylated dimer **258** via RLi. *Reagents and conditions:* i) $n\text{-BuLi}$, -78°C , THF, 1 h ii) H_2O , 0.5 h iii) DDQ, 1 h.

Again using TPP as the comparison, it was anticipated that introducing a n -butyl group at the β -position of fused symmetric dimer **214** would generate a fused porphyrin-chlorin dimer **257**. These triply-fused chlorin dimers, again from an optical application viewpoint, should be advantageous as a further enhancement of absorption would be anticipated on generation for the chlorin. Only a few examples of chlorin fused dimers exist but these involved cycloaddition reactions for generation.^[182-183] Adopting a method developed by Senge *et al.*, whereby TPP was monobutylated at the β -position in 17 % yield, the fused dimer **214** was butylated under standard organolithium conditions.^[257, 302] The reaction proceeded well, although, as with all fused dimers, difficulties arose on purification. Dimer **258** was isolated in a yield of 15 %, with the main other component being unreacted starting material **214**. Only trace quantities of the dibutylated dimer were detected.

NMR analysis

The ^1H NMR spectrum of **258** shows the typical chlorin CH_2 peaks around 4.5 ppm, along with the butyl peaks at 4.0, 2.3 and 0.9 ppm. The aromatic region changes dramatically from that of dimer **214**, as there is a disruption to the symmetry, shown in

Figure 5.4, increasing the number of signals observed. Such differences point towards the generation of **258**, the structure of which was confirmed via HRMS. More detailed studies on the functionalisations of fused dimers via organolithium methods, however, are required.

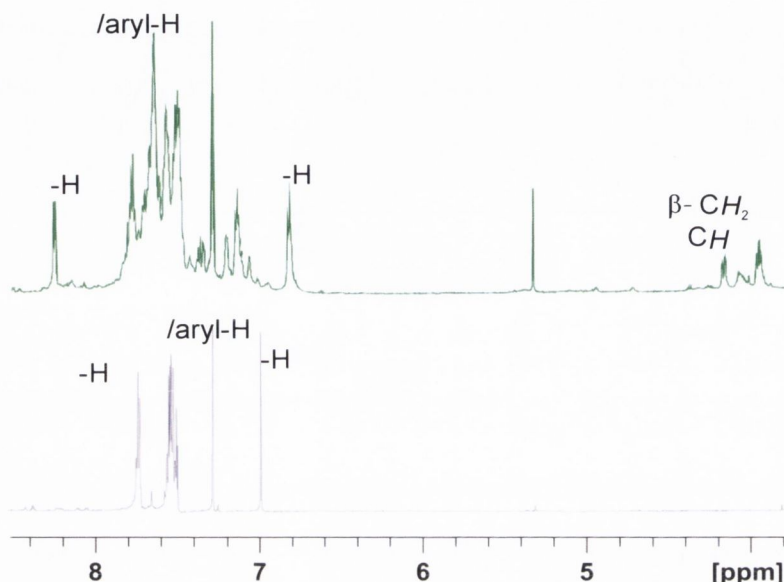


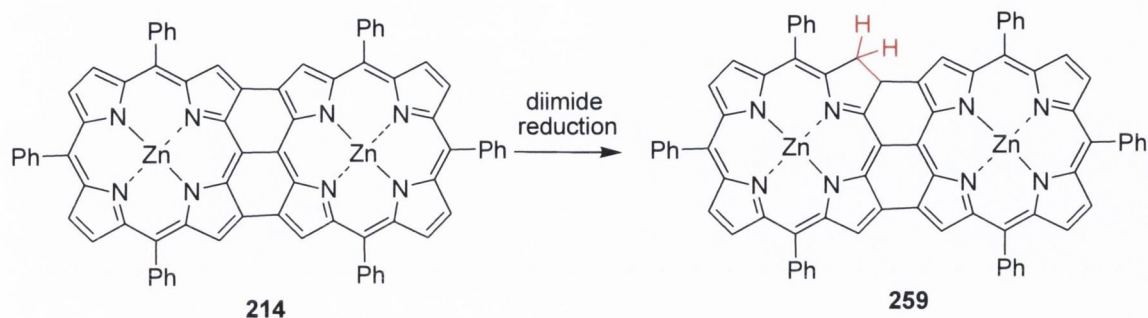
Figure 5.8: Aryl and chlorin regions of ¹H NMR spectra of fused dimer **214** (blue) and chlorin dimer **258** (green) in CDCl₃.

5.6 Diimide reduction

The classic reduction of the porphyrin periphery to generate a chlorin species was also attempted. The diimide reduction of monomeric porphyrins, developed by Whitlock *et al.*, to their respective chlorins and bacteriochlorins, is widely known.^[303-304] Under these reductive conditions, the porphyrin pyrrolic double bond is reduced via diimide, which is generated *in situ*. The diimide species hydrogenates the double bond to generate the chlorin or bacteriochlorin, depending on the quantity of diimide generated. It was envisaged that similar principles could be applied to dimeric porphyrins to generate a novel fused porphyrin-chlorin dimer.

Using conditions, optimised by Senge and co-workers, dimer **214** was subjected to diimide reduction. Using UV/vis/NIR analysis, initial studies show that the reaction was successful as a bathochromic shift of 50 nm, with respect to **214** was observed. This red shift in the absorption profile is to be expected with chlorins, although the absorption profile as a whole almost mimicked that of dimer **214**. Preliminary ¹H NMR analysis

proved inconclusive and thus further investigations into the reduction of fused dimers are necessary.



Scheme 5.10: Diimide reduction of fused dimer **214**. *Reagents and conditions:* Tosyl hydrazine, β -picoline, K_2CO_3 , 120 °C, 20 h.

5.7. Conclusions

Numerous strategies towards the functionalisation of porphyrin arrays were investigated. For directly linked dimers, the reactivity reflects that of monomeric porphyrins with brominations and cycloadditions achievable in high yields. For fused arrays, the reactivity is somewhat diminished due to the poor solubility of the arrays. However, these investigations showed that fused dimers can be functionalised directly, via organolithium reactions, and indirectly via palladium catalysed coupling reactions with pre-installed activators such as bromine. Such post-fusing modifications demonstrate the ability to fine-tune the arrays for optical applications, as there is an enhancement of bathochromic shift, and although further investigations are necessary, preliminary studies are promising. Further research into the diimide reduction reaction is necessary, and this would provide a straightforward route to chlorin fused dimers. By the introduction of more solubilising substituents, an improved reactivity of the bromo-dimers should be observed and this needs to be investigated. Also, via debromination methods, there is a possibility to generate fused dimers bearing free meso positions. Employing organolithium methods, the meso reactivity of fused dimers could be probed.

CHAPTER 6:
Carbazole-linked Porphyrin Dimers as
Organic Light Emitting Diodes
(OLEDs)

6.1 Introduction

Polymers of known chromophoric molecules such as fluorenes, carbazoles and oxadiazoles have proven to be extremely efficient as host matrices in OLED devices due to their high stability and as they are green and blue emitters.^[93-94, 99] For example, the polymeric carbazole, poly(*N*-vinylcarbazole) (PVK)^[102] and polyfluorene (PFO),^[305] have been shown to be highly efficient as a host material in OLEDs and are used in commercial devices. To fine-tune the colour of the OLED, photoluminescent dyes can be doped into the host matrices producing devices.^[306] As porphyrins are highly chromophoric and strongly emissive materials, there is much research into the development of such for use in OLEDs.^[97, 104] Most previous studies on porphyrin-based OLED materials focused on substituted monomeric porphyrin dopants^[107, 307] and whilst these studies are promising, showing significant enhancement of devices, we wanted to open a different approach by constructing porphyrin dimers linked via a carbazole entity followed by the analysis of the properties of such arrays.

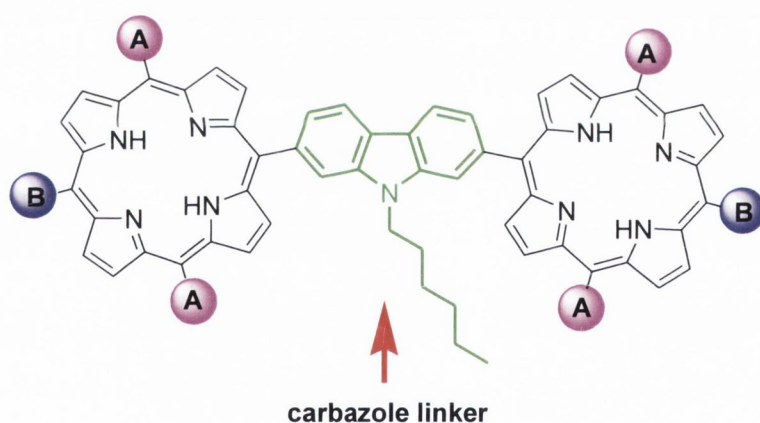


Figure 6.1: Model system for carbazole linked porphyrin dimers.

Published studies have incorporated chromophores such as fluorenes and carbazoles into the porphyrin periphery.^[308-310] Recently, it was shown that polymeric porphyrin-fluorene arrays exhibit a lower turn on voltage in comparison to TPP doped into a PFO matrix.^[311-312] As there is a limit to the scope of dopants into polymeric layers as the porphyrins self-aggregate, an approach of synthesising polymeric-fluorene porphyrins units is attractive.^[313] Following on from the theme of conjugated porphyrin oligomers, our aim was to develop synthetic methods for the introduction of bulky substituents, namely carbazole units, to the porphyrin macrocycle (Figure 6.1). This should reduce self-aggregation and potentially give new materials suitable as substrates in OLEDs. In

addition, we envisaged that the additional porphyrin unit, along with the conduction properties of the carbazole, would act to improve the light emitting properties of OLED devices. Furthermore, if these materials prove promising, there is scope to develop these arrays in a similar fashion to Fei *et al.*^[312] for enhanced optical properties. Here, synthesis of such porphyrins materials using Suzuki type coupling reactions is discussed. Single layer organic light emitting diodes (OLEDs) were created to demonstrate the optical properties of these materials.

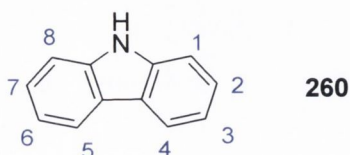


Figure 6.1: Carbazole structure **260** with IUPAC numbering system.

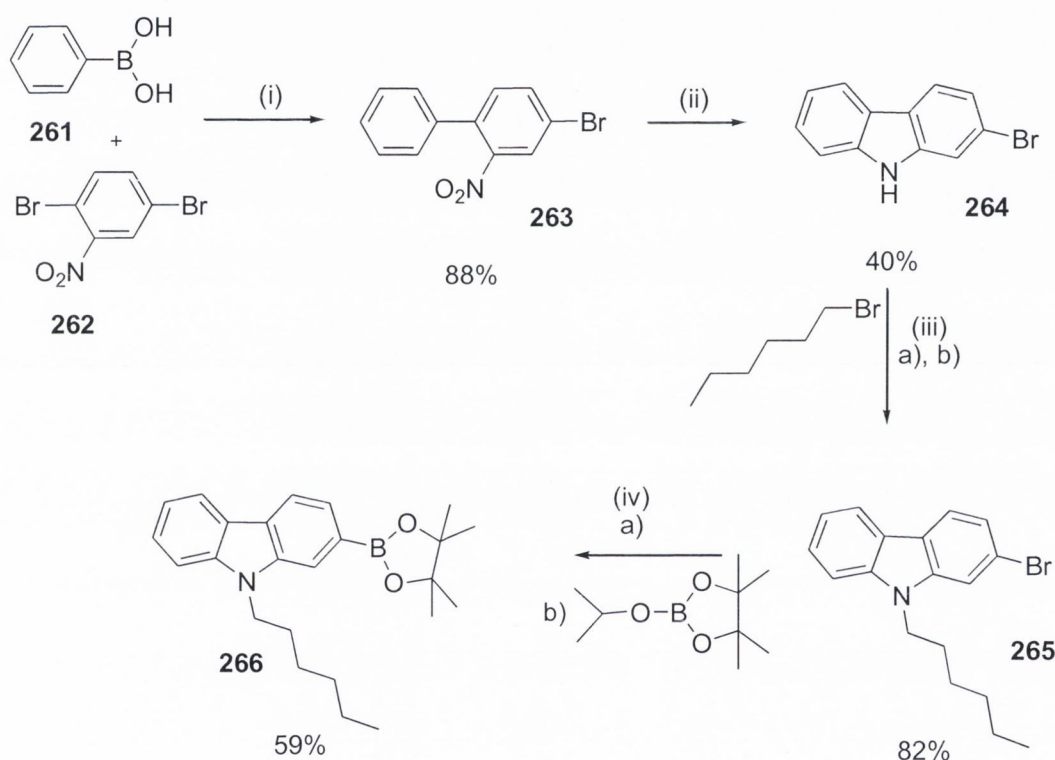
6.2 Synthesis

Carbazole substituted porphyrin monomers and dimers were synthesised with the aim of enhancing the optical properties of the porphyrin. Based on the general applicability of Suzuki-Miyaura reactions^[236, 239] in porphyrin chemistry and our current developments thereof^[40, 314-315] we focused on the coupling of respective bromo and borylated building blocks. Carbazoles are tricyclic aromatic compounds (Figure 6.1) and for our work substitution at the 2- and 7- positions are desirable as the overall target generated will have a better conjugation, unlike the 3-, 6- substituted derivatives.^[316] For their incorporation into the porphyrin periphery they need to be activated at such positions.

6.2.1 Synthesis of carbazole precursors

The synthesis of carbazoles has been extensively explored with numerous methods available to generate such moieties. Substitution at the 3 and 6 positions is easily achieved after generation of the carbazole tricyclic system as these are most reactive enabling almost exclusive bromination at these sites allowing for further modifications.^[317] The synthesis of the desired 2- and 7- substituted carbazoles is not as clear-cut as functional groups cannot be directly inserted to these positions. Thus, prior cyclisation modifications are necessary to activate these positions, with numerous routes available to do so.^[318-320] The strategies employed all involved the generation of biaryl compounds via known coupling methods such as Suzuki-Miyaura^[321] and Ullmann from commercially available starting materials. Subsequent cyclisations to produce the carbazole moiety can be achieved via nitro, amino and azido intermediates.

For the synthesis of monomeric porphyrin-carbazole conjugates, we chose the monoborylated carbazole **266** as the building block. This was synthesised via a procedure developed by Tavasli *et al.*^[322] from phenyl boronic acid **261** and 2,5-dibromonitrobenzene **262**, under Suzuki coupling conditions, to give a 2-bromo-nitrobiphenyl **263** (Scheme 6.1). Subsequent Cadogan carbazole synthesis^[320] via an intramolecular cyclisation using triethyl phosphite, gave carbazole **264**. This method, developed in 1965, is a widely adopted procedure for the generation of carbazoles in moderate yields.

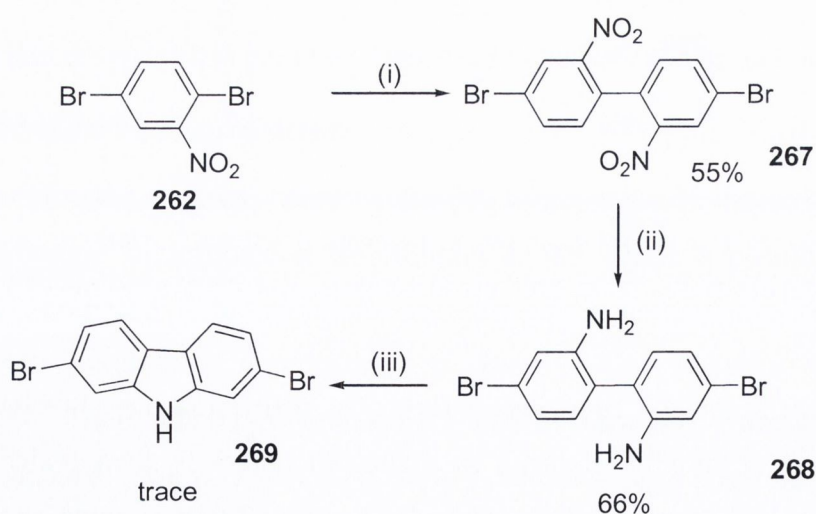


Scheme 6.1. Synthesis of monoborylated carbazole precursors. *Reagents and conditions:* i) Pd(PPh)_3 , Na_2CO_3 , toluene, 90°C , 6 h. ii) $(\text{EtO})_3\text{P}$, 160°C , overnight. iii) a) $t\text{-BuOK}$, DMF, rt, 2 h. b) bromohexane, 130°C , 24 h. iv) a) $n\text{-BuLi}$, -78°C , THF, 3 h. b) 2-Isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane, rt, 24 h.

The mechanism for the ring-closing carbazole generation step involves the overall deoxygenation of the nitro biphenyl via nucleophilic attack by the trivalent phosphorous atom, with the elimination of the phosphine oxide. There is some speculation as to whether or not the cyclisation goes through a nitrene intermediate and generally two plausible mechanistic routes are accepted.^[320, 323] The *N*-ethylated side product of **264** which can form from the presence of triethyl phosphite lowers these yields and methods have been developed whereby this phosphite is substituted with triphenyl phosphine and

yields are improved by up to 20 %.^[323] Other modifications of this Calogan-type synthesis have appeared, one of noteworthy mention involving a microwave assisted carbazole synthesis from the 2-nitro derivative of **260** and an aryl bromide generating biaryls via Suzuki coupling and subsequent cyclisation. This method reduces the extent of protodeboronation, as it has been optimised using a weaker base, observed in aryl residues containing an *ortho* electron withdrawing substituent. Thus, the synthesis of biaryl, 2-substituted carbazoles and other fused heterocycles can be obtained in excellent yields.^[324] The next step in the synthesis is the base-mediated *N*-protection of **264** using bromohexane to give **265** in a yield of 82 %, necessary to eliminate any side reactions at this position later steps of the synthesis. Subsequent borylation under organolithium conditions yielded the borylated carbazole **266** in good yield of 59 %.

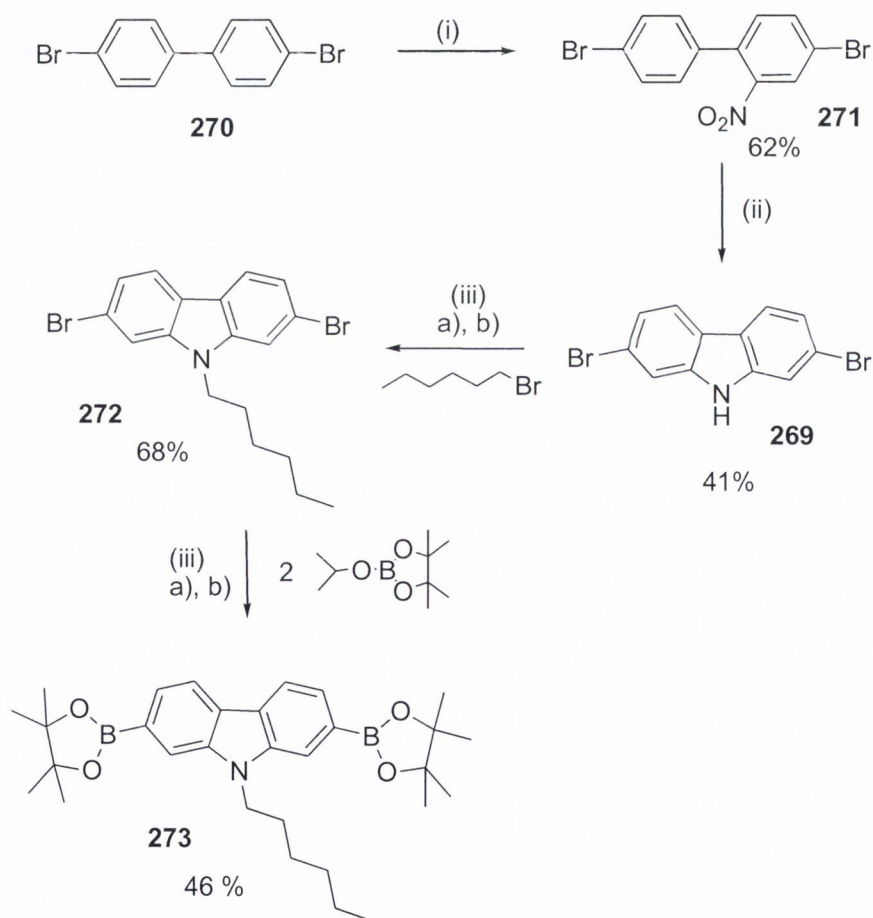
Access to carbazole-linked porphyrin dimers requires a disubstituted carbazole and for the generation of such, an initial strategy was adopted from a procedure developed by Sonntag *et al.*^[325] subjecting 2,5-dibromonitrobenzene **262** to Ullmann coupling using activated copper (Scheme 6.2). This is a useful strategy for the synthesis of symmetrical biaryl compounds and the mechanism involves oxidative addition of copper to aryl halide and this activated species undergoes another oxidative addition with the aryl halide to give the symmetrical biaryl **267** in a yield of 55 %. The nitro groups on **267** were then reduced to bis-amino biaryl **268** in a yield of 66 % under standard reducing conditions.



Scheme 6.2: Synthesis of dibromo carbazole **269** via alternative strategy. *Reagents and conditions:* i) Cu/Zn, DMF, 120 °C, 20 h. ii) Sn, HCl, EtOH, 100 °C, 3 h. iii) H₃PO₄, 190 °C, 24 h.

The subsequent acid catalysed ring closing reaction to form carbazole **269** proved difficult and only trace quantities of the desired carbazole was synthesised. An alternative

strategy was thus needed and it was decided to adopt the Cadogan method, as employed for the generation of mono-substituted carbazole **264** (Scheme 6.1). The strategy followed was that of a procedure by Tang *et al.*,^[326] from the commercially available dibromo-biphenyl **270** as starting material (Scheme 6.3). Nitration was achieved using standard fuming nitric acid conditions, generating **271** in 62 % yield. Intramolecular cyclisation via the Cadogan method gave dibromo-carbazole **269** in a yield of 41 %. Base-mediated *N*-protection using a hexyl group produced **272** in a yield of 68 %, and subsequent diborylation under organolithium conditions to give the desired diborylated carbazole **273** in a yield of 46 % following recrystallisation.

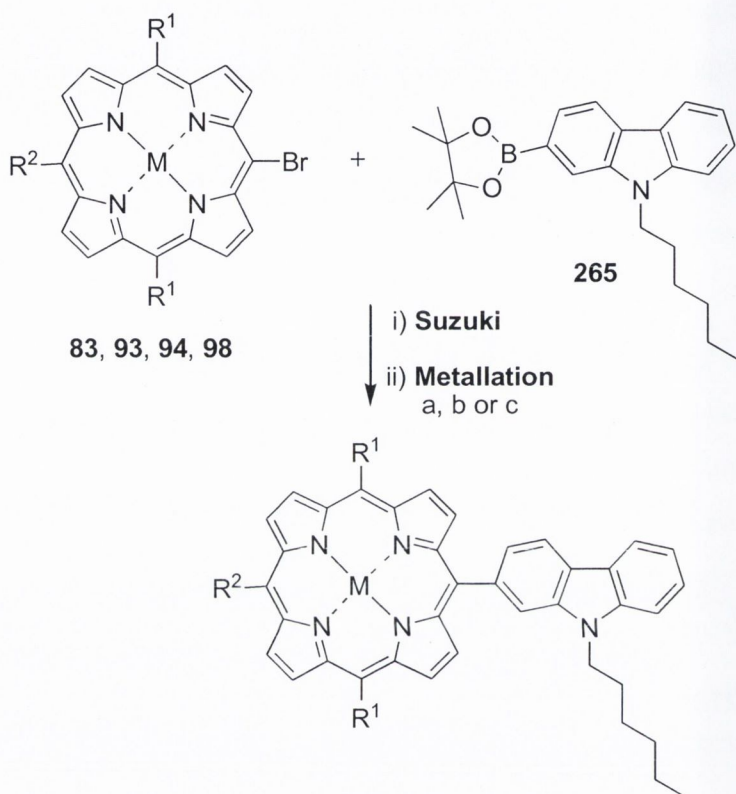


Scheme 6.3: Synthesis of diborylated carbazole precursor **273**. *Reagents and conditions:* i) HNO_3 , AcOH , $120\text{ }^\circ\text{C}$, 20 h. ii) $(\text{EtO})_3\text{P}$, $160\text{ }^\circ\text{C}$, overnight. ii) a) *t*-BuOK, DMF, rt, 2 h. b) bromohexane, $130\text{ }^\circ\text{C}$, 16 h. iii) a) *n*-BuLi, $-78\text{ }^\circ\text{C}$, THF, 3 h. b) 2-isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane, rt, 20 h.

6.2.2 Synthesis of porphyrin-carbazole units

These borylated and brominated carbazole building blocks, **265**, **266**, **272** and **273** were subjected to Suzuki-Miyaura coupling with the desired porphyrins. The general strategy

adopted for the synthesis of monomeric conjugates is shown in Scheme 6.4, whereby borylated carbazole **266** underwent Suzuki coupling with either the monobrominated porphyrins **83**, **93** and **94** or the dibrominated porphyrin **98** yielded the desired monomeric carbazole porphyrin compounds **274**, **275**, **277** and **281** in good coupling yields of 75-85%.

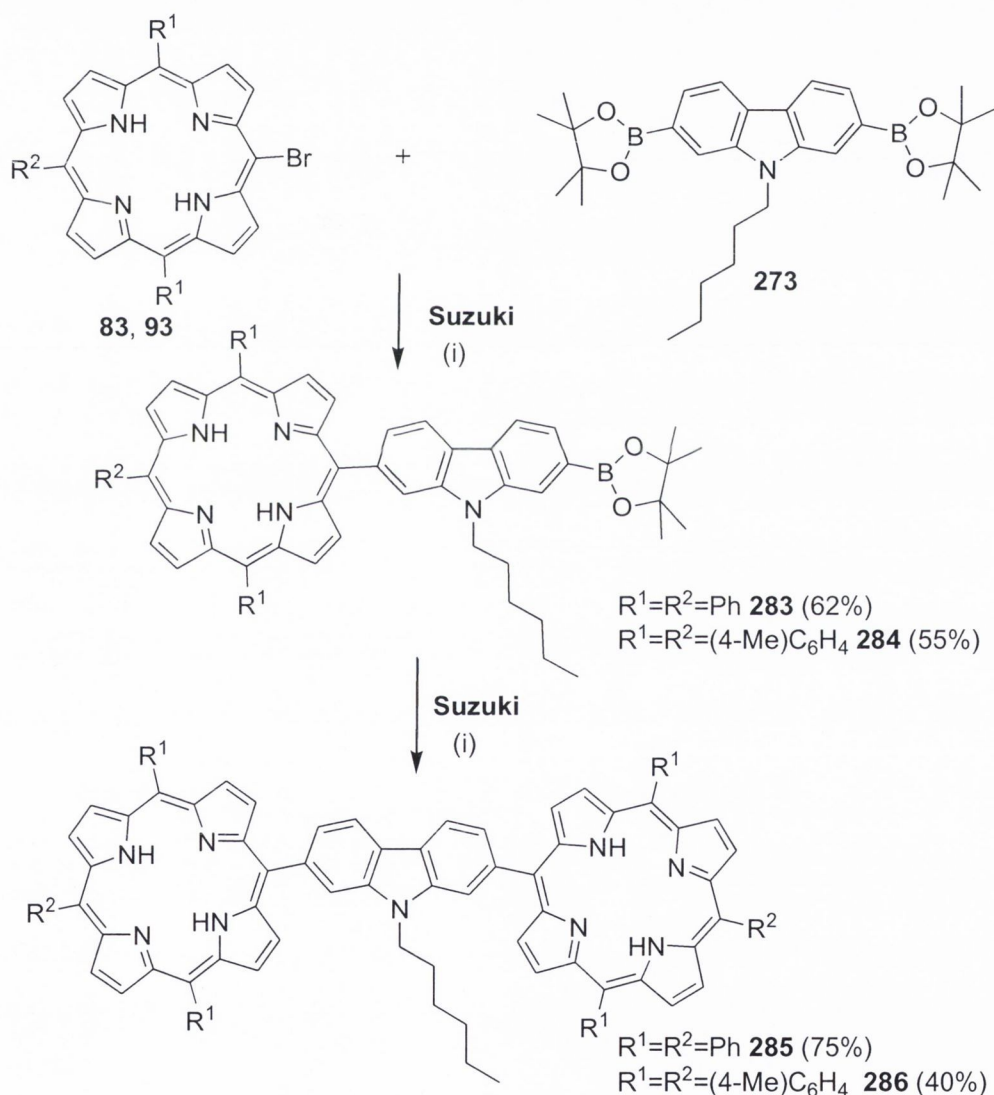


R ¹	R ²	M	#	Yield %
Ph	Ph	2H	274	75
	H	2H	275	61
	Ph	Zn ^{II}	276	74
4-Me-C ₆ H ₄	4-Me-C ₆ H ₄	2H	277	86
		Zn ^{II}	278	81
		Pd ^{II}	279	89
		InCl	280	59
Ph	Carbazole	2H	281	76
		Zn ^{II}	282	81

Scheme 6.4. Synthesis of carbazole porphyrins via Suzuki coupling and metallations. *Reagents and conditions:* i) Borylated carbazole, Pd(PPh₃)₄, THF, K₃PO₄, 67 °C, 16 h. ii) a) Zn(OAc)₂, MeOH, 70 °C, 0.5 h. b) Pd(OAc)₂, toluene, 120 °C, 20 h., c) InCl₃, AcOH, 24 h.

Attempts to execute the reverse strategy, i.e. Suzuki coupling of borylated porphyrin **128** and bromo-carbazole **265**, proved ineffective as the main product isolated was deborylated starting material **128**. In this reaction there is also the possibility of a dimeric directly linked bisporphyrin side product to form (see Section 4.3.2).

Different metals were introduced to the porphyrin core, namely zinc,^[8] palladium^[8, 327] and indium chloride^[328] to improve the optical properties via known procedures. This gave the metallated porphyrins **276**, **278-280** and **282** in moderate to excellent yields ranging from 59 to 89%.



Scheme 6.5. Synthesis of carbazole linked porphyrin dimers **285** and **286**. *Reagents and conditions:* Pd(PPh₃)₄, THF, K₃PO₄, 67 °C, 16-20 h.

For the synthesis of carbazole-linked porphyrin dimers a two-step approach was adopted. The first Suzuki coupling was carried out to attach the borylated carbazole **273** with the desired bromoporphyrin to form the porphyrin carbazoles **283** and **284** in yields of 62%

and 55%, respectively. A second Suzuki coupling of **283** and **284** with the bromoporphyrins **83** or **93** yielded the desired dimers **285** and **286** in yields of 75% and 40%, respectively. We found this two-step Suzuki coupling approach to be more successful than a one-step approach where only trace amounts of dimer was formed, although Therien and coworkers^[239] reported good yields for this one-step method for other species. The main products from this approach were the deborylated porphyrin-carbazoles **274** and **277**, along with starting materials. Also, the reverse strategy was attempted using dibromocarbazole **272** and borylated porphyrin **132**, but this again was unsuccessful, with only trace quantities of desired dimer formed, the main product being deborylated starting material.

6.3 Spectroscopic Studies

6.3.1 NMR analysis

Figure 6.2 shows a ^1H NMR spectral comparative of the aromatic regions of borylated carbazole **266** and porphyrin-carbazole conjugate **274**. The typical signals of a 2-substituted carbazole are reflected in the NMR spectrum of **266**. The most downfield resonances are for H4 and H5, occurring at 8.1 ppm as a multiplet as the signals overlap. A singlet at 7.9 ppm is for H3 and H7, H8 and H6 occur as a triplet, doublet and triplet respectively at 7.55, 7.50 and 7.4 ppm. These signals are typical for 2-mono-substituted carbazoles. On attachment to the porphyrin as shown in **274**, there is a deshielding effect by the porphyrin on all carbazole signals of approximately 0.3 ppm, but the pattern remains the same.

The β -porphyrin signals occur as two doublets and a broad singlet all in the 8.8-8.9 ppm region, differing considerably to the bromo starting material **83**, whereby a downfield doublet is seen at 9.7 ppm, reflecting the protons adjacent the bromo substituent. The aromatic carbazole substituent has a shielding effect on the adjacent β -protons, with respect to **83**, resulting in an upfield shift for these signals. The porphyrin aryl signals resonate at 7.7 and 8.2 ppm, similar to those of **83** (where **83** = 5-bromo-10,15,20-triphenylporphyrin). A similar effect is seen with porphyrin-carbazole dimers **285** and **286**, although being more symmetric only exhibit three carbazole signals.

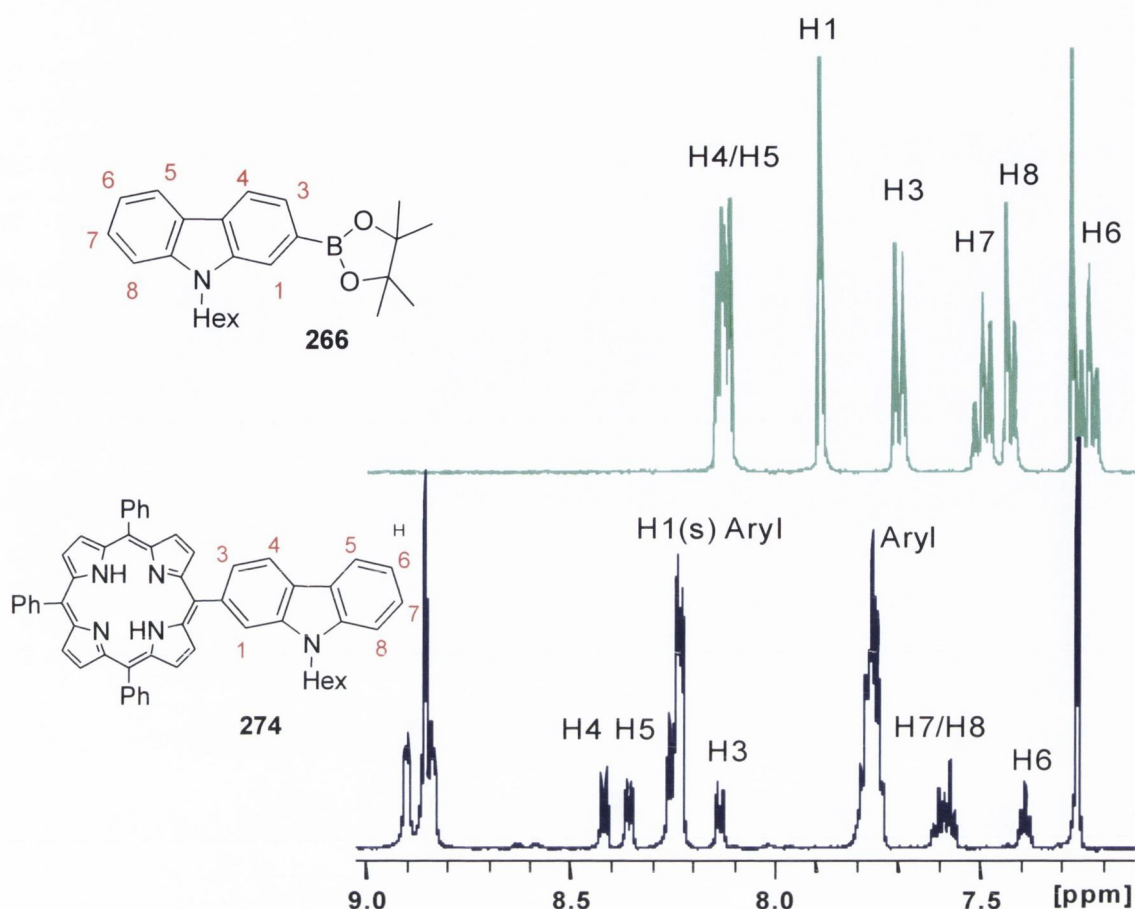


Figure 6.2: ^1H NMR comparison of **274** (blue) and borylated carbazole **266** (green) in CDCl_3

The structure of **282** was proposed by a preliminary X-ray data analysis (Figure 6.3). The molecular structure is characterised by a planar macrocycle with a hexacoordinated zinc center carrying two axial THF molecules and was crystallised from dichloromethane-THF as solvate. As the present crystal quality was insufficient to give a high resolution a recollection of diffraction data with better crystals is necessary for this compound.

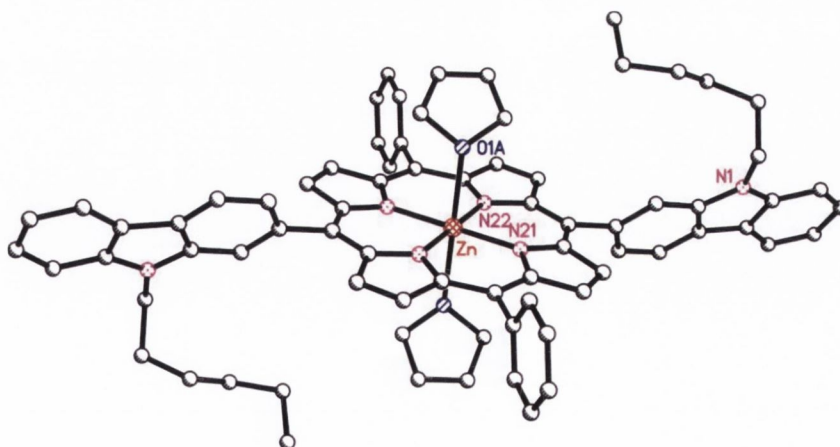


Figure 6.3: X-ray crystal structure of **282**

6.3.2 Photophysical studies

Photophysical studies were carried out on all porphyrin-carbazole monomers and dimers and for comparative purposes on the bromoporphyrin precursors. The dimeric porphyrins **285** and **286** exhibit almost identical UV absorption and emission spectra with regard to their monomeric counterparts. Dimer **286** shows a slight red shift in the Soret and Q band absorptions of 6 and 9 nm, respectively, compared to that of the monomer **277**. Dimer **285** did not display any bathochromic shift, although there was significant broadening of the Soret band with respect to monomer **274** as shown in Figure 6.4. Both dimers exhibited deep-red emission at 659 and 719 nm for **285** and 682 and 722 nm for **286**, also similar to the monomers but showing a higher intensity. This deep red emission is similar to that of other porphyrins developed as OLEDs e.g. porphyrin-fluorene derivatives.^[313]

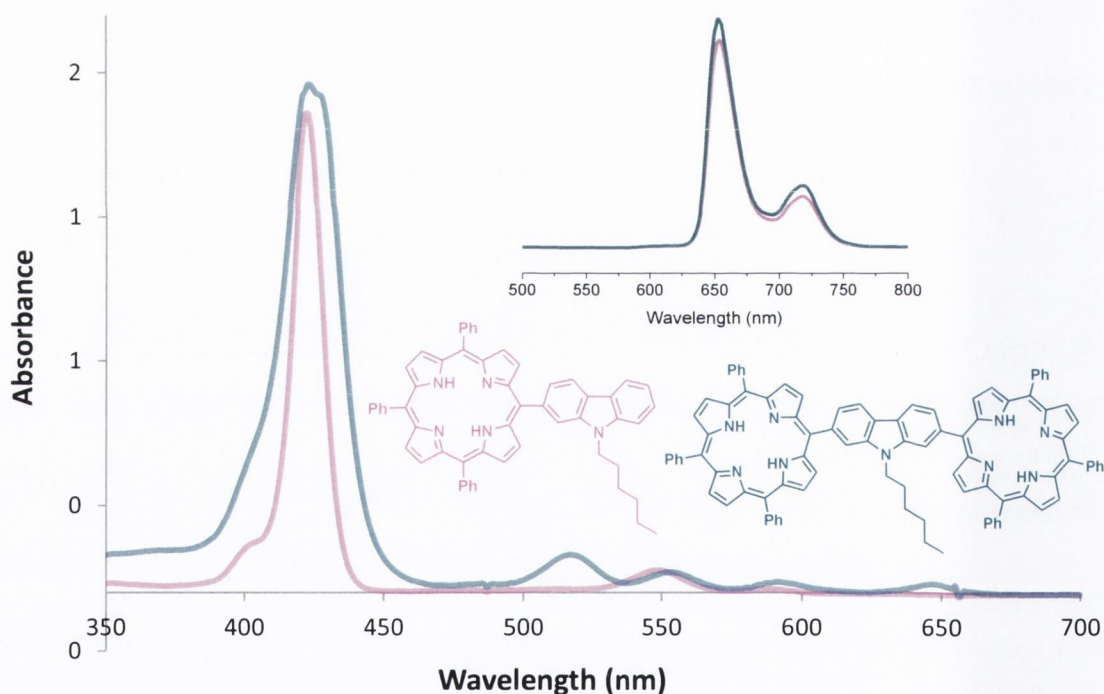


Figure 6.4: UV-vis absorption spectrum of **274** (pink) and **285** (cyan) in CH_2Cl_2 . Inset: Emission spectrum of dimer **285** versus monomer **274**

6.4 OLED studies

OLEDs have a multilayered structure which at its very basic is an organic electroluminescent material in between a cathode and anode (Figure 1.9). When a voltage

is applied to the device, the dye material is put into an excited state, with the emission of light on return to its ground state, a phenomenon known as electroluminescence. Here, the porphyrin-carbazole materials (15 mg/mL toluene solutions) were spin-coated onto photolithography etched indium tin oxide substrates, Aluminium electrodes are then evaporated onto the single layer devices after solvent evaporation. The dicarbazole porphyrins **281** and **282** show improved stability and performance when compared to porphyrins with only one carbazole attached (e.g., **274** and **276**). The OLED results for porphyrin **282** are shown in Figure 6.5. The electroluminescence spectrum shows a red emission centered at 656 nm at a current density of 1.3 mA.mm⁻². All OLED measurements were carried out by Brian Tuffy, under the supervision of Prof. Werner Blau, School of Physics, Trinity College Dublin.

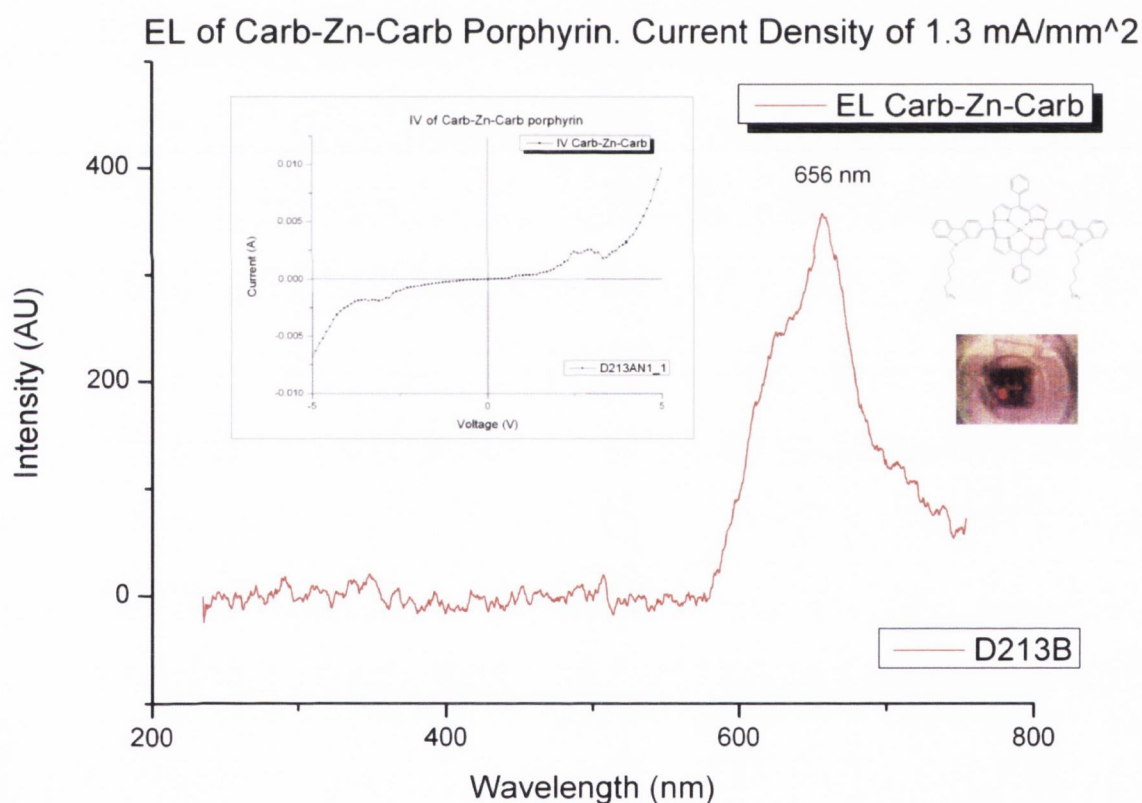


Figure 6.5: Electroluminescence spectrum of **282** with current-voltage plot and working device photo (inset). Current density was 1.3 mA.mm⁻².

The current-voltage plot shows poor rectification but emission was achieved with a low turn-on voltage of 4 V. The chemical structure and a photo of a working device are also inset. Stable emission of red light across the full active area is shown and an estimate of the quantum efficiency was calculated to be 0.02% for this single layer device.

The dimers **285** and **286** were also investigated for their optical properties. Figure 6.6 shows the electroluminescence for dimer **286**, similar to that of **282**, with a red-emission centered at 659 nm, blue-shifted from that of its monomer **277**, which emitted at 677 nm. Unfortunately, the dimers did not exhibit an increase in emission intensity in comparison to the monomers. This is most likely due to the aggregation quenching effect of the neighboring porphyrin unit.

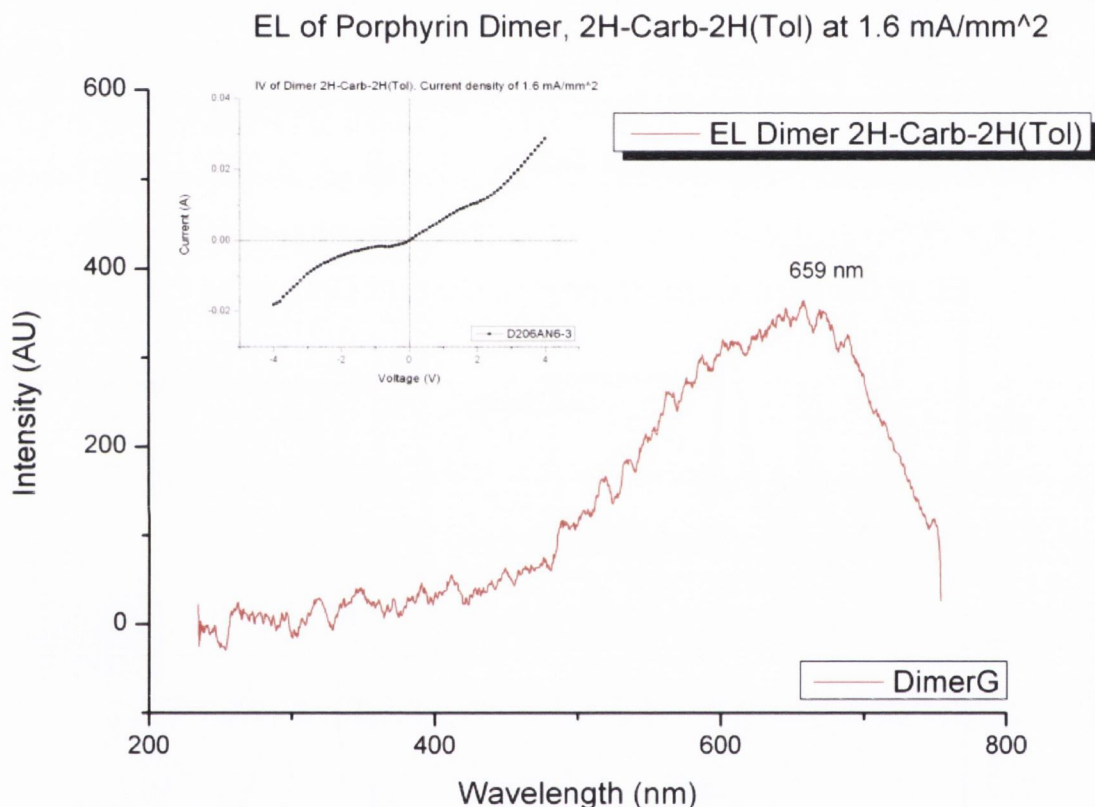


Figure 6.6: Electroluminescence spectrum of **286** with current-voltage plot (inset). Current density was 1.6 mA.mm⁻².

The current-voltage plot inset shows an ohmic dominated response with poor rectification but electroluminescence is observed at as low as 3 V with 1.6 mA.mm⁻². Turn-on voltages for the metallated porphyrins **278**, **279** and **280** were 6V, 3V and 4V, respectively, showing the effect of metal substitution. The free-base porphyrin **277** had a turn-on voltage of 6V.

Material	Absorption (nm)	Emission (nm)	Turn-on (V)	EL
PFO	385	422, 442	13	++
274	422	658, 720	4	+
276	423	615, 656	6	++
277	424	656, 722	6	+
278	422	616, 655	3	+
279	421	611, 652	3	+
280	431	617, 658	4	+
282	424	613, 655	4	++
285	423	659, 719	4	+
286	429	657, 722	3	+

Table 6.1: Summary of the optical properties of carbazole-porphyrin materials.

6.5 Conclusions

A range of porphyrin-carbazole derivatives, both monomeric and dimeric, and their metallated counterparts were synthesised in good coupling yields via a novel synthetic strategy. These compounds all exhibit enhanced photoluminescence, with respect to the unsubstituted porphyrins. These carbazole porphyrins produced OLED devices emitting in the red, with greater emission intensity and stable emission than the bromo substituted porphyrin precursors. The dicarbazole porphyrin shows better results when compared to the single carbazole group demonstrating its enhancement of the emission. The dimer did not show significant enhancement of the emission when compared to the monomer as was thought. This may be due to an aggregation quenching effect from the close proximity of the second porphyrin unit, extra defect sites in the thin film or energy transfer away from the radiative paths. Despite this problem, the dimers exhibit low-turn on voltage and thus good potential for use in OLEDs. Further work on the development of polymeric porphyrin-carbazoles via a similar synthetic strategy should eliminate this aggregation defect and enhance the emissive properties. Also, via the application of the oxidative fusing methods discussed in Chapters 4 and 5, a similar principle could be applied with porphyrin-carbazole conjugates. These novel carbazole-triply fused arrays could act as potential NIR emitters, having OLED applications in areas such as night-vision.

CHAPTER 7:

Experimental

7.1 General considerations and instrumentation:

All commercial chemicals used were of analytical grade, were supplied by Sigma Aldrich, Frontier Scientific, Inc. and Tokyo Chemical Industry (TCI) and used without further purification unless otherwise stated. Anhydrous THF and diethylether distilled over sodium/benzophenone and dichloromethane dried over P_2O_5 were used. 1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (400 MHz for 1H NMR; 100.6 MHz for ^{13}C NMR) and/or Bruker AV 600 (600 MHz for 1H NMR; 150.9 MHz for ^{13}C NMR). Chemical shifts are reported in ppm referred to TMS set at 0.00 ppm. The assignment of signals was confirmed by 2D spectra (COSY, HSQC) except for those porphyrins with low solubility. CHN analyses were not attained.^[329] HRMS spectra were measured on MaldiQ-Tof Premier Micromass and Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray ionisation source (ESI). Melting points were acquired on a Stuart SMP-10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 (fluorescence indicator F₂₅₄;Merck) pre-coated aluminium sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230-400 mesh) and aluminium oxide (neutral, activated with 6.5 % H_2O , Brockmann Grade III). Photophysical measurements were performed in ethylacetate, THF, CH_2Cl_2 and toluene. Fluorescence spectra were recorded on Perkin-Elmer Precisely LS-55 spectrometer. UV-vis absorption measurements were performed with a Shimadzu MultiSpec-1501. Electrical characterisation (current/voltage) was carried out using a Keithley 2400 source meter. Electroluminescence spectra were obtained using an Andor Solis intensified CCD camera coupled with an Oreil Spectrometer.

7.2 Synthesis of porphyrin monomer precursors

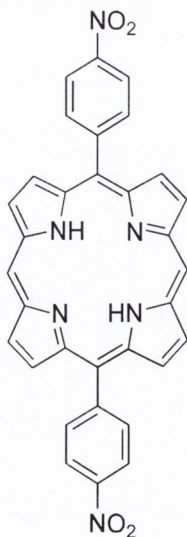
Dipyrromethane **35** was synthesised via standard procedures and spectroscopic data corresponded to that reported in the literature.^[330]

7.2.1 Synthesis of 5,15-disubstituted porphyrins

General Procedure A:

5,15-Disubstituted porphyrins **44-51**^[142, 185-190] were synthesised in accordance with the literature using condensation reactions. The procedure was adapted from Lindsey and co-workers.^[26] Dry CH_2Cl_2 (1800 mL) was placed in a two-litre three-necked round-bottomed flask, equipped with magnetic stirrer, and argon inlet. The flask was shielded from ambient light. Dipyrromethane **35** (3.3 g, 22.3 mmol) and the corresponding aldehyde (24 mmol) were added. The solvent was degassed with a stream of argon for 30 minutes. Trifluoroacetic acid (0.17 mL, 2.3 mmol) was added dropwise to the reaction vessel via a syringe. The reaction was allowed to stir for 3.5 hours under argon at room temperature. DDQ (11.1 g, 49 mmol) was added and the reaction was allowed to stir for 30 minutes open to the air. Triethylamine (12 mL) was added to quench the excess acid catalyst and the mixture was allowed to stir for 1 hour. The mixture was passed through a large silica plug, using CH_2Cl_2 as eluent. The porphyrin containing fractions were collected and solvent was removed *in vacuo*. The dark purple residue was recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to produce purple crystals.

5,15-Bis(4-nitrophenyl)porphyrin (**49**):

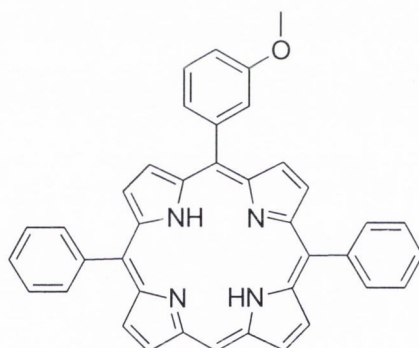


Synthesised according to general procedure A using 4-nitrobenzaldehyde **41** and DPM **35**. Recrystallised from DCM/MeOH to yield **49** (220 mg, 0.399 mmol, 4 %) as a purple solid. M.p. >300 °C; R_f = 0.2 (DCM : ethyl acetate = 10 : 1, v/v); ^1H NMR (600 MHz, $\text{CDCl}_3/\text{d-TFA}$, 10:1): δ = 8.73 (d, $^3J_{\text{H-H}}$ = 8.4 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.92 (d, $^3J_{\text{H-H}}$ = 8.4 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 9.05 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 4H, H_β), 9.63 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 4H, H_β), 11.05 (s, 2H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 107.5, 111.2, 113.1, 114.9, 119.7, 123.5, 129.7, 130.4, 148.1, 143.5, 143.8, 145.0, 149.1, 158.0, 158.3 ppm; UV/vis ($\text{CH}_2\text{Cl}_2/\text{MeOH}$): λ_{max} (log ϵ) = 428 (4.87), 555 (3.11), 594 (3.24), 656 (3.06) nm; HRMS (MS ES+) m/z calcd. for $[\text{C}_{32}\text{H}_{21}\text{N}_6\text{O}_4](\text{M}+\text{H})^+$: 553.1624, found 553.1641.

7.2.2. Synthesis of 5,10,15 trisubstituted porphyrins via organolithium methods

5,10,15-Trisubstituted porphyrins **61-81**^[40, 116, 190, 207-212] were synthesised via methods developed by Senge *et al.* using organolithium reagents and spectroscopic data were in accordance to those reported in the literature.

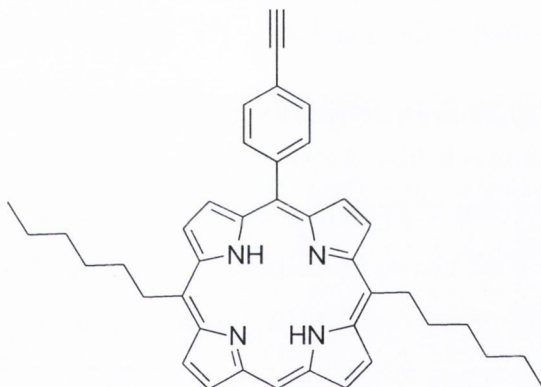
5-(3-Methoxyphenyl)-10,20-diphenylporphyrin (**61**):



n-BuLi (12.97 mmol, 5.2 mL) was added slowly to a cooled (0 °C) solution of 3-bromoanisole (12.97 mmol, 1.64 mL) in freshly distilled diethyl ether (8 mL). After the addition was complete the reaction mixture was allowed to warm to room temperature. This mixture was then transferred to a cooled (-20 °C) solution of 5,15-diphenylporphyrin **44** (1.08 mmol, 500 mg), in freshly distilled THF (20 mL). The suspension was allowed to warm to room temperature and stirred for 19 hours. Water (6 mL) was added carefully and after 30 min DDQ (5.40 mmol, 1.23 g) was added and the mixture allowed to stir for 1.5 h after which time the suspension was passed through a short column of silica gel and the product mixture was eluted with DCM. The solvents were removed under reduced pressure and the residue was purified using silica gel column chromatography (*n*-hexane : CH_2Cl_2 , 1 : 1, v/v) to give purple solid **61** as the

first fraction, with the second fraction containing **81** as a side product (4 %). Solvents removed to yield **61** as a purple solid. Yield: (187 mg, 0.329 mmol, 30%). M.p. >300 °C; $R_f = 0.53$ (CH_2Cl_2 : n -hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.97$ (s, 2H, NH), 4.01 (s, 3H, OCH_3), 7.35-7.38 (m, 1H, C_6H_4 -H), 7.65-7.69 (t, $^3J_{\text{H-H}} = 15.6$ Hz, 1H, C_6H_4 -H), 7.83 (m, 8H, Ph-H), 8.28 (m, 4H, Ph-H), 8.93-8.96 (m, 4H, H_β), 9.04-9.05 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.36-9.38 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β) 10.26 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 13.7, 21.3, 22.2, 28.9, 29.3, 31.1, 31.5, 55.0, 104.4, 113.1, 119.2, 119.7, 120.0, 126.4, 126.9, 127.3, 130.3, 131.0, 134.3, 141.3, 143.4, 146.7, 157.4$ ppm; UV/vis (THF): λ_{max} (log ϵ) = 411 (5.65), 508 (4.20), 541 (3.44), 581 (3.77), 640 (3.50) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{39}\text{H}_{29}\text{N}_4\text{O}](\text{M}^+)$: 568.2263, found 568.2254.

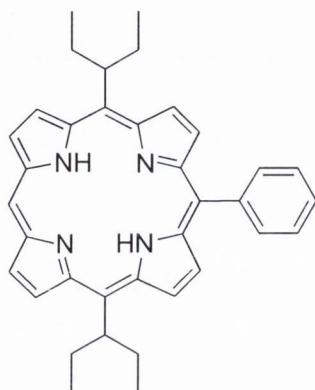
5-(4-Ethynylphenyl)-10,20-dihexylporphyrin (**66**):



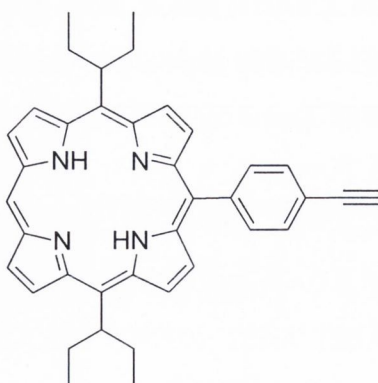
Following the procedure given for **61**, using p -bromophenylethyne (0.91 g, 5.0 mmol), n -BuLi (4 mL of a 2.5M solution in n -hexane, 10 mmol) and 5,15-dihexylporphyrin **45** (200 mg, 0.418 mmol) as the starting material. The desired product was isolated following column chromatography (CH_2Cl_2 : n -hexane, 1 : 6, v/v) to yield two fractions, the first of which was starting material **45** and the second yielding the desired product **66**, which upon recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (72 mg, 0.125 mmol, 30%). M.p. >300 °C; $R_f = 0.57$ (CH_2Cl_2 : n -hexane = 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): $\delta = -2.84$ (s, 2H, NH), 0.96-0.98 (t, $^3J_{\text{H-H}} = 14.9$ Hz, 6H, CH_3), 1.43 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 1.85 (m, 4H, CH_2), 2.55 (m, 4H, CH_2), 3.36 (s, 1H, $\text{C}\equiv\text{CH}$), 5.01 (t, $^3J_{\text{H-H}} = 15.8$ Hz 4H, CH_2), 7.91-7.93 (d, $^3J_{\text{H-H}} = 6.3$ Hz, 2H, C_6H_4 -H), 8.18-8.19 (d, $^3J_{\text{H-H}} = 6.3$ Hz, 2H, C_6H_4 -H), 8.88-8.89 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β), 9.36-9.37 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β), 9.46-9.47 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β), 9.55-9.56 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β), 10.07 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz,

CDCl_3): $\delta = 14.0, 25.6, 29.6, 30.1, 34.8, 38.5, 78.0, 83.7, 118.0, 119.4, 121.3, 127.4, 128.0, 130.1, 131.4, 131.6, 134.2, 143.7, 144.7, 147.2$ ppm; UV/vis (THF): λ_{max} ($\log \epsilon$) = 411 (5.43), 511 (4.12), 542 (3.54), 592 (3.38), 644 (3.19) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{40}\text{H}_{43}\text{N}_4](\text{M}+\text{H})^+$: 579.3488, found 579.3463.

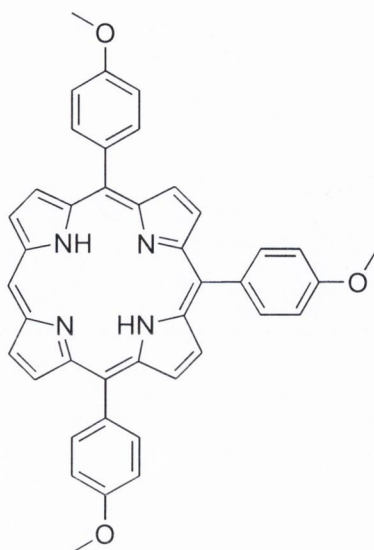
5,15-Bis(1-ethylpropyl)-10-phenylporphyrin (67):



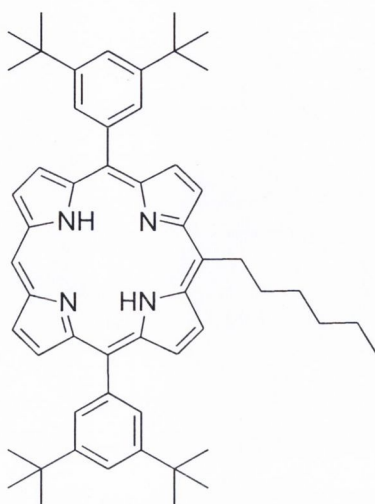
5,15-Bis(1-ethylpropyl)porphyrin **46** (450 mg, 0.998 mmol) was dissolved in THF (40 mL) and cooled to 0 °C. Phenyllithium (1.8 M in hexane, 4.4 mL, 7.9 mmol) was added dropwise over 5 min. After addition, the solution was stirred at room temperature for 30 mins, over which a time the solution turned brown. Saturated NH_4Cl (2 mL) was added and stirring continued for 10 min. DDQ (907 mg, 3.99 mmol) was added and the solution stirred for 45 min. The reaction mixture was then filtered through a plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* and the dark residue was recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give purple crystals. Yield: 422 mg (0.801 mmol, 80%). M.p. >300 °C; $R_f = 0.67$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = -2.45$ (s, 2H, NH), 0.95-0.99 (t, $^3J_{\text{H-H}} = 14.8$ Hz, 12H, CH_3), 2.82 (m, 4H, CH_2), 2.98 (m, 4H, CH_2), 5.05 (m, 2H, CH), 7.77 (m, 3H, Ph-H), 8.22-8.24 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, Ph-H), 8.88 (m, 2H, H_β), 9.40-9.41 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 9.58 (m, 2H, H_β), 9.70-9.73 (m, 2H, H_β), 10.16 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.1, 34.6, 49.9, 103.9, 122.5, 126.6, 127.6, 128.8, 131.7, 131.9, 134.2, 143.8, 146.7, 149.4$ ppm; UV/Vis (EtOAc): λ_{max} ($\log \epsilon$) = 409 (5.34), 509 (4.07), 541 (3.50), 585 (3.43), 641 (3.21) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{36}\text{H}_{39}\text{N}_4](\text{M}+\text{H})^+$: 527.3175, found 527.3175.

5,15-Bis(1-ethylpropyl)-10-(4-ethynylphenyl)porphyrin (68):

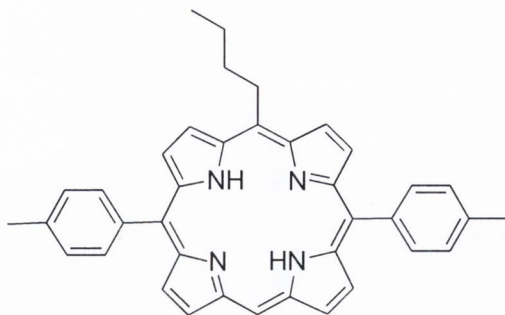
A 100 ml Schlenk flask containing *p*-bromophenylethyne (0.91 g, 5.0 mmol) was dried under high vacuum and purged with argon. Dry diethyl ether (10 mL) was added to this solution and it was cooled to -70 °C. *n*-BuLi (4 mL of a 2.5M solution in *n*-hexane, 10 mmol) was added dropwise to the flask over a period of one hour. The reaction mixture was then warmed to -40 °C and dry THF was added dropwise until a white-pink suspension formed. A solution of 5,15-bis(1-ethylpropyl)porphyrin **46** (200 mg, 0.43 mmol) in dry THF (80 mL) was added rapidly to the vigorously stirred reaction mixture under argon. The reaction was left to stir for approximately 16 hours, forming a brown solution. Saturated NH₄Cl (2 mL) was then added and the solution turned bright green. DDQ was added and the solution turned red and was left to stir for a further one hour. The crude mixture was then filtered through a silica plug using CH₂Cl₂ as eluent. Solvents removed in vacuo and crude residue subjected to column chromatography using CH₂Cl₂ : *n*-hexane (1 : 7, v/v) as eluent. Three fractions were obtained, the first being starting material **46**, the second was the desired product **68**, whilst the third was an inseparable mixture of mono and disubstituted butylated starting material. Recrystallisation of product **68** from CH₂Cl₂/MeOH yielded purple crystals (86 mg, 0.156 mmol, 35%). M.p. >300 °C; *R*_f = 0.47 (CH₂Cl₂ : *n*-hexane = 3 : 2, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.49 (s, 2H, NH), 0.94-0.97 (t, ³*J*_{H-H} = 15.2 Hz, 12H, CH₃), 2.82 (m, 4H, CH₂), 2.97 (m, 4H, CH₂), 3.37 (s, 1H, C≡CH), 5.04 (m, 2H, CH), 7.90-7.92 (d, ³*J*_{H-H} = 7.7 Hz, 2H, C₆H₄-H), 8.19-8.20 (d, ³*J*_{H-H} = 7.7 Hz, 2H, C₆H₄-H), 8.84 (m, 2H, *H*_β), 9.39-9.40 (m, 2H, *H*_β), 9.59-9.60 (m, 2H, *H*_β), 9.69-9.71 (m, 2H, *H*_β), 10.16 (s, 1H, *H*_{meso}) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 13.9, 29.6, 34.4, 49.8, 77.9, 83.7, 121.3, 122.5, 129.9, 131.4, 131.7, 134.0, 144.4 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 410 (5.51), 510 (4.26), 542 (3.70), 588 (3.66), 644 (3.38) nm; HRMS (ESI) *m/z* calcd. for [C₃₈H₃₉N₄](M+H)⁺: 551.3175, found 551.3170.

5,10,15-Tris(4-methoxyphenyl)porphyrin (70):^[212]

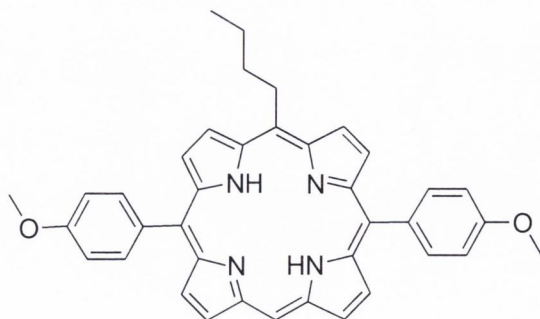
n-BuLi (12.97 mmol, 5.2 mL) was added slowly to a cooled (0 °C) solution of 4-bromoanisole (12.97 mmol, 1.64 mL) in freshly distilled diethyl ether (8 mL). After the addition was complete the reaction mixture was allowed to warm to room temperature. This mixture was then transferred to a cooled (-20 °C) solution of 5,15-bis(4-methoxyphenyl)porphyrin **51** (1.08 mmol, 500 mg), in freshly distilled THF (20 mL). The suspension was allowed to warm to room temperature and stirred for 19 hours. Water (6 mL) was added carefully and after 30 min DDQ (5.40 mmol, 1.23 g) was added. The mixture continued to stir for 1.5 h after which time the suspension was passed through a short column of silica gel and the product mixture was eluted with CH₂Cl₂. The solvents were removed under reduced pressure and the residue was purified using silica gel column chromatography (CH₂Cl₂ : *n*-hexane, 1 : 1, v/v) to give two main fractions, the first of which contained desired product **70** and the second of which yielded butylated side product **80**. Solvents were removed *in vacuo* to give purple solid **70** (187 mg, 0.297 mmol, 31%). M.p. = 220-222 °C; *R*_f = 0.44 (CH₂Cl₂ : *n*-hexane = 2 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS) δ = -2.99 (s, 2H, NH), 4.04 (m, 6H, OCH₃) 4.13 (s, 3H, OCH₃), 7.37-7.39 (d, ³*J*_{H-H} = 8.5 Hz, 2H, C₆H₄-*H*), 7.70 (m, 2H, C₆H₄-*H*), 7.83 (m, 4H, C₆H₄-*H*), 8.14 (m, 4H, C₆H₄-*H*), 8.92-8.93 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 8.96-8.97 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.08-9.09 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.36-9.37 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 10.24 ppm (s, 1H, *H*_{meso}); UV/vis (THF): λ_{max} (log ε) = 413 (5.58), 509 (4.14), 544 (3.50), 585 (3.69), 639 nm (3.54); HRMS (MALDI) *m/z* calcd. for [C₄₁H₃₂O₃N₄](M⁺): 628.2474, found 628.2482. This compound was mentioned by Wojaczyński *et al.* but no experimental data were given.^[212]

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-hexylporphyrin (75):

5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrin **47** (100 mg, 0.145 mmol) was dissolved in THF (40 mL) and cooled to -78°C . *n*-Hexyllithium (2.5 M in hexane, 1.0 mL, 2.5 mmol) was added dropwise over 30 min. After addition, the solution was stirred for 15 min at -78°C before warming to room temperature. $\text{H}_2\text{O} : \text{THF}$ (1 : 1, v/v, 5 mL) was added and stirring continued for 10 min. DDQ (329 mg, 1.45 mmol) was added and the solution stirred for 20 min. All solvents were removed, the brown residue dissolved in CH_2Cl_2 (20 mL) and filtered through a plug of silica. The purple solution was purified by column chromatography (silica, $\text{CH}_2\text{Cl}_2 : n\text{-hexane}$, 1 : 2, v/v) to yield a purple solid. Yield: 84.1 mg (0.109 mmol, 75%). M.p. $>300^{\circ}\text{C}$; $R_f = 0.35$ ($\text{CH}_2\text{Cl}_2 : n\text{-hexane} = 1 : 1$, v/v); $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS): $\delta = -2.91$ (s, 2H, NH), 0.94–1.00 (t, $^3J_{\text{H-H}} = 14.9$ Hz, 3H, CH_3), 1.49 (m, 4H, CH_2), 1.60 (s, 36H, *t*-butyl-*H*), 1.88 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 5.13 (t, $^3J_{\text{H-H}} = 15.9$ Hz, 2H, CH_2), 7.82 (m, 2H, Ar-*H*), 8.14 (m, 4H, Ar-*H*), 9.04–9.08 (dd, $^3J_{\text{H-H}} = 7.2$ Hz, 4.6 Hz, 4H, H_β), 9.30–9.31 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.59–9.60 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 10.13 (s, 1H, H_{meso}) ppm; $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): $\delta = 13.9, 14.0, 30.2, 30.3, 34.9, 35.2, 121.1, 121.3, 128.6, 128.7, 128.9, 129.6, 134.2, 138.9, 140.8, 140.9, 144.0, 145.3, 146.5, 148.6, 148.7, 150.5$ ppm; UV/vis (THF): λ_{max} (log ϵ) = 413 (5.48), 510 (4.04), 544 (3.62), 588 (3.63), 644 (3.70) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{54}\text{H}_{67}\text{N}_4](\text{M}+\text{H})^+$: 771.5366, found 771.5360.

5-(*n*-Butyl)-10,20-bis(4-methylphenyl)porphyrin (77):

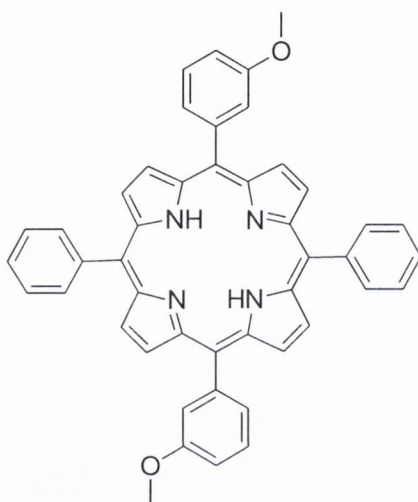
Following the general procedure I, 5,15-bis(4-methylphenyl)porphyrin **48** (245 mg, 0.49 mmol), *n*-BuLi (1.19 mL, 2.99 mmol), H₂O 0.5 mL and DDQ (445 mg, 1.96 mmol) were used. The crude reaction mixture was purified by column chromatography (silica, *n*-hexane : ethyl acetate, 20 : 1, v/v), and gave the desired product (267 mg, 0.44 mmol, 61 %) as purple crystals. M.p. >300 °C; *R_f* = 0.5 (*n*-hexane : ethyl acetate = 20 : 1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 1.18 (t, ³*J*_{H-H} = 14.9 Hz, 3H, CH₃), 1.90 (m, 2H, CH₂), 2.60 (m, 2H, CH₂), 2.80 (s, 6H, tolyl-CH₃), 5.13 (t, ³*J*_{H-H} = 15.3 Hz, 2H, CH₂), 7.65 (d, ³*J*_{H-H} = 7.9 Hz, 4H, C₆H₄-H), 8.14 (d, ³*J*_{H-H} = 7.9 Hz, 4H, C₆H₄-H), 9.08 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H_β*), 9.10 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H_β*), 9.39 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H_β*), 9.69 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H_β*), 10.18 (s, 1H, *H_{meso}*) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 21.3, 23.6, 35.4, 41.0, 104.8, 119.8, 121.7, 127.9, 128.6, 131.1, 131.9, 132.4, 136.8, 139.2, 149.5, 149.6, 149.7, 149.8 ppm; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 415 (5.07), 452 (3.89), 544 (3.53), 580 (3.50), 639 (3.51) nm; HRMS (MALDI) *m/z* calcd. for [C₃₈H₃₄N₄](M⁺): 546.2783, found 546.2774.

5-(*n*-Butyl)-10,20-bis(4-methoxyphenyl)porphyrin (80):

This compound was isolated from the synthesis of **70**. It is a side-product derived from the direct reaction of butyllithium on **51**, to give a purple powder of **80**. Yield (183 mg, 0.316 mmol, 33%). M.p. = 240-242 °C; *R_f* = 0.43 (*n*-hexane : CH₂Cl₂ = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.99 (s, br., 1H, NH), 1.14 (d, ³*J*_{H-H} = 14.9 Hz,

3H, CH_3), 1.87-1.79 (m, 2H, CH_2), 2.59-2.51 (m, 2H, CH_2), 4.13 (s, 6H, OCH_3), 5.14-5.05 (m, 2H, CH_2), 7.32 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.15 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.99 (t, $^3J_{\text{H-H}} = 5.1$ Hz, 4H, H_β), 9.29-9.23 (m, 2H, H_β), 9.57-9.52 (m, 2H, H_β), 10.09 (s, 1H, H_{meso}) ppm; ^{13}C -NMR (150 MHz, CDCl_3): $\delta = 14.1, 22.5, 23.8, 29.9, 31.8, 35.6, 41.1, 55.6, 112.4, 118.8, 134.2, 135.6, 135.7, 159.6$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 414 (5.48), 511 (4.10), 544 (3.49), 583 (3.66), 640 (3.50) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{38}\text{H}_{35}\text{N}_4\text{O}_2](\text{M}+\text{H})^+$: 579.2760, found 579.2751.

5,15-Bis(3-methoxyphenyl)-10,20-diphenylporphyrin (**81**):



Compound **81** was isolated as a tetrasubstituted side product from the organolithium reaction to synthesise **61**, as a purple powder **81** (21 mg, 0.031 mmol, 4%). M.p. >300 °C; $R_f = 0.41$ (CH_2Cl_2 : n -hexane, 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.77$ (s, 2H, NH), 4.01 (s, 6H, OCH_3), 7.34-7.37 (dd, $^3J_{\text{H-H}} = 5.3, 2.3$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.65-7.69 (t, $^3J_{\text{H-H}} = 15.2$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.79 (m, 10H, Ph-H), 8.24-8.25 (d, $^3J_{\text{H-H}} = 5.8$ Hz, 4H, Ph-H), 8.86-8.87 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 4H, H_β), 8.91-8.92 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 55.3, 55.8, 113.6, 115.6, 120.3, 122.2, 122.4, 124.2, 126.5, 127.3, 127.7, 127.8, 128.2, 128.9, 129.8, 131.7, 134.4, 138.8, 139.7, 143.3, 145.8, 145.9, 157.8, 159.1$ ppm; UV/vis (THF): λ_{max} (log ϵ) = 417 (5.41), 513 (4.05), 547 (3.73), 588 (3.71), 647 (3.66) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{46}\text{H}_{34}\text{N}_4\text{O}_2](\text{M}+\text{H})^+$: 675.2760, found 675.2748.

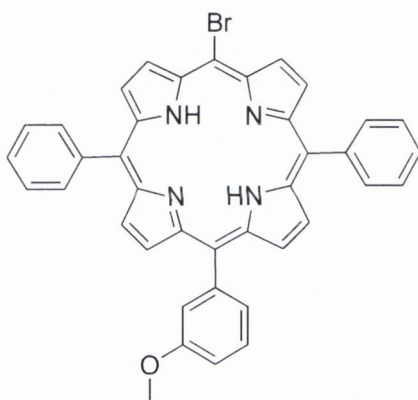
7.2.3 Brominated precursors

Bromoporphyrins **83-85**,^{[222] [223] [211]} **87**,^[210] **93**,^[129] **94**,^[215] **96-102**,^{[218] [216] [217] [224] [220]} were synthesised via methods developed by Boyle and co-workers^[215] and NMR data were in accordance to those reported in the literature.

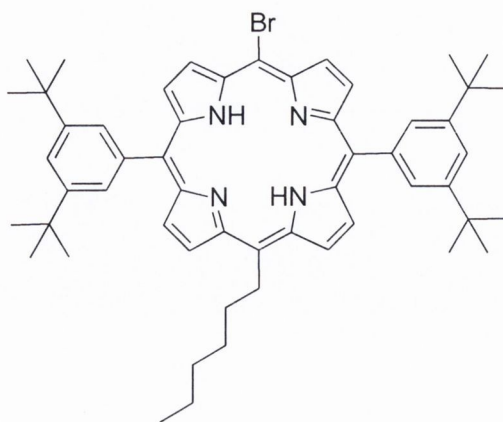
General Procedure B: Bromination

The porphyrin (1 equiv.) was dissolved into CHCl_3 and NBS (0.8 - 2.1 equiv.) and pyridine (0.1 mL) were added. The reaction progression was monitored by TLC using CHCl_3 : *n*-hexane (1 : 1, v/v). The reaction was stopped when all the starting material was consumed. The mixture was then filtered through a silica gel plug and recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

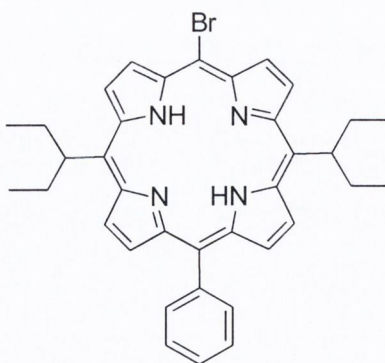
5-Bromo-15-(3-methoxyphenyl)-10,20-diphenylporphyrin (82):



Produced from **61** (100 mg, 0.176 mmol) and NBS (47 mg, 0.263 mmol) in 60 mL CHCl_3 , following general procedure B to give the purple product **82** (110 mg, 97%). M.p. >300 °C; R_f = 0.41 (CH_2Cl_2 : *n*-hexane, 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -2.74 (s, 2H, NH) 4.00 (s, 3H, OCH_3), 7.34-7.36 (m, 1H, $\text{C}_6\text{H}_4\text{-H}$), 7.66 (m, 1H, $\text{C}_6\text{H}_4\text{-H}$) 7.76 (m, 8H, $\text{C}_6\text{H}_4/\text{Ph-H}$), 8.21-8.23 (d, $^3J_{\text{H-H}}$ = 7.5 Hz, 4H, Ph-H), 8.81-8.83 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 8.87-8.88 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 8.92-8.93 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 9.69-9.71 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 55.3, 102.8, 113.5, 120.3, 130.5, 120.6, 126.6, 127.7, 134.4, 141.6, 143.0, 157.9 ppm. UV/vis (THF): λ_{max} (log ϵ) = 419 (5.46), 517 (4.09), 550 (3.81), 595 (3.64), 655 (3.77) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{39}\text{H}_{27}\text{BrON}_4](\text{M}^+)$: 646.1368, found 646.1368.

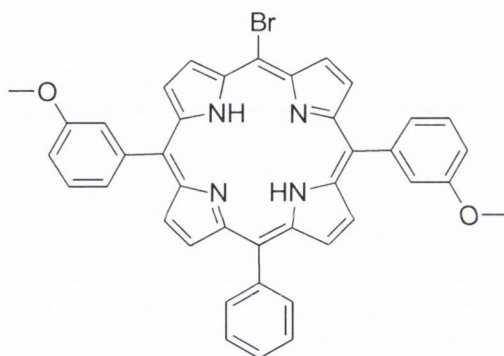
5-Bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-hexylporphyrin (86):

Produced from **75** (75 mg, 0.097 mmol) and NBS (20 mg, 0.112 mmol) in 150 mL CHCl_3 , following the general procedure B. After 50 min the solvent was removed *in vacuo* and the residue purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 2, v/v) to yield a purple solid. Yield: 75 mg (0.088 mmol, 91%). M.p. $>300^\circ\text{C}$; $R_f = 0.53$ (CH_2Cl_2 : *n*-hexane, 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.64$ (s, 2H, NH), 0.94-0.98 (t, $^3J_{\text{H-H}} = 14.5$ Hz, 3H, CH_3), 1.41 (m, 2H, CH_2), 1.57 (s, 36H, *t*-butyl-*H*), 1.66 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 2.57 (m, 2H, CH_2), 4.99 (m, 2H, CH_2), 7.85 (m, 2H, C_6H_3 -*H*), 8.05-8.07 (m, 4H, C_6H_3 -*H*), 8.92 (m, 4H, H_β), 9.46-9.47 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 9.62-9.63 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 13.5, 20.9, 30.2, 34.9, 35.2, 38.7, 101.5, 121.0, 121.3, 121.4, 123.5, 124.7, 127.7, 128.3, 128.6, 128.7, 129.6, 134.2, 138.9, 140.9, 144.0, 146.5, 146.6, 148.6, 150.5$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 421 (5.86), 486 (4.39), 557 (4.52), 659 (4.42) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{54}\text{H}_{66}\text{BrN}_4](\text{M}+\text{H})^+$: 849.4471, found 849.4436.

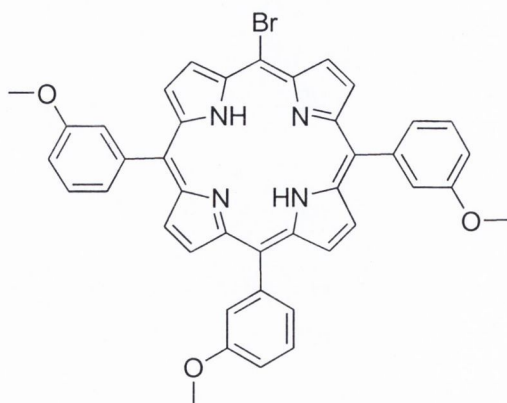
5-Bromo-10,20-bis(1-ethylpropyl)-15-phenylporphyrin (88):

Following the general procedure B, 5,15-bis(1-ethylpropyl)-10-phenylporphyrin **67** (300 mg, 0.570 mmol) and NBS (203 mg, 1.139 mmol) gave 290 mg (0.643 mmol, 84 %) of a purple solid after recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. M.p. $>300^\circ\text{C}$; $R_f = 0.78$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = -2.40$ (s, 2H, *NH*), 0.95-0.98 (t, $^3J_{\text{H-H}} = 14.8$ Hz, 12H, *CH*₃), 2.81 (m, 4H, *CH*₂), 2.93 (m, 4H, *CH*₂), 4.98 (m, 2H, *CH*), 7.78 (m, 3H, *Ph-H*), 8.18-8.19 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, *Ph-H*), 8.79-8.80 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, *H* _{β}), 9.51 (s, 2H, *H* _{β}), 9.64 (s, 2H, *H* _{β}), 9.80-9.82 (d, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, *H* _{β}) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.2, 34.6, 50.1, 123.7, 126.5, 127.7, 128.4, 129.6, 132.0, 132.9, 134.2, 143.0, 148.0$ ppm; UV/vis (EtOAc): λ_{max} (log ϵ) = 417 (5.32), 520 (3.97), 553 (3.68), 602 (3.33), 657 (3.47) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{36}\text{H}_{38}\text{N}_4\text{Br}](\text{M}+\text{H})^+$: 605.2280; found 605.2272.

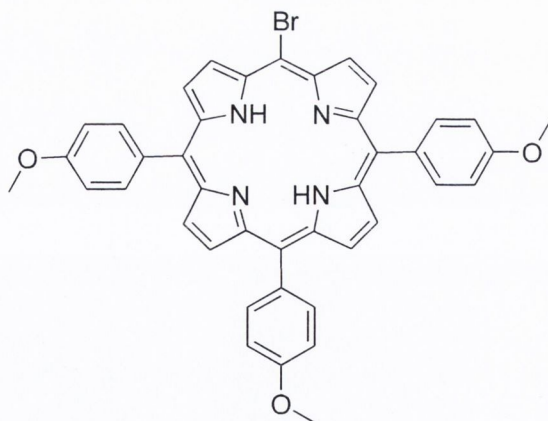
5-Bromo-10,20-bis(3-methoxyphenyl)-15-phenylporphyrin (**89**):



Following the general procedure B, 5,15-bis(3-methoxyphenyl)-10-phenylporphyrin **78** (450 mg, 0.752 mmol) and NBS (268 mg, 1.503 mmol) gave 460 mg (0.678 mmol, 90 %) of a purple solid after recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. M.p. = $260\text{--}263^\circ\text{C}$; $R_f = 0.33$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = -2.73$ (s, 2H, *NH*), 4.03 (s, 6H, *OCH*₃), 7.36-7.39 (dd, $^3J_{\text{H-H}} = 8.3$ Hz, 2.8 Hz, 2H, *C*₆*H*₄-*H*), 7.66-7.71 (t, $^3J_{\text{H-H}} = 15.7$ Hz, 2H, *C*₆*H*₄-*H*), 7.78 (m, 7H, *Ph/C*₆*H*₄-*H*), 8.20-8.21 (d, $^3J_{\text{H-H}} = 6.2$ Hz, 2H, *Ph-H*), 8.82-8.83 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, *H* _{β}), 8.86-8.87 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, *H* _{β}), 8.97-8.98 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, *H* _{β}), 9.86-9.87 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, *H* _{β}) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.5, 102.9, 113.7, 120.5, 126.8, 127.1, 127.6, 127.7, 127.9, 131.6, 134.4, 139.6, 141.8, 143.1, 157.9$ ppm; UV/Vis (EtOAc): λ_{max} (log ϵ) = 418 (5.41), 516 (4.05), 550 (3.69), 596 (3.45), 651 (3.40) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{40}\text{H}_{29}\text{N}_4\text{O}_2\text{Br}](\text{M}^+)$: 676.1474; found 676.1479.

5-Bromo-10,15,20-tris(3-methoxyphenyl)porphyrin (90):

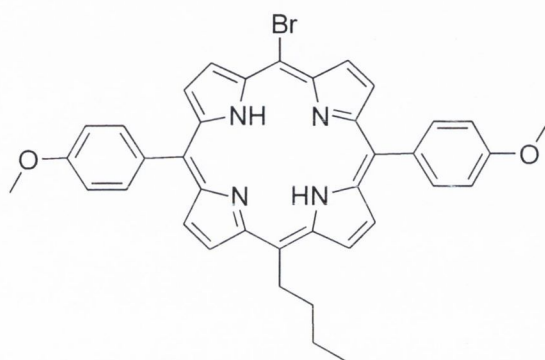
Produced from **69** (157 mg, 0.25 mmol) and NBS (93 mg, 0.52 mmol) following general procedure B. Purple crystals were isolated as **90** (122 mg, 0.172 mmol, 69%). M.p. >300 °C; R_f = 0.45 (CH_2Cl_2 : n -hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -2.75 (s, 2H, NH), 4.00 (s, 3H, OCH_3), 4.02 (s, 6H, OCH_3), 7.36 (m, 4H, C_6H_4 -H), 7.67 (m, 4H, C_6H_4 -H), 7.79 (m, 4H, C_6H_4 -H), 8.86 (s, 4H, H_β), 8.97 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.69 ppm (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 55.4, 55.5, 102.9, 113.6, 113.7, 120.4, 120.5, 120.6, 127.5, 127.6, 127.7, 131.9, 143.1, 143.2, 158.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 421 (5.46), 517 (4.11), 553 (3.76), 595 (3.57), 652 (3.47) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{41}\text{H}_{32}\text{BrN}_4\text{O}_3](\text{M}+\text{H})^+$: 707.1658, found 707.1655.

5-Bromo-10,15,20-tris(4-methoxyphenyl)porphyrin (91):

Following general procedure B, **91** was produced from **70** (164 mg, 0.26 mmol) and NBS (70 mg, 0.39 mmol). Purple crystals were isolated (112 mg, 0.159 mmol, 61%). M.p. >300 °C; R_f = 0.41 (CH_2Cl_2 : n -hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -2.74 (s, 2H, NH), 4.09 (s, 3H, OCH_3), 4.11 (s, 6H, OCH_3), 7.30 (d, $^3J_{\text{H-H}}$ =

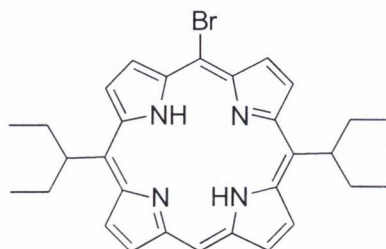
8.6 Hz, 6H, C₆H₄-H), 8.09 (m, 6H, C₆H₄-H), 8.82 (s, 4H, *H*_β), 8.92 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.66 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 55.4, 55.5, 102.4, 112.2, 120.3, 120.7, 120.5, 134.1, 134.2, 135.2, 135.4, 135.5, 159.3, 159.4 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 423 (5.56), 522 (4.20), 556 (4.02), 599 (3.71), 655 (3.81) nm; HRMS (ESI) *m/z* calcd. for [C₄₁H₃₂BrN₄O₃](M⁺): 707.1658, found 707.1671.

5-Bromo-15-(*n*-butyl)-10,20-bis(4-methoxyphenyl)porphyrin (92):



Produced from **80** (79 mg, 0.13 mmol) and NBS (46 mg, 0.26 mmol) using general procedure B. Purple crystals were isolated (50 mg, 0.070 mmol, 55%). M.p. >300 °C; *R*_f = 0.36 (CH₂Cl₂ : *n*-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.70 (s, 2H, NH) 1.12 (t, ³*J*_{H-H} = 15.2 Hz, 3H, CH₃), 1.80 (m, 2H, CH₂), 2.50 (m, 2H, CH₂), 4.12 (s, 6H, OCH₃), 4.97 (m, 2H, CH₂), 7.30 (d, ³*J*_{H-H} = 8.3 Hz, 4H, Ph-H), 8.09 (d, ³*J*_{H-H} = 8.3 Hz, 4H, Ph-H), 8.88 (m, 4H, *H*_β), 9.44 (d, ³*J*_{H-H} = 4.8 Hz, 2H, *H*_β), 9.59 (d, ³*J*_{H-H} = 4.8 Hz, 2H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 14.2, 23.6, 35.3, 40.8, 55.5, 55.6, 101.8, 112.2, 119.9, 121.5, 134.4, 135.4, 135.5, 159.5 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 423 (5.33), 522 (4.01), 557 (3.79), 600 (3.45), 656 (3.57) nm; HRMS (ESI) *m/z* calcd. for [C₃₈H₃₄BrN₄O₂](M+H)⁺: 657.1865, found 657.1854.

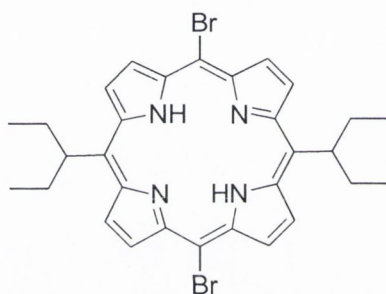
5-Bromo-10,20-bis(1-ethylpropyl)porphyrin (95):



Produced from porphyrin **46** (300 mg, 0.665 mmol) and NBS (95 mg, 0.532 mmol) in 250 mL CHCl₃, following general procedure B. Column chromatography (*n*-hexane :

toluene, 3 : 1, v/v) gave three fractions: starting material **46** first, the second containing the desired target **95** and the third was dibrominated product **101**. Solvents removed to yield a purple product **95** (190 mg, 0.358 mmol, 54%). M.p. >300 °C; R_f = 0.52 (CH_2Cl_2 : n -hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS) δ = -2.48 (s, 2H, NH), 0.96 (t, $^3J_{\text{H-H}}$ = 14.6 Hz, 3H, CH_3), 2.82 (m, 4H, CH_2), 3.05 (m, 4H, CH_2), 5.00 (m, 2H, CH), 9.34-9.35 (d, $^3J_{\text{H-H}}$ = 3.1 Hz, 2H, H_β), 9.66 (m, 4H, H_β), 9.87 (d, $^3J_{\text{H-H}}$ = 3.4 Hz, 4H, H_β), 10.11 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 13.9, 14.0, 34.7, 50.4, 77.2, 124.8, 132.7 ppm; UV/vis: λ_{max} (log ϵ) = 414 (5.44), 514 (4.14), 546 (3.64), 592 (3.54), 648 (3.42) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{30}\text{H}_{34}\text{N}_4\text{Br}](\text{M}+\text{H})^+$: 529.1967, found 529.1967.

5,15-Dibromo-10,20-bis(1-ethylpropyl)porphyrin (**101**):



Produced from porphyrin **46** (300 mg, 0.493 mmol) and NBS (184 mg, 1.036 mmol) following general procedure B, to yield purple the product **101** (356 mg, 0.585 mmol, 88%). M.p. >300 °C; R_f = 0.61 (CH_2Cl_2 : n -hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS) δ = -2.34 (s, 2H, NH), 0.97 (t, $^3J_{\text{H-H}}$ = 15.0 Hz, 12H, CH_3), 2.81 (m, 4H, CH_2), 2.89 (m, 4H, CH_2), 4.92 (m, 2H, CH), 9.57 (m, 4H, H_β), 9.75 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 13.8, 24.4, 34.4, 50.0, 67.0, 124.4, 129.8, 133.1 ppm; UV/vis (THF): λ_{max} (log ϵ) = 422 (5.55), 524 (4.16), 558 (4.05), 606 (3.60), 664 (3.84) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{30}\text{H}_{33}\text{N}_4\text{Br}_2](\text{M}+\text{H})^+$: 607.1072 found 607.1066.

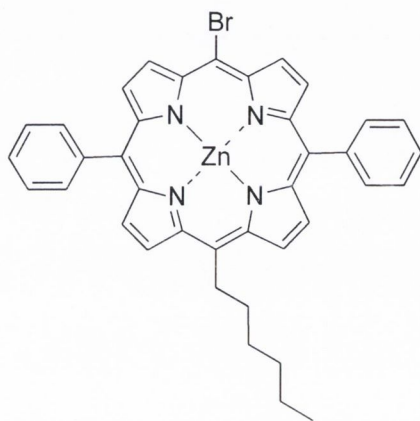
7.2.4 Metallated porphyrins

General procedure C – Zinc(II) insertion:

Porphyrins **103-105**,^[119, 129] **107**,^[216] **109**,^[129] **112**,^[46] **115**,^[40] **116**,^[40] **120**,^[119] **122**,^[187] **123**^[228] were metallated with zinc(II) according to standard procedure and spectroscopic data agreed with that in the literature. Adapting a method by Buchler,^[226] porphyrin (1 equiv.) was dissolved in CHCl_3 (25 - 50 mL) and heated to reflux at 60 °C

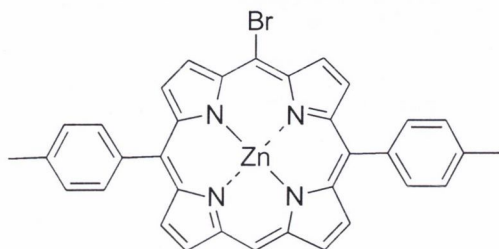
for 10 min. Zinc(II) acetate (5 equiv.) in MeOH (1 mL) was added and the reaction heated under reflux for 30 min. Following reaction completion, solvents were removed *in vacuo* and the residue was redissolved in CH₂Cl₂. This solution was passed through a plug of silica using CH₂Cl₂ as eluent. Solvents were removed *in vacuo* to give a pink/purple solid followed by recrystallisation CH₂Cl₂/MeOH.

{5-Bromo-15-hexyl-10,20-diphenyl-porphyrinato}zinc(II) (106):



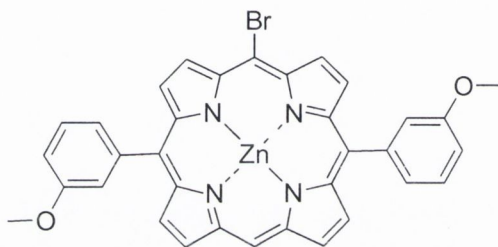
Produced from **84** (100 mg, 0.159 mmol) dissolved in CHCl₃ (25 mL) and zinc(II)acetate (170 mg, 0.795 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (92 mg, 0.133 mmol, 84%). M.p. >300 °C; $R_f = 0.61$ (CH₂Cl₂ : *n*-hexane = 2 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): $\delta = 0.94$ - 0.97 (t, ³*J*_{H-H} = 12.8 Hz, 3H, CH₃), 1.40 (m, 2H, CH₂), 1.51 (m, 2H, CH₂), 1.82 (m, 2H, CH₂), 2.54 (m, 2H, CH₂), 4.98 (m, 2H, CH₂), 7.81 (m, 6H, Ph-*H*), 8.19-8.21 (d, ³*J*_{H-H} = 7.9 Hz, 4H, Ph-*H*), 8.88 (m, 4H, *H*_β), 9.46-9.47 (d, ³*J*_{H-H} = 4.3 Hz, 2H, *H*_β), 9.61-9.62 (d, ³*J*_{H-H} = 4.3 Hz, 2H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): $\delta = 14.2, 22.8, 29.8, 30.4, 31.9, 35.4, 38.9, 120.9, 122.1, 126.6, 127.6, 128.8, 132.3, 132.4, 133.0, 134.5, 142.4, 149.5, 149.6, 149.9$ ppm; UV/vis (CH₂Cl₂): λ_{max} (log ϵ) = 423 (5.33), 557 (3.79), 646 (3.57) nm; HRMS (MALDI) *m/z* calcd. for [C₃₈H₃₁BrN₄Zn](M⁺): 686.1024, found 686.1027.

{5-Bromo-10,20-bis(4-methylphenyl)porphyrinato}zinc(II) (108):

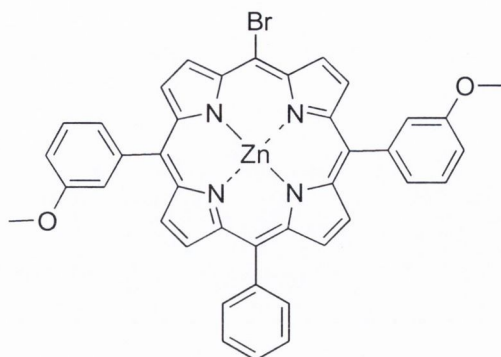


Produced from bromoporphyrin **97** (275 mg, 0.482 mmol) dissolved in CHCl_3 (40 mL) and zinc(II)acetate (200 mg, 0.913 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (280 mg, 0.442 mmol, 92%). M.p. $>300^\circ\text{C}$; $R_f = 0.31$ (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 2.75$ (s, 6H, tolyl- CH_3), 7.57-7.59 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 4H, C_6H_4 -*H*), 8.10-8.12 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 4H, C_6H_4 -*H*), 9.00-9.02 (t, $^3J_{\text{H-H}} = 8.7$ Hz, 4H, H_β), 9.29-9.31 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.74-9.76 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 10.10 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 21.5, 106.1, 120.7, 127.2, 131.7, 134.6, 136.9, 140.1, 149.2, 150.1, 150.5, 150.6$ ppm; UV/vis (EtOAc): λ_{max} ($\log \epsilon$) = 418 (5.47), 552 (4.03), 591 (3.16) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{34}\text{H}_{23}\text{N}_4\text{ZnBr}](\text{M}^+)$: 630.0398; found 630.0387.

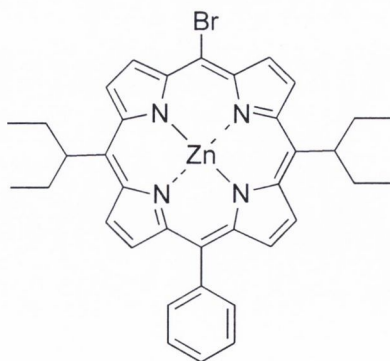
{5-Bromo-10,20-bis(3-methoxyphenyl)porphyrinato}zinc(II) (110**):**



Produced from **96** (490 mg, 0.814 mmol) dissolved in CHCl_3 (60 mL) and zinc(II)acetate (300 mg, 0.137 mmol) dissolved in methanol (3 mL), according to standard procedure C to give a purple solid (350 mg, 0.526 mmol, 65%). M.p. = 272-275 $^\circ\text{C}$; $R_f = 0.40$ (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^1H NMR (400 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$, 20 : 1): $\delta = 3.99$ (s, 6H, OCH_3), 7.32-7.35 (dd, $^3J_{\text{H-H}} = 8.3$ Hz, 2.7 Hz, 2H, C_6H_4 -*H*), 7.62-7.66 (t, $^3J_{\text{H-H}} = 15.1$ Hz, 2H, C_6H_4 -*H*), 7.79 (m, 4H, C_6H_4 -*H*), 9.02 (m, 4H, H_β), 9.26-9.28 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 9.74-9.75 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 10.09 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$ 20:1): $\delta = 55.4, 104.3, 106.2, 112.9, 113.0, 120.4, 120.8, 127.2, 127.9, 131.8, 132.5, 132.6, 132.8, 144.4, 149.3, 150.2, 150.3, 157.8$ ppm; UV/vis (EtOAc): λ_{max} ($\log \epsilon$) = 417 (5.37), 550 (3.98), 592 (3.14) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{34}\text{H}_{23}\text{N}_4\text{O}_2\text{ZnBr}](\text{M}^+)$: 662.0296; found 662.0311.

{5-Bromo-10,20-bis(3-methoxyphenyl)-15-phenylporphyrinato}zinc(II) (111):

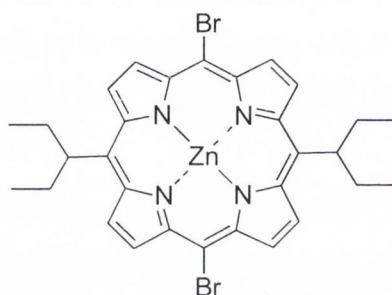
Produced from bromoporphyrin **89** (300 mg, 0.442 mmol) dissolved in CHCl_3 (40 mL) and zinc(II)acetate (250 mg, 1.141 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (245 mg, 0.331 mmol, 75%). M.p. = 261–263 °C; R_f = 0.42 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): δ = 4.01 (s, 6H, OCH_3), 7.33–7.35 (dd, $^3J_{\text{H-H}}$ = 8.7 Hz, 2.0 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.62–7.66 (t, $^3J_{\text{H-H}}$ = 15.3 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.74 (m, 7H, $\text{Ph/C}_6\text{H}_4\text{-H}$), 8.17–8.18 (d, $^3J_{\text{H-H}}$ = 6.5 Hz, 2H, Ph-H), 8.83–8.84 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 8.88–8.89 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 8.98–8.99 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.71–9.72 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$, 10:1): δ = 53.4, 55.8, 103.9, 113.0, 120.6, 120.9, 121.4, 126.3, 127.1, 127.3, 127.8, 134.4, 135.2, 143.2, 144.5, 148.3, 148.8, 149.6, 157.7 ppm; UV/vis (EtOAc): λ_{max} (log ϵ) = 423 (5.71), 558 (4.24), 598 (3.72) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{40}\text{H}_{27}\text{N}_4\text{O}_2\text{ZnBr}](\text{M}^+)$: 738.0609; found 738.0606.

{5-Bromo-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (113):

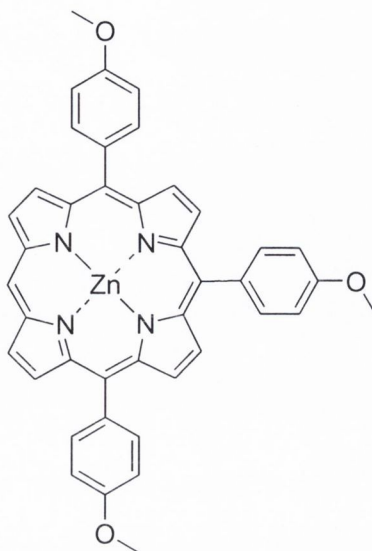
Produced from **88** (300 mg, 0.495 mmol) dissolved in CHCl_3 (40 mL) and zinc(II)acetate (250 mg, 1.142 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (260 mg, 0.389 mmol, 79%). M.p. >300 °C;

$R_f = 0.57$ ($\text{CH}_2\text{Cl}_2 : n\text{-hexane} = 1 : 1$, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 0.90\text{--}0.93$ (t, $^3J_{\text{H-H}} = 14.7$ Hz, 12H, CH_3), 2.81 (m, 4H, CH_2), 2.98 (m, 4H, CH_2), 5.12 (m, 2H, CH), 7.75 (m, 3H, Ph-H), 8.16–8.18 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, Ph-H), 8.84 (s, 2H, H_β), 9.62 (s, 2H, H_β), 9.75 (m, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.2$, 35.0, 50.5, 122.6, 122.8, 123.0, 123.8, 126.2, 127.2, 129.6, 130.0, 130.5, 131.7, 132.3, 134.3, 143.9, 147.4, 149.7, 152.6 ppm; UV/vis (EtOAc): λ_{max} ($\log \epsilon$) = 423 (5.65), 561 (4.15), 605 (3.85) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{36}\text{H}_{35}\text{N}_4\text{ZnBr}](\text{M}^+)$: 666.1337; found 666.1312.

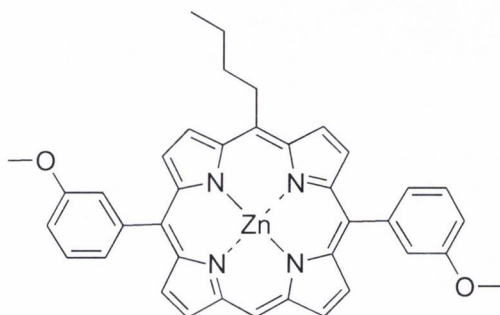
5,15-Dibromo-10,20-bis(1-ethylpropyl)porphyrinato}zinc(II) (114):



Produced from porphyrin **101** (200 mg, 0.329 mmol) dissolved in CHCl_3 (40 mL) and $\text{Zn}(\text{OAc})_2$ (301 mg, 1.645 mmol), following general procedure C to yield pink crystals (194 mg, 0.289 mmol, 88%). M.p. >300 °C; $R_f = 0.39$ ($\text{CHCl}_3 : n\text{-hexane} = 1 : 1$, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 0.93$ (t, $^3J_{\text{H-H}} = 14.8$ Hz, 12H, CH_3), 2.81 (m, 4H, CH_2), 2.96 (m, 4H, CH_2), 5.06 (m, 2H, CH), 9.57 (m, 4H, H_β), 9.69 (m, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 13.9$, 34.4, 50.4, 77.2, 124.8, 131.2, 132.7 ppm; UV/vis (THF): λ_{max} ($\log \epsilon$) = 428 (5.58), 566 (4.02), 614 (3.94) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{30}\text{H}_{30}\text{N}_4\text{ZnBr}_2](\text{M}^+)$: 668.0129, found 668.0136.

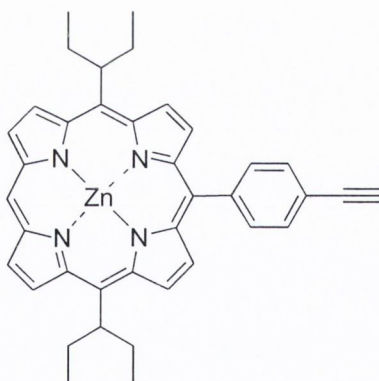
{5,10,15-Tris(4-methoxyphenyl)porphyrinato}zinc(II) (119):

Produced from **70** (80 mg, 0.127 mmol) dissolved in CHCl_3 (25 mL) and zinc(II)acetate (80 mg, 0.365 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (82 mg, 0.119 mmol, 94%). M.p. = 162-165 °C; R_f = 0.17 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 3.99 (s, 6H, OCH_3), 4.09 (s, 3H, OCH_3), 7.27 (s, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.33-7.36 (dd, $^3J_{\text{H-H}} = 2.2$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.66-7.70 (t, $^3J_{\text{H-H}} = 15.7$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.81 (s, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.85-7.87 (d, $^3J_{\text{H-H}} = 7.4$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.13-8.15 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 9.02-9.03 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.05-9.06 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.14-9.15 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.39-9.40 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 10.23 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 55.5, 55.6, 105.8, 112.0, 113.4, 120.3, 120.4, 127.4, 127.7, 131.7, 131.8, 132.1, 132.6, 135.4, 144.1, 149.9, 150.0, 150.2, 157.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 415 (5.27), 543 (4.09), 579 (3.50) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{41}\text{H}_{30}\text{N}_4\text{O}_3\text{Zn}](\text{M}^+)$: 690.1609; found 690.1629.

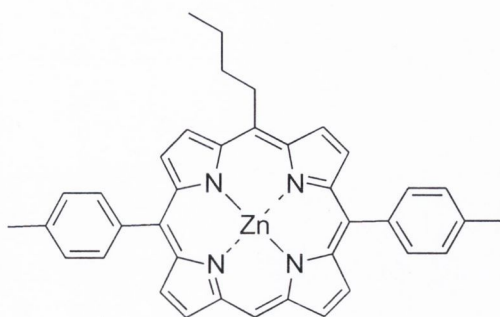
{5-(*n*-Butyl)-10,20-bis(3-methoxyphenyl)porphyrinato}zinc(II) (120):

Produced from **79** (30 mg, 0.052 mmol) dissolved in CHCl_3 (25 mL) and zinc(II)acetate (30 mg, 0.137 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (29 mg, 0.046 mmol, 88%). M.p. = 191-194 °C; R_f = 0.37 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 1.16-1.20 (t, $^3J_{\text{H-H}}$ = 14.8 Hz, 3H, CH_3), 1.90 (m, 2H, CH_2), 2.61 (m, 2H, CH_2), 4.02 (s, 6H, OCH_3), 2.64 (s, 12H, tolyl- CH_3), 5.09-5.14 (t, $^3J_{\text{H-H}}$ = 16.1 Hz, 2H, CH_2), 7.36-7.37 (dd, $^3J_{\text{H-H}}$ = 3.2, 1.8 Hz, 1H, $\text{C}_6\text{H}_4\text{-H}$), 7.38-7.39 (dd, $^3J_{\text{H-H}}$ = 3.2, 1.8 Hz, 1H, $\text{C}_6\text{H}_4\text{-H}$), 7.66-7.71 (t, $^3J_{\text{H-H}}$ = 15.7 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.81 (m, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.87 (m, 2H, $\text{C}_6\text{H}_4\text{-H}$), 9.09-9.13 (q, $^3J_{\text{H-H}}$ = 11.6, 4.7 Hz, 4H, H_β), 9.34-9.35 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.64-9.65 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 10.14 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 14.3, 23.8, 35.7, 41.3, 55.5, 105.2, 113.4, 119.7, 120.4, 122.1, 127.3, 127.6, 128.9, 131.5, 132.1, 132.6, 144.2, 149.5, 149.7, 150.1, 157.9 ppm; UV/vis (EtOAc): λ_{max} (log ϵ) = 416 (5.56), 550 (4.14), 589 (3.30) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{38}\text{H}_{32}\text{N}_4\text{O}_2\text{Zn}](\text{M}^+)$: 640.1817; found 640.1849.

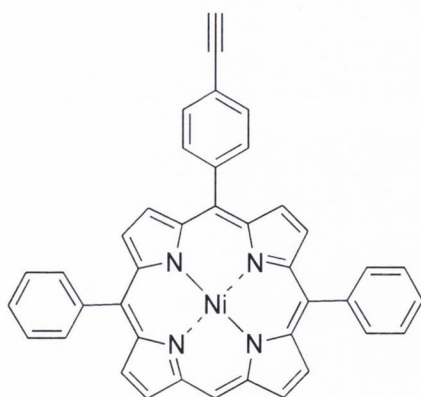
{5,15-Bis(1-ethylpropyl)-10-(4-ethynylphenyl)porphyrinato}zinc(II) (121**):**



Produced from porphyrin **68** (100 mg, 0.181 mmol) dissolved in CHCl_3 and $\text{Zn}(\text{OAc})_2$ (166 mg, 0.907 mmol), following standard procedure C to yield purple crystals (90 mg, 0.147 mmol, 81%). M.p. >300 °C; R_f = 0.43 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.98-1.02 (t, $^3J_{\text{H-H}}$ = 14.6 Hz, 12H, CH_3), 2.88 (m, 4H, CH_2), 3.05 (m, 4H, CH_2), 3.37 (s, 1H, $\text{C}\equiv\text{CH}$), 5.21 (m, 2H, CH), 7.94-7.96 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.24-8.26 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 9.01-9.03 (m, 2H, H_β), 9.37 (m, 2H, H_β), 9.85 (m, 4H, H_β), 10.19 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.2, 29.7, 34.9, 50.5, 77.2, 77.8, 86.5, 123.0, 131.0, 131.3, 131.5, 134.3 ppm; UV/vis (THF): λ_{max} (log ϵ) = 420 (5.73), 554 (4.31), 594 (3.64) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{38}\text{H}_{37}\text{N}_4\text{Zn}](\text{M}+\text{H})^+$: 613.2310, found 613.2297.

{5-(*n*-Butyl-10,20-bis(4-methylphenyl)porphyrinato}zinc(II) (124):

Produced from **77** (150 mg, 0.259 mmol) dissolved in CHCl_3 (25 mL) and zinc(II)acetate (150 mg, 0.685 mmol) dissolved in methanol (2 mL), according to standard procedure C to give a purple solid (148 mg, 0.243 mmol, 94%). M.p. = 284 °C; R_f = 0.33 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 1.14-1.18 (t, $^3J_{\text{H-H}}$ = 14.7 Hz, 3H, CH_3), 1.88 (m, 2H, CH_2), 2.77 (s, 6H, $\text{C}_6\text{H}_4\text{-CH}_3$), 5.07-5.10 (t, $^3J_{\text{H-H}}$ = 15.9 Hz, 2H, CH_2), 7.60-7.62 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.12-8.14 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 9.07 (m, 4H, H_β), 9.30-9.31 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 2H, H_β), 9.61-9.62 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 10.09 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.3, 21.6, 23.8, 35.7, 41.3, 105.0, 119.9, 121.9, 127.3, 128.7, 131.3, 132.1, 132.5, 134.5, 137.0, 140.1, 149.7, 149.8, 1149.9, 150.0 ppm; UV/vis (EtOAc): λ_{max} (log ϵ) = 416 (5.61), 550 (4.18), 590 (3.54) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{38}\text{H}_{32}\text{N}_4\text{Zn}](\text{M}^+)$: 608.1918; found 608.1938.

{5-(4-Ethynylphenyl)-10,20-diphenylporphyrinato}nickel(II) (125):

Porphyrin **62** (100 mg, 0.178 mmol) and $\text{Ni}(\text{acac})_2$ (49 mg, 0.191 mmol) were dissolved in toluene (75 mL) in a 100 mL flask and heated at reflux for 3 hours. The solvent was then removed *in vacuo* and product isolated after filtering the redissolved residue through a plug of silica gel using CH_2Cl_2 as eluent. Recrystallisation of the product

using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ yielded red-purple crystals (199 mg, 90%). M.p. $>300\text{ }^\circ\text{C}$; $R_f = 0.53$ ($\text{CH}_2\text{Cl}_2 : n\text{-hexane} = 1 : 1$, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 3.31$ (s, 1H, $\text{C}\equiv\text{CH}$), 7.74 (m, 6H, Ph-*H*), 7.83-7.85 (d, $^3J_{\text{H-H}} = 7.9$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.01-8.03 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.05-8.07 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 2H, Ph-*H*), 8.77-8.78 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 8.82-8.83 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 8.91-8.92 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 9.15-9.16 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 9.85 (s, 1H, H_{meso}) ppm; ^{13}C -NMR (150 MHz, CDCl_3): $\delta = 83.4, 104.6, 118.2, 121.5, 126.7, 127.6, 130.5, 131.6, 132.1, 132.3, 132.5, 133.5, 140.7, 141.6, 141.9, 142.7, 142.8$ ppm; UV/vis (THF): λ_{max} (log ϵ) = 407 (5.46), 521 (4.29), 557 (3.60) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{40}\text{H}_{24}\text{N}_4\text{Ni}](\text{M}^+)$: 618.1354, found 618.1380.

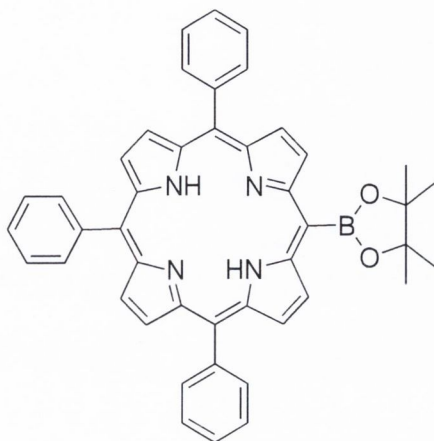
7.2.5 Borylation

Porphyrins **128**,^[240] **129**,^[219] **130**,^[241] **132**^[242] and **133**^[239] were borylated according to standard procedures and spectroscopic data agreed with those in the literature.

General Procedure D – Borylation of haloporphyrins:

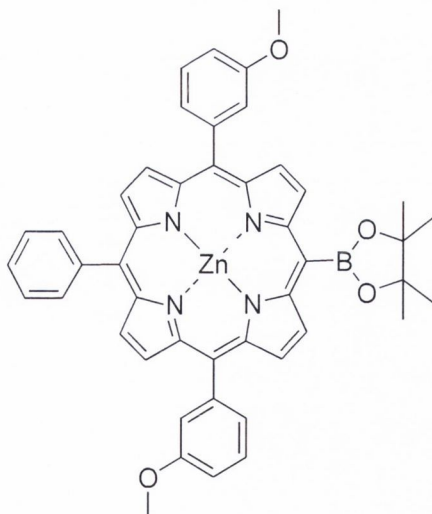
The borylation of haloporphyrins was carried out adapting a procedure by Therien and coworkers.^[239] Bromoporphyrin (1 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (0.2 equiv.) were charged to a Schlenk flask and dried under high vacuum. 1,2-Dichloroethane (10 mL) and NEt_3 (0.2 mL) were then added and the solution was degassed via three freeze-pump-thaw cycles, before the flask was purged with argon. Pinacolborane (15 equiv.) was then added and the flask was sealed and stirred at $90\text{ }^\circ\text{C}$. The reaction was followed by TLC using $\text{CH}_2\text{Cl}_2 : n\text{-hexane}$ (2 : 1, v/v). Once the starting material was consumed, the reaction was quenched with a saturated KCl solution (10 mL), washed with water, and dried over MgSO_4 . The solvent was removed *in vacuo* and the residue was subjected to column chromatography using $\text{CH}_2\text{Cl}_2 : n\text{-hexane}$ (1 : 1, v/v).

5,10,15-Triphenyl-20-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)porphyrin (128):^[240]



Produced from **83** (63 mg, 0.102 mmol) with $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.020 mmol) and pinacolborane (1.530 mmol, 0.20 mL) following general procedure D. After purification using column chromatography, **128** was obtained as a purple solid (37 mg, 0.056 mmol, 54%,). M.p. $>300^\circ\text{C}$; $R_f = 0.31$ (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); Spectroscopic data agreed with literature.

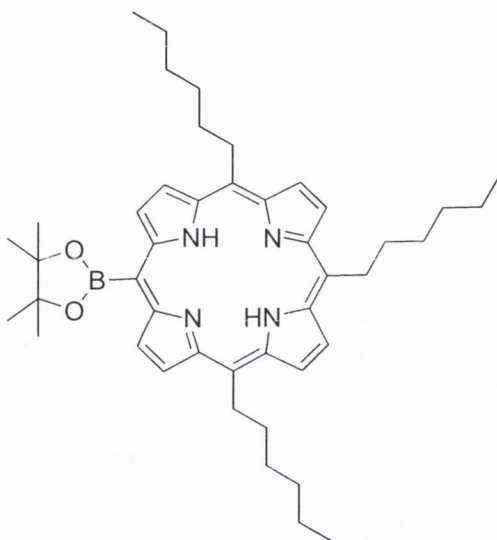
{5,15-Bis(3-methoxyphenyl)-10-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-20-phenylporphyrinato}zinc(II) (131):



Produced from **111** (150 mg, 0.202 mmol), borolane (0.25 mL, 1.700 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (7 mg, 0.010 mmol), DCE (10 mL) and TEA (0.6 mL) dissolved in CHCl_3 (25 mL) according to standard procedure D to give a purple solid (89 mg, 0.113 mmol, 56%). M.p. $>300^\circ\text{C}$; $R_f = 0.31$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz,

CDCl_3 , TMS): $\delta = 1.90$ (s, 12H, CH_3), 3.95 (s, 6H, OCH_3), 7.30-7.32 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.65-7.69 (t, $^3J_{\text{H-H}} = 15.7$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.77 (m, 5H, $\text{Ph/C}_6\text{H}_4\text{-H}$), 7.85-7.87 (d, $^3J_{\text{H-H}} = 7.3$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.24-8.26 (d, $^3J_{\text{H-H}} = 7.3$ Hz, 2H, Ph-H), 8.99-9.00 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.02-9.03 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.16-9.17 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.95-9.97 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 25.3, 55.5, 85.3, 113.5, 120.3, 120.7, 126.5, 127.3, 127.5, 127.7, 131.5, 131.1, 132.8, 133.0, 134.4, 142.8, 149.9, 150.3, 154.5, 157.8$ ppm; UV/vis (EtOAc): λ_{max} ($\log \epsilon$) = 419 (5.58), 551 (4.17), 591 (3.39) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{46}\text{H}_{39}\text{N}_4\text{O}_4\text{ZnB}](\text{M}^+)$: 786.2356; found 786.2351.

5,10,15-Trihexyl-20-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)porphyrin (134):



Produced from **85** (64 mg, 0.100 mmol) with $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.020 mmol) and pinacolborane (1.500 mmol, 0.13 mL), following general procedure D with a reaction time of 7 h. After purification, **134** was obtained as a purple solid (35 mg, 0.051 mmol, 51%). M.p. >300 °C; $R_f = 0.32$ (CH_2Cl_2 : n -hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.65$ (s, 2H, NH) 0.95 (m, $^3J_{\text{H-H}} = 14.8$ Hz, 12H, CH_3), 1.42 (m, 6H, CH_2), 1.53 (m, 6H, CH_2), 1.80 (m, 6H, CH_2), 1.87 (s, 12H, CH_3), 2.54 (m, 6H, CH_2), 4.95 (m, 6H, CH_2), 9.46 (d, $^3J_{\text{H-H}} = 4.2$ Hz, 2H, H_β), 9.58-9.48 (m, 4H, H_β), 9.84 (d, $^3J_{\text{H-H}} = 4.2$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.0, 22.6, 25.1, 30.1, 30.2, 31.8, 35.4, 35.7, 38.5, 38.7, 84.9, 118.7, 121.2, 128.1$ ppm; UV/vis: λ_{max} ($\log \epsilon$) = 421(5.46), 517 (4.11), 553 (3.76), 595 (3.57), 652 (3.47) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{44}\text{H}_{62}\text{N}_4\text{O}_2\text{B}](\text{M}+\text{H})^+$ 689.4966, found 689.4977.

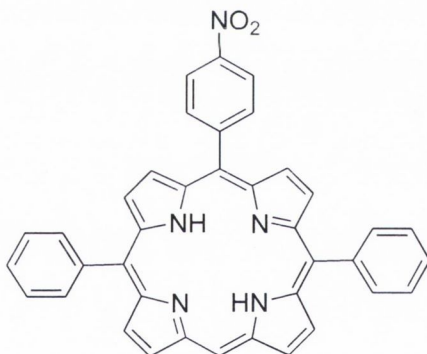
7.2.6 Suzuki coupling

Porphyrins **63**, **138**^[209] and **141**^[246] were synthesised according to Suzuki coupling procedures and spectroscopic data of **141** agreed with that in the literature.

General procedure E – Suzuki coupling:

A Schlenk flask was charged with K₃PO₄ (20 equiv.) and anhydrous THF (60 mL) under an argon atmosphere, then porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and Pd(PPh₃)₄ (0.1 equiv.) were added. The reaction was heated to reflux for 7-10 hours (TLC control) and protected from light. After completion, the solvent was evaporated and the residue was dissolved in CH₂Cl₂. This mixture was washed with saturated NaHCO₃, H₂O, and brine, and then dried over Na₂SO₄. The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallisation from CH₂Cl₂/MeOH to give the desired compound.

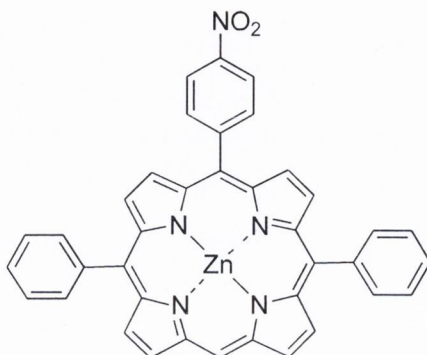
5-(4-Nitrophenyl)-10,20-diphenylporphyrin (63):



Following the general procedure E, 5-bromo-10,20-diphenylporphyrin **94** (150 mg, 0.277 mmol), K₃PO₄ (1469 mg, 6.92 mmol), 4-nitrophenyl boronic pinacol ester **135** (862 mg, 3.462 mmol) and Pd(PPh₃)₄ (32 mg, 0.028 mmol) gave 138 mg (0.236 mmol, 85%) of a purple solid after recrystallisation from CH₂Cl₂/MeOH. M.p. >300 °C; *R*_f = 0.42 (CH₂Cl₂ : *n*-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -3.00 (s, 2H, NH), 7.83 (m, 6H, Ph-*H*), 8.27 (d, ³*J*_{H-H} = 8.8 Hz, 4H, Ph-*H*), 8.42 (d, ³*J*_{H-H} = 8.8 Hz, 2H, C₆H₄-*H*), 8.65 (d, ³*J*_{H-H} = 8.8 Hz, 2H, C₆H₄-*H*), 8.79 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 8.98 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.07 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.39 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 10.29 (s, 1H, *H*_{meso}) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 105.2, 116.6, 117.0, 120.7, 120.9, 121.5, 125.4, 126.4, 127.2, 127.6, 130.1, 131.2, 134.7, 141.1, 144.4, 145.4, 146.3, 147.3, 148.5, 149.2 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) =

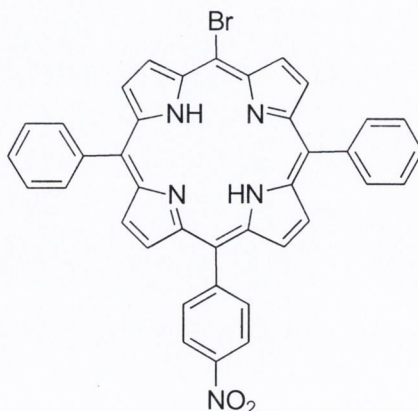
414 (4.88), 511 (3.66), 544 (3.22), 581 (3.23), 637 (2.71) nm; HRMS (ESI) m/z calcd. for $[C_{38}H_{26}N_5O_2](M+H^+)$: 584.2087, found 584.2093.

{5-(4-Nitrophenyl)-10,20-diphenylporphyrinato}zinc(II) (137):



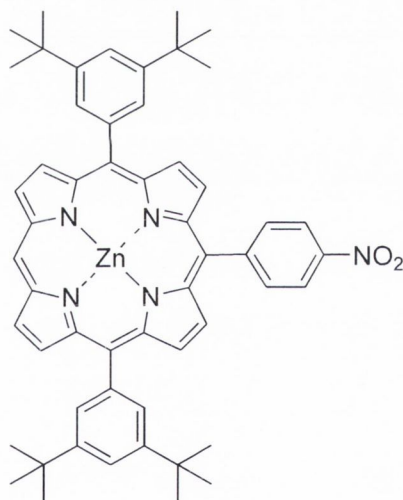
Following the general procedure E, **105** (150 mg, 0.248 mmol), K_3PO_4 (526 mg, 2.480 mmol), 4-nitrophenyl boronic pinacol ester **135** (247 mg, 0.992 mmol) and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) gave 138 mg (0.213 mmol, 86%) of a purple solid after recrystallisation from $CH_2Cl_2/MeOH$. M.p. = 120–123 °C; R_f = 0.35 (CH_2Cl_2 : n -hexane = 1 : 1, v/v); 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.82 (m, 6H, Ph- H), 7.97–8.00 (d, $^3J_{H-H}$ = 8.5 Hz, 4H, Ph- H), 8.39–8.41 (d, $^3J_{H-H}$ = 8.7 Hz, 2H, C_6H_4 - H), 8.64–8.66 (d, $^3J_{H-H}$ = 8.7 Hz, 2H, C_6H_4 - H), 8.87–8.88 (d, $^3J_{H-H}$ = 4.7 Hz, 2H, H_β), 9.05–9.07 (d, $^3J_{H-H}$ = 4.6 Hz, 2H, H_β), 9.15–9.17 (d, $^3J_{H-H}$ = 4.7 Hz, 2H, H_β), 9.46–9.47 (d, $^3J_{H-H}$ = 4.6 Hz, 2H, H_β), 10.23 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 121.0, 121.6, 122.4, 126.6, 127.6, 128.2, 128.3, 130.4, 131.0, 131.3, 131.4, 132.1, 132.5, 132.8, 134.5, 135.0, 135.7, 142.6, 148.7, 150.0, 150.2, 150.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 416 (5.05), 546 (4.02), 585 (3.30) nm; HRMS (MALDI) m/z calcd. for $[C_{38}H_{23}N_5O_2Zn](M^+)$: 645.1143, found 645.1157.

5-Bromo-15-(4-nitrophenyl)-10,20-diphenylporphyrin (138):



Following the general procedure E, **98** (100 mg, 0.161 mmol) and **135** (40 mg, 0.161 mmol) gave three fractions, starting material **98** (25%), fraction 2 yielded the desired product **138** and the third yielded disubstituted product **139** (22%). Yield **138** 38 mg (0.054 mmol, 36%) of a purple solid after recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. M.p. $>300^\circ\text{C}$; $R_f = 0.24$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.73$ (s, 2H, *NH*), 7.82 (m, 6H, *Ph-H*), 8.21 (d, $^3J = 7.0$ Hz, 4H, *Ph-H*), 8.38 (d, $^3J_{\text{H-H}} = 8.8$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.65 (d, $^3J_{\text{H-H}} = 8.8$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.72 (d, $^3J_{\text{H-H}} = 4.1$ Hz, 2H, H_β), 8.87 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 8.94 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.71 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 103.7, 104.1, 107.9, 117.3, 121.1, 121.8, 126.7, 127.9, 132.1, 134.4, 134.8, 141.3, 147.7, 148.7$ ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 421 (4.98), 518 (3.75), 555 (3.57), 599 (3.35), 651 (3.33) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{38}\text{H}_{25}\text{N}_5\text{O}_2\text{Br}](\text{M}+\text{H}^+)$: 662.1192, found 662.1179.

5,15-bis(3,5-di-*tert*-butyl-phenyl)-10-(4-nitrophenyl)porphyrinato}zinc(II) (140**):**



Following the general procedure E, **123** (65 mg, 0.078 mmol), K_3PO_4 (165 mg, 0.780 mmol), 4-nitrophenyl boronic pinacol ester **135** (78 mg, 0.314 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (9 mg, 0.008 mmol) gave 52 mg (0.060 mmol, 77 %) of a purple solid following filtration through a plug of silica using CH_2Cl_2 as eluent. M.p. = $189\text{--}191^\circ\text{C}$; $R_f = 0.54$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 1.57$ (s, 36H, *t*-butyl-*H*), 7.86–7.87 (t, $^3J_{\text{H-H}} = 3.6$ Hz, 2H, *Ar-H*), 8.14–8.15 (d, $^3J_{\text{H-H}} = 1.8$ Hz, 4H, *Ar-H*), 8.43–8.44 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.65–8.67 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.90–8.91 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.11–9.13 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.20–9.21 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β), 9.47–9.48 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β), 10.36 (s, 1H, H_{meso}) ppm;

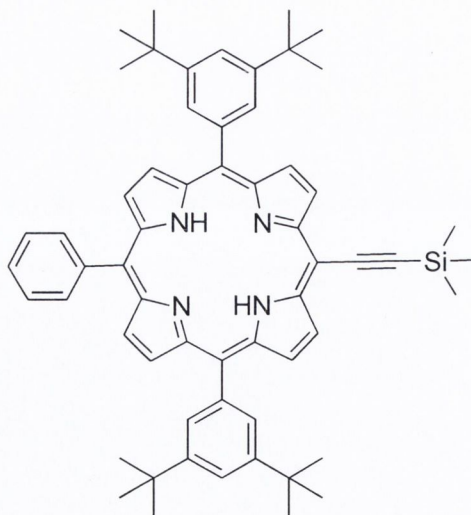
^{13}C NMR (100 MHz, CDCl_3): $\delta = 31.8, 106.6, 121.0, 121.6, 124.4, 128.3, 129.9, 130.9, 132.0, 132.9, 133.2, 135.0, 146.7, 150.0$ ppm; UV/vis (EtOAc): λ_{max} ($\log \epsilon$) = 418 (5.39), 550 (4.08), 591 (3.28) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{54}\text{H}_{55}\text{N}_5\text{O}_2\text{Zn}_2]$ (M^+): 869.3647, found 869.3654.

7.2.7 Sonogashira coupling

Trimethylsilyl porphyrins **142–146**^[45, 119, 228, 247, 249] and **148**^[250] were synthesised according to standard procedures and spectroscopic data was in agreement with that in the literature.

General Procedure F – Preparation of ethyne porphyrins via Sonogashira coupling: Bromoporphyrin (1 equiv.), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.2 equiv.) and CuI (0.3 equiv.) were added to a Schlenk flask and dried under high vacuum. Triethylamine (40 mL) and THF (10 mL) were added and the solution was degassed via three freeze-pump-thaw cycles. Trimethylsilylacetylene (10 equiv.) was added, the flask was sealed and heated to 50–65 °C and stirred for 18 hours. The reaction was followed by TLC using CHCl_3 : *n*-hexane (1 : 2, v/v). Once the starting material was consumed, the solvent was removed *in vacuo* and the residue was dry-loaded onto silica using CHCl_3 : *n*-hexane (1 : 3, v/v) as an eluent. The desired compound was collected and recrystallised using $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

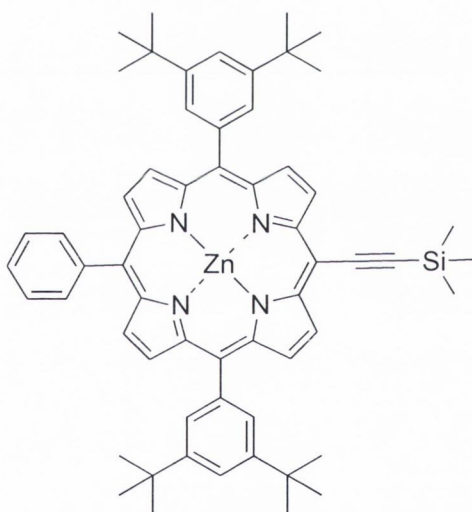
5,15-Bis(3,5-di-*tert*-butylphenyl)-10-trimethylsilylethynyl-20-phenylporphyrin (**147**):



Produced from 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin **87** (180 mg, 0.214 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (10.0 mg, 0.143 mmol), CuI (4.0 mg, 5.3 mmol) and ethynyl(trimethyl)silane (0.20 g, 2.04 mmol) according to procedure F. All solvents

were removed and the brown residue purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 2, v/v) to yield a purple solid (154 mg, 0.179 mmol, 83%). M.p. >300 °C; R_f = 0.55 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = -2.32 (s, 2H, NH), 0.60 (s, 9H, TMS- CH_3), 1.54 (s, 36H, *t*-butyl-*H*), 7.76 (m, 3H, Ph-*H*), 7.84 (m, 2H, Ar-*H*), 8.09 (d, $^3J_{\text{H-H}}$ = 1.5 Hz, 4H, Ar-*H*), 8.20-8.21 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 2H, Ph-*H*), 8.78-8.79 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 8.83-8.84 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 8.95-8.96 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 9.69-9.70 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 31.6, 34.9, 98.5, 101.5, 107.2, 121.0, 121.8, 122.3, 126.6, 127.7, 129.7, 134.1, 140.6, 142.1, 148.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 428 (5.12), 529 (3.73), 566 (3.88), 602 (3.35), 663 (3.51) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{59}\text{H}_{67}\text{N}_4\text{Si}](\text{M}+\text{H})^+$ 859.5135, found 859.5145.

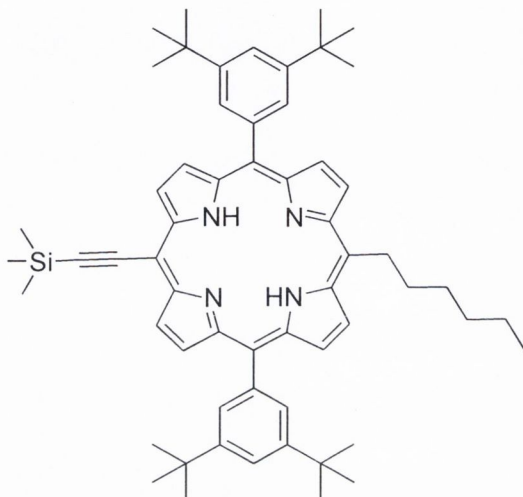
{5,15-Bis(3,5-di-*tert*-butylphenyl)-10-trimethylsilylethynyl-20-phenyl porphyrinato}zinc(II) (148):



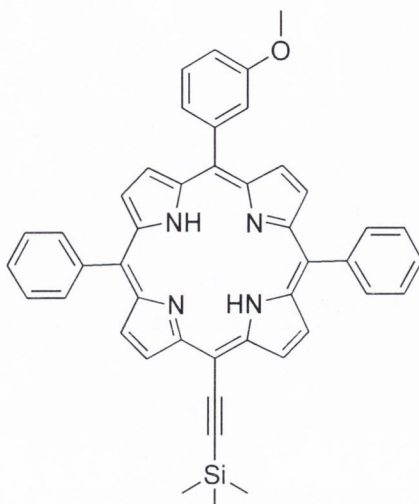
Produced from **112** (50.0 mg, 0.552 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (20.0 mg, 28.6 μmol), CuI (5.0 mg, 0.262 mmol) and ethynyl(trimethyl)silane (0.20 g, 2.04 mmol) following general procedure F. All solvents were removed and the brown residue purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 3, v/v) to yield a purple solid (23.2 mg, 0.254 mmol, 46%). M.p. >300 °C; R_f = 0.52 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = 0.64 (s, 9H, TMS- CH_3), 1.58 (s, 36H, *t*-butyl-*H*), 7.77 (m, 3H, Ph-*H*), 7.85 (m, 2H, Ar-*H*), 8.10-8.11 (d, $^3J_{\text{H-H}}$ = 1.7 Hz, 4H, Ar-*H*), 8.21-8.22 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 2H, Ph-*H*), 8.90-8.91 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 8.95-8.96 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.06-9.07 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.80-9.81 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 31.7, 35.0, 120.9, 122.7, 123.4,

126.5, 127.5, 129.7, 130.9, 132.1, 133.2, 134.2, 141.4, 148.7, 149.8, 150.3, 150.8, 152.5 ppm; UV/vis (THF): λ_{max} ($\log \epsilon$) = 433 (5.49), 569 (4.09), 613 (4.13) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{59}\text{H}_{64}\text{N}_4\text{SiZn}](\text{M}^+)$ 920.4192, found 920.4191.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-hexyl-20-(trimethylsilyl)ethynylporphyrin (149):



Following general procedure F, using bromoporphyrin **86** (65 mg, 0.076 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (20 mg, 0.029 mmol), CuI (10.0 mg, 0.052 mmol) and ethynyl(trimethyl)silane (0.20 g, 2.04 mmol). The solution was stirred for 20 h at 50 °C. All solvents were removed and the brown residue purified by column chromatography (silica gel, CH_2Cl_2 : *n*-hexane, 1 : 3, v/v) to yield a purple solid (23 mg, 0.254 mmol, 36%). Mp: >300 °C; R_f = 0.58 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -2.29 (s, 2H, NH), 0.61 (s, 9H, TMS- CH_3), 0.94-0.98 (t, $^3J_{\text{H-H}}$ = 14.6 Hz, 3H, CH_3), 1.43 (m, 4H, CH_2), 1.57 (s, 36H, *t*-butyl-*H*), 1.85 (m, 2H, CH_2), 2.56 (m, 2H, CH_2), 4.99 (t, $^3J_{\text{H-H}}$ = 16.4 Hz, 2H, CH_2), 7.84 (m, 2H, Ar-*H*), 8.78-8.81 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 4H, C_6H_3 -*H*), 8.90 (m, 4H, H_β), 9.44-9.45 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.60-9.61 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β) ppm; ^{13}C -NMR (150 MHz, CDCl_3): δ = 14.4, 22.6, 30.3, 31.6, 34.8, 38.9, 97.6, 101.1, 107.2, 120.9, 121.5, 121.9, 122.5, 129.5, 134.0, 141.0, 148.3, 150.6 ppm; UV/vis (THF): λ_{max} ($\log \epsilon$) = 424 (5.15), 527 (3.71), 565 (3.78), 607 (3.33), 665 (3.53) nm; HRMS (Maldi) m/z calcd. for $[\text{C}_{59}\text{H}_{74}\text{N}_4\text{Si}](\text{M}^+)$: 866.5683, found 866.5677.

5-(3-Methoxyphenyl)-15-trimethylsilanylethynyl-10,20-diphenylporphyrin (150):

Following general procedure F, using bromoporphyrin **82** (120 mg, 0.185 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (19.5 mg, 0.028 mmol), CuI (8.8 mg, 0.047 mmol) and ethynyl(trimethyl)silane (0.26 mL, 1.85 mmol). The solution was stirred for 12 h at 50 °C. All solvents removed and residue purified via column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 2, v/v) to yield a purple product as the main fraction. Yield 59.2 mg (0.089 mmol, 48%). Mp: >300 °C; R_f = 0.48 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = -2.39 (s, 2H, NH), 0.65 (s, 9H, TMS- CH_3) 4.00 (s, 3H, OCH_3), 7.34-7.36 (dd, $^3J_{\text{H-H}}$ = 6.0, 2.5 Hz, 1H, C_6H_4 -H), 7.64-7.67 (t, $^3J_{\text{H-H}}$ = 15.8 Hz, 2H, C_6H_4 -H), 7.81 (m, 8H, $\text{C}_6\text{H}_4/\text{Ph}$ -H), 8.23-8.24 (d, $^3J_{\text{H-H}}$ = 6.5 Hz, 4H, Ph-H), 8.79-8.80 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 8.85-8.86 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 8.92-8.93 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.69-9.70 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β) ppm; ^{13}C -NMR (150 MHz, CDCl_3): δ = 13.9, 22.5, 29.6, 31.4, 55.3, 98.9, 101.8, 106.9, 113.5, 120.2, 120.9, 121.5, 126.6, 127.4, 127.7, 130.9, 134.4, 141.5, 143.1, 157.8 ppm; UV/vis (THF): λ_{max} (log ϵ) = 427 (5.27), 525 (3.90), 563 (4.02), 602 (3.43), 654 (3.35) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{44}\text{H}_{37}\text{N}_4\text{OSi}](\text{M}+\text{H})^+$: 665.2737, found 665.2759.

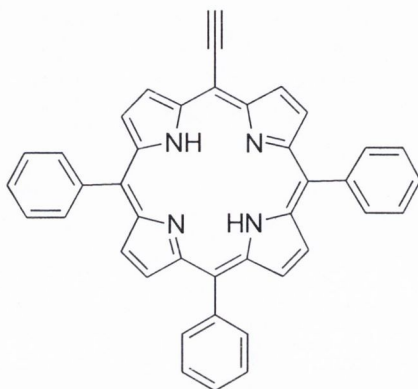
Deprotection of trimethylsilanylethynylporphyrins

Alkynyl porphyrins **152-155**^[119, 209, 228, 248] and **157**^[250] were prepared from the corresponding trimethylsilanylporphyrins via standard procedure. Spectroscopic data agreed with those in the literature.

General procedure G – Deprotection of trimethylsilyl alkynylporphyrins: Trimethylsilylethynylporphyrin (1 equiv.) was dissolved in CH_2Cl_2 and TBAF (1M, 1 mL) was added. The reaction was followed by TLC using CH_2Cl_2 : *n*-hexane (1 : 1,

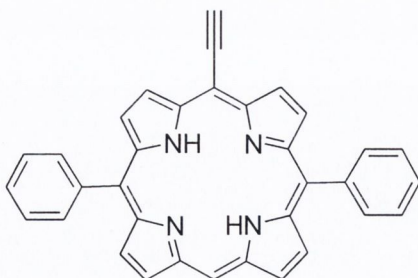
v/v). Upon completion, the solution was filtered through a plug of silica using CH_2Cl_2 as eluent. Solvent was removed *in vacuo* and the residue recrystallised using $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

5-Ethynyl-10,15,20-triphenylporphyrin (**152**):^[248]



Produced from **142** (43 mg, 0.08 mmol) following general procedure G. Purple crystals were isolated (27 mg, 0.05 mmol, 61%). M.p. $>300\text{ }^\circ\text{C}$; $R_f = 0.34$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.49$ (s, 2H, NH), 4.19 (s, 1H, $\text{C}\equiv\text{CH}$), 7.76 (m, 9H, Ph-*H*), 8.25–8.14 (m, 6H, Ph-*H*), 8.78 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_β), 8.91 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 9.69 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 53.2, 83.8, 85.4, 97.3, 120.9, 122.1, 126.5, 126.6, 127.7, 130.8, 134.2, 134.3, 141.5, 141.8$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 425 (5.56), 525 (4.28), 560 (4.17), 599 (3.73), 655 (3.71) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{40}\text{H}_{27}\text{N}_4](\text{M}+\text{H})^+$: 563.2236, found 563.2231. Locos *et al.* reported the synthesis of **152** but no experimental details were given.

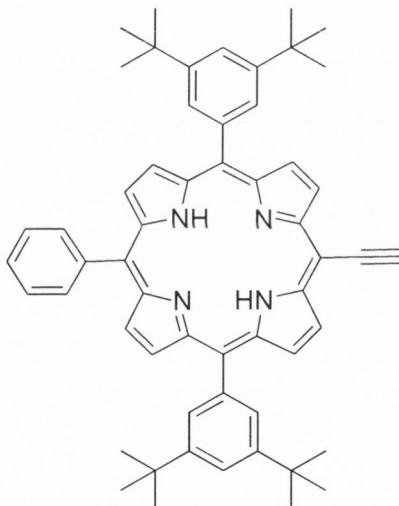
5-Ethynyl-10,20-diphenylporphyrin (**153**):^[209]



Following the general procedure G, 0.2 mL (0.0002 mmol) of 1 M solution of TBAF in THF was added to a solution of 10-trimethylsilanylethynyl-5,15-diphenylporphyrin **144** (75 mg, 0.133 mmol) in 20 mL CH_2Cl_2 . The reaction mixture was stirred for 20 minutes. The solvent was removed under reduced pressure and the residue dissolved in

CH_2Cl_2 and filtered over a short silica gel column. Recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (60 mg, 0.123 mmol, 92 %). M.p. > 300 °C; R_f = 0.52 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -2.70 (s, 2H, NH), 4.23 (s, 1H, $\text{C}\equiv\text{CH}$), 7.83 (m, 6H, Ph-*H*), 8.26 (m, 4H, Ph-*H*), 8.98 (d, $^3J_{\text{H-H}}$ = 4.1 Hz, 2H, H_β), 9.01 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.33 (d, 3J = 4.7 Hz, 2H, H_β), 9.79 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 10.27 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 83.7, 85.7, 97.8, 106.6, 120.3, 126.7, 127.7, 130.5, 131.0, 131.4, 131.6, 134.4, 141.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 420 (4.76), 517 (3.38), 552 (3.28), 592 (3.28), 649 (2.98) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{34}\text{H}_{23}\text{N}_4](\text{M}+\text{H})^+$: 487.1910, found 487.1923. This compound was mentioned by Fazekas *et al.* but no experimental details were given.

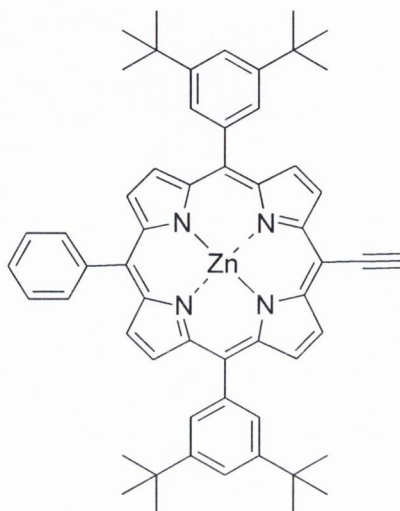
5,15-Bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin (156):



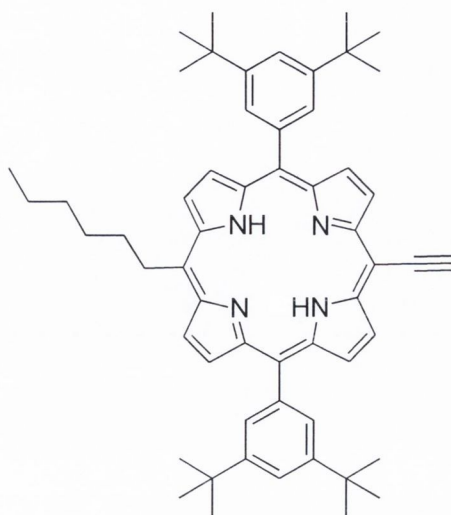
Produced from **147** (130 mg, 0.151 mmol) in CH_2Cl_2 (80 mL) and TBAF in THF (1 M, 0.5 mL, 0.5 mmol) following general procedure G. After 20 min, the solution was filtered through a plug of silica and washed with CH_2Cl_2 (50 mL). All solvents were removed to yield a purple solid. Yield: 112 mg (0.142 mmol, 94%). M.p. >300 °C; R_f = 0.49 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = -2.37 (s, 2H, NH), 1.51 (s, 36H, *t*-butyl-*H*), 4.19 (s, 1H, $\text{C}\equiv\text{C-H}$), 7.70-7.80 (m, 3H, Ph-*H*), 7.81-7.83 (m, 2H, Ar-*H*), 8.05-8.09 (m, 4H, Ar-*H*), 8.18-8.21 (m, 2H, Ph-*H*), 8.79 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 8.82 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 8.97 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.70 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 31.6, 34.9, 83.6, 85.7, 121.1, 121.8, 122.3, 126.5, 127.7, 129.8, 134.2, 140.5, 142.0, 148.8 ppm; UV/vis

(CH₂Cl₂): λ_{max} (log ϵ) = 427 (5.79), 527 (4.39), 562 (4.36), 602 (3.93), 659 (4.00) nm; HRMS (ESI) m/z calcd. for [C₅₆H₅₉N₄](M+H)⁺: 787.4727, found 787.4740.

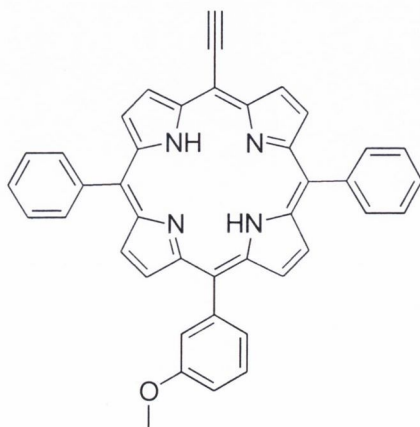
{5,15-Bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrinato}zinc(II)
(157):



Following general procedure G, **157** was produced from **148** (100 mg, 0.117 mmol) in CH₂Cl₂ (30 mL) and TBAF in THF (1 M, 0.5 mL, 0.500 mmol). After stirring for 20 min the solution was filtered through a plug of silica and washed with CH₂Cl₂. All solvents were removed *in vacuo* to yield a purple solid. Yield: 86 mg (0.109 mmol, 94%). M.p. >300 °C; R_f = 0.51 (CH₂Cl₂ : *n*-hexane = 1 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = 1.59 (s, 36H, *t*-butyl-*H*), 4.09 (s, 1H, C $\equiv$ C-*H*), 7.78 (m, 3H, Ph-*H*), 7.86 (m, 2H, Ar-*H*), 8.12-8.13 (d, ³ $J_{\text{H-H}}$ = 1.7 Hz, 4H, Ar-*H*), 8.22-8.23 (d, ³ $J_{\text{H-H}}$ = 6.5 Hz, 2H, Ph-*H*), 8.93-8.94 (d, ³ $J_{\text{H-H}}$ = 4.6 Hz, 2H, *H* _{β}), 8.97-8.98 (d, ³ $J_{\text{H-H}}$ = 4.6 Hz, 2H, *H* _{β}), 9.08-9.09 (d, ³ $J_{\text{H-H}}$ = 4.6 Hz, 2H, *H* _{β}), 9.76-9.77 (d, ³ $J_{\text{H-H}}$ = 4.6 Hz, 2H, *H* _{β}) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 21.0, 29.5, 30.2, 31.6, 34.9, 83.1, 86.0, 97.8, 120.8, 122.7, 123.2, 125.4, 126.4, 127.4, 128.1, 129.6, 130.6, 132.0, 133.3, 134.1, 135.6, 141.3, 142.5, 148.6, 149.7, 150.2, 150.8, 151.4, 152.5 ppm; UV/vis (THF): λ_{max} (log ϵ) = 429 (5.31), 566 (3.91), 608 (3.76) nm; HRMS (ESI) m/z calcd. for [C₅₆H₅₆N₄Zn](M⁺): 848.3796, found 848.3836.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-hexylporphyrin (158):

Produced from **149** (23 mg, 0.025 mmol) in CH_2Cl_2 (10 mL) and TBAF in THF (1 M, 0.1 mL, 0.1 mmol) following general procedure G. After stirring for 20 min, the solution was filtered through a plug of silica and washed with CH_2Cl_2 (50 mL). All solvents were removed to yield a purple solid. Yield: 20 mg (0.023 mmol, 93%). M.p. $>300^\circ\text{C}$; $R_f = 0.54$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.33$ (s, 2H, NH), 0.94-0.98 (t, $^3J_{\text{H-H}} = 14.5$ Hz, 3H, CH_3), 1.42 (m, 4H, CH_2), 1.58 (s, 36H, *t*-butyl-*H*), 1.86 (m, 2H, CH_2), 2.57 (m, 2H, CH_2), 4.17 (s, 1H, $\text{C}\equiv\text{CH}$), 5.00 (m, 2H, CH_2), 7.84 (s, 4H, Ar-*H*), 8.07 (m, 2H, Ar-*H*), 8.91 (m, 4H, H_β), 9.45-9.46 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.63-9.64 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β) ppm; ^{13}C -NMR (150 MHz, CDCl_3): $\delta = 13.9, 22.6, 30.2, 31.7, 34.9, 35.7, 38.7, 83.3, 35.6, 96.2, 120.9, 121.7, 122.7, 129.5, 129.6, 140.8, 148.7$ ppm; UV/vis (THF): λ_{max} (log ϵ) = 428 (5.48), 525 (4.10), 562 (4.14), 603 (3.69), 661 (3.79) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{56}\text{H}_{67}\text{N}_4](\text{M}+\text{H})^+$: 795.5366, found 795.5378.

5-Ethynyl-15-(3-methoxyphenyl)-10,20-diphenylporphyrin (159):

Produced from trimethylsilylethynyl porphyrin **150** (25 mg, 0.038 mmol) following the general procedure G to yield a purple solid (20 mg, 0.034 mmol, 90%). Mp: >300 °C; R_f = 0.40 (CH₂Cl₂ : *n*-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.45 (s, 2H, NH), 4.00 (s, 3H, OCH₃), 4.22 (s, 1H, C $\equiv$ CH), 7.35-7.37 (m, 3H, aryl-*H*), 7.64-7.68 (m, 2H, aryl-*H*), 7.81 (m, 6H, aryl-*H*), 8.22-8.24 (d, ³*J*_{H-H} = 6.8 Hz, 2H, Ph-*H*), 8.79-8.80 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H* _{β}), 8.85-8.86 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H* _{β}), 8.93-8.94 (d, ³*J*_{H-H} = 4.1 Hz, 2H, *H* _{β}) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 25.5, 29.6, 30.2, 34.1, 55.6, 37.8, 83.8, 85.4, 97.4, 112.5, 120.3, 120.9, 121.7, 125.4, 126.7, 127.4, 127.7, 131.1, 134.4, 135.7, 141.5, 143.1, 157.8 ppm; UV/vis (THF): $\lambda_{\max}$ (log ϵ) = 423 (5.58), 523 (4.19), 558 (4.13), 601 (3.66), 662 (3.38) nm; HRMS (ESI) *m/z* calcd. for [C₄₁H₂₉N₄O](M+H)⁺: 593.2327, found 593.2341.

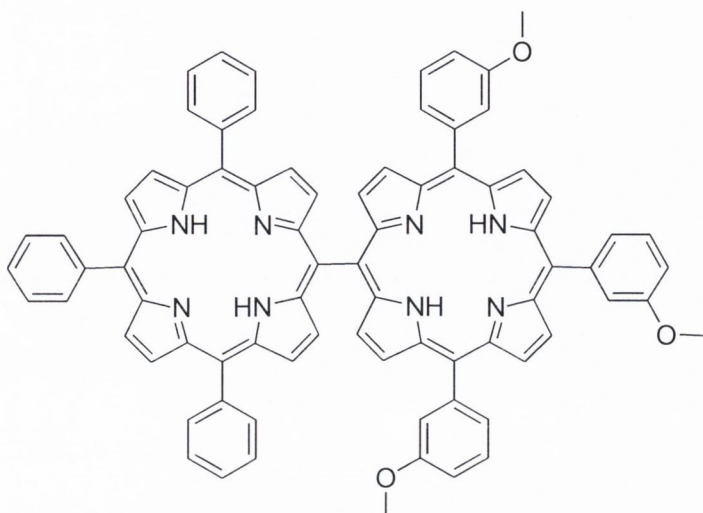
7.3 Conjugated Arrays

7.3.1 Directly linked dimers

General procedure H – Suzuki coupling for the synthesis of directly-linked dimers:

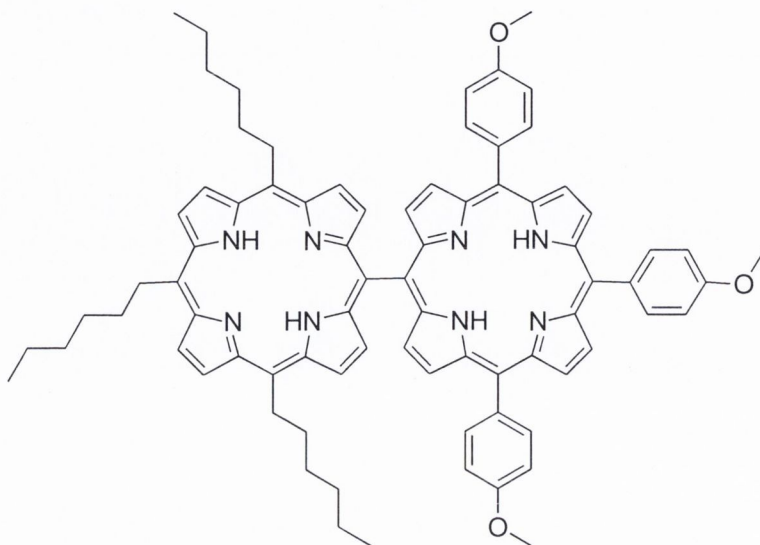
A Schlenk tube was charged with bromoporphyrin (1 equiv.), porphyrinyl boronate (1 equiv.) and Cs₂CO₃ (1.5 equiv.) and dried under high vacuum. Dry DMF (1 mL) and dry toluene (2 mL) were then added, and the mixture was degassed via three freeze-pump-thaw cycles. Pd(PPh₃)₄ (0.2 equiv.) was then added, the flask sealed and stirred at 80 °C. The reaction was followed by TLC. Once the starting material was consumed, the reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over MgSO₄, evaporated to dryness, and subjected to column chromatography

5-(10',15',20'-Triphenylporphyrin-5'-yl)-10,15,20-tris(3-methoxyphenyl)porphyrin (160):



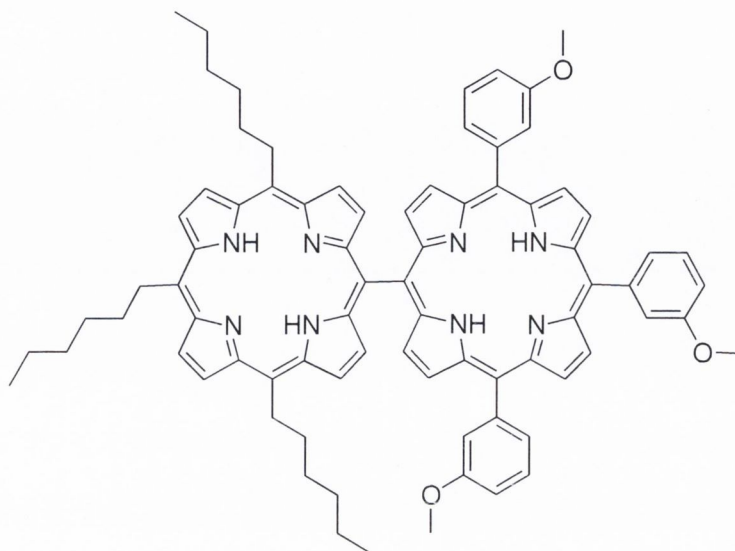
Produced from **128** (5 mg, 0.0075 mmol), **90** (5 mg, 0.007 mmol), Cs₂CO₃ (6 mg, 0.03 mmol) and Pd(PPh₃)₄ (1 mg, 0.0008 mmol) following general procedure H. After purification, a dark purple solid was isolated (3 mg, 0.003 mmol, 29%). M.p. >300 °C; *R*_f = 0.37 (CH₂Cl₂ : *n*-hexane = 3 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.24-2.28 (m, 4H, NH), 3.94 (s, 3H, OCH₃), 4.07 (s, 3H, OCH₃), 7.57 (m, 3H, aryl-*H*), 7.71 (m, 8H, aryl-*H*), 7.83 (m, 8H, aryl-*H*), 7.89-7.83 (m, 3H, aryl-*H*), 8.09-8.10 (d, ³*J*_{H-H} = 4.8 Hz, 4H, *H*_β), 8.24-8.26 (d, ³*J*_{H-H} = 6.8 Hz, 4H, aryl-*H*), 8.31-8.34 (d, ³*J*_{H-H} = 5.8 Hz, 4H, aryl-*H*), 8.61-8.62 (d, ³*J*_{H-H} = 4.8 Hz, 2H, *H*_β), 8.65-8.66 (d, ³*J*_{H-H} = 4.8 Hz, 2H, *H*_β), 8.97 (m, 8H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 55.4, 113.2, 126.6, 126.7, 127.7, 128.8, 134.4, 143.5, 144.8 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 406 (5.20), 503 (3.94), 533 (3.53), 574 (3.48) nm; HRMS (MALDI) *m/z* calcd. for [C₇₉H₅₆N₈O₃](M⁺) 1165.4554, found 1165.4497.

5-(10',15',20'-Trihexylporphyrin-5'-yl)-10,15,20-tris(4-methoxyphenyl)porphyrin (161):



Produced from **134** (10 mg, 0.015 mmol), **91** (12 mg, 0.02 mmol), Cs_2CO_3 (4 mg, 0.02 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.003 mmol) following general procedure H, to give green solid (6 mg, 0.005 mmol, 37%). M.p. $>300^\circ\text{C}$; $R_f = 0.32$ (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.14$ (s, 2H, NH), -2.05 (s, 2H, NH), 0.91-0.82 (t, $^3J_{\text{H-H}} = 15.0$ Hz, 12H, CH_3), 1.38 (m, 6H CH_2), 1.45 (m, 6H, CH_2), 1.76 (m, 4H, CH_2), 1.92 (m, 2H, CH_2), 2.54 (m, 4H, CH_2), 2.63 (m, 2H, CH_2), 4.04 (s, 6H, OCH_3), 4.18 (s, 3H, OCH_3), 4.94 (m, 4H, CH_2), 5.11-5.15 (t, $^3J_{\text{H-H}} = 15.6$ Hz, 2H, CH_2), 7.24-7.25 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.38-7.39 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.05-8.06 (d, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, H_β), 8.08-8.09 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 8.16-8.18 (d, $^3J_{\text{H-H}} = 8.8$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$) 8.25-8.26 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$) 8.63-8.64 (d, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, H_β), 8.96-8.97 (d, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, H_β), 9.00-9.01 (d, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, H_β), 9.13-9.14 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 9.58-9.60 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 9.66-9.67 ppm (d, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, H_β); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 13.9$, 14.0, 22.5, 22.7, 29.5, 29.6, 30.1, 30.2, 31.7, 31.9, 38.5, 55.3, 112.0, 112.1, 135.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 410 (5.67), 450 (5.01), 507 (4.48), 567 (3.95), 599 (3.87), 666 (3.49) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{79}\text{H}_{81}\text{N}_8\text{O}_3](\text{M}+\text{H})^+$: 1189.6432, found 1189.6428.

5-(10',15',20'-Trihexylporphyrin-5'-yl)-10,15,20-tris(3-methoxyphenyl)porphyrin (162):



Produced from **134** (10 mg, 0.015 mmol), **90** (8 mg, 0.010 mmol), Cs_2CO_3 (4 mg, 0.02 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (2 mg, 0.002 mmol) following general procedure H to give a purple solid. Yield (8 mg, 0.007 mmol, 51%). M.p. $>300^\circ\text{C}$; $R_f = 0.30$ (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.16$ (s, 2H, NH) -2.07 (s, 2H, NH), 0.86 (m, 12H, CH_3), 1.00 (m, 6H CH_2), 1.36-1.30 (m, 6H, CH_2), 1.77 (m, 6H, CH_2), 1.92-1.86 (m, 6H, CH_2), 2.50 (m, 4H, CH_2), 2.62 (m, 2H, CH_2), 4.01 (s, 6H, OCH_3), 4.14 (s, 3H, OCH_3), 4.94-4.85 (m, 4H, CH_2), 5.14-5.06 (m, 2H, CH_2), 7.21 (d, $^3J_{\text{H-H}} = 8.6$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.03 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 8.07 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 8.14 (d, $^3J_{\text{H-H}} = 8.6$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.22 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.61 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 8.96 (dd, $^3J_{\text{H-H}} = 13.2, 4.7$ Hz, 4H, H_β), 9.11 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β), 9.56 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.63 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 13.9, 14.0, 22.8, 29.6, 30.1, 30.3, 38.6, 55.7, 110.0, 112.0, 113.4, 134.1, 135.3, 137.1$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 413 (4.97), 452 (4.10), 525 (4.34), 564 (3.96), 601 (3.87), 661 (3.79) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{79}\text{H}_{81}\text{N}_8\text{O}_3](\text{M}+\text{H})^+$: 1189.6432, found 1189.6471.

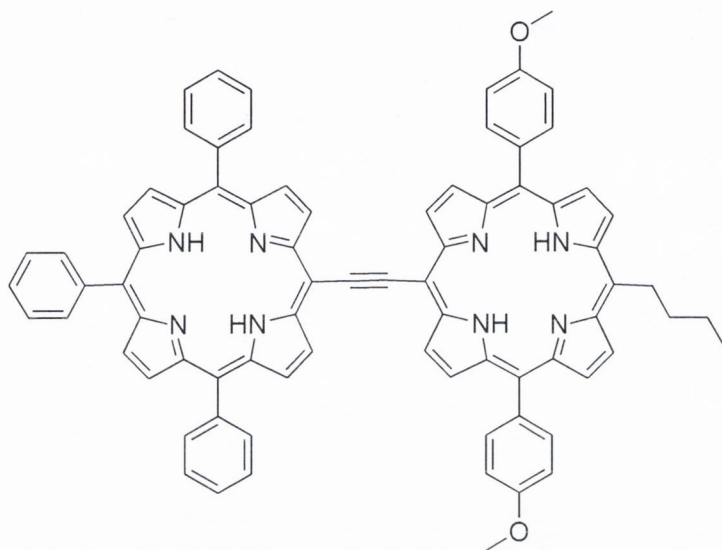
7.3.2 Alkynyl linked dimers

General procedure I – Copper-free Sonogashira coupling of porphyrin dimers:

This procedure was adapted from a method by Wagner *et al.*^[126] Bromoporphyrin (1 equiv.), ethynylporphyrin (1 equiv.), $\text{Pd}_2(\text{dba})_3$ (0.4 equiv.) and AsPh_3 (1 equiv.) were added to a Schlenk tube and dried under high vacuum. The flask was purged with argon

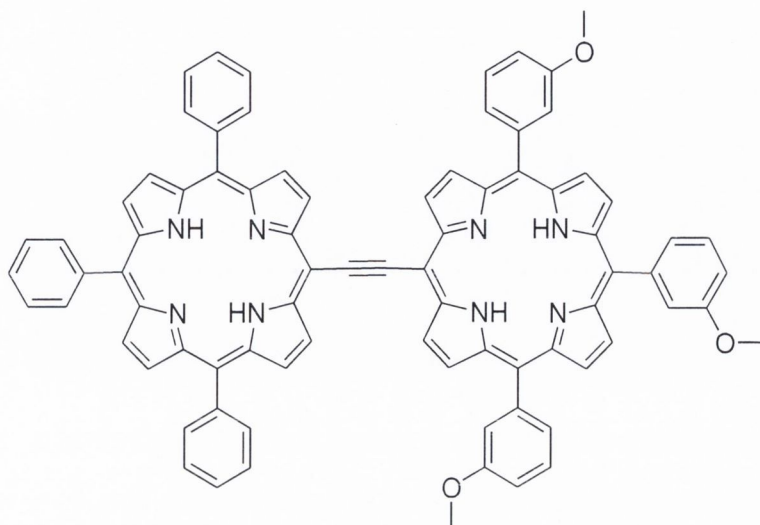
and dry THF (10 mL) and NEt_3 (1 mL) were added. The solution was degassed via three freeze-pump-thaw cycles and the reaction heated to 65 °C. The reaction was followed by TLC using CH_2Cl_2 : *n*-hexane (1 : 1, v/v). Once the starting material was consumed, the solvent was removed and the residue dry-loaded onto silica.

5-(*n*-Butyl)-15-(5'-ethynyl-10',15',20'-triphenylporphyrin)-10,20-bis(4-methoxyphenyl)porphyrin (163):



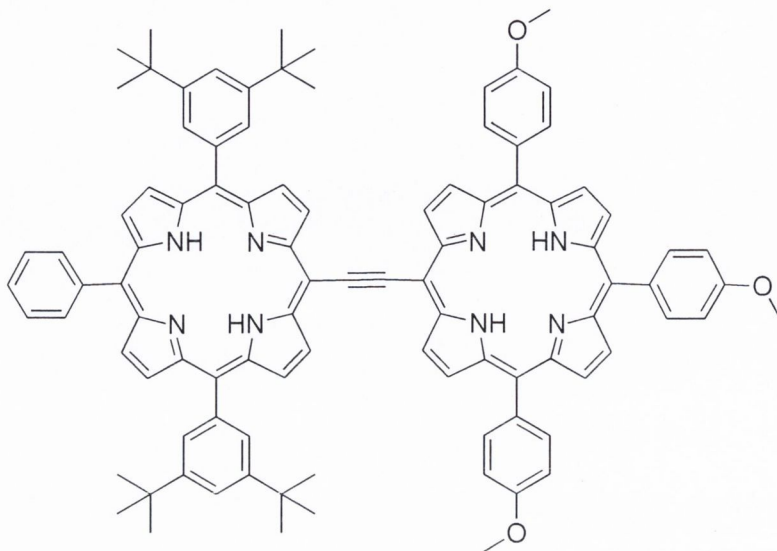
Produced from **151** (10 mg, 0.018 mmol), **92** (12 mg, 0.018 mmol), AsPh_3 (4 mg, 0.013 mmol) and $\text{Pd}_2(\text{dba})_3$ (5 mg, 0.001 mmol) following procedure I. After purification dark green crystals were isolated (5 mg, 0.004 mmol, 29%). M.p. >300 °C; R_f = 0.37 (CH_2Cl_2 : *n*-hexane = 4 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -2.02 (s, 2H, NH), -1.93 (s, 2H, NH), 1.15 (t, $^3J_{\text{H-H}}$ = 15.4 Hz, 3H, CH_3), 1.88-1.81 (m, 2H, CH_2), 2.57-2.51 (m, 2H, CH_2), 4.14 (s, 6H, OCH_3), 4.98 (m, 2H, CH_2), 7.35 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.80 (m, 9H, Ph-H), 8.17 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.22 (m, 2H, Ph-H), 8.29 (m, 4H, Ph-H), 8.80 (m, 4H, H_β), 8.90-8.91 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.07 (m, 4H, H_β), 9.44 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 2H, H_β), 10.24 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 10.32 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.0, 14.1, 22.5, 23.5, 29.2, 29.6, 29.9, 31.8, 55.5, 112.2, 120.7, 127.8, 128.2, 128.7, 128.8, 130.3, 134.3, 134.4, 134.7, 135.4, 141.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 415 (4.73), 470 (4.72), 518 (3.89), 620 (3.93), 717 (4.00) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{78}\text{H}_{58}\text{N}_8\text{O}_2](\text{M})^+$ 1138.4683, found 1138.4803.

5-(5',10',20'-Triphenylporphyrin)-ethynyl-10,15,20-tris(3-methoxyphenyl)porphyrin (164):



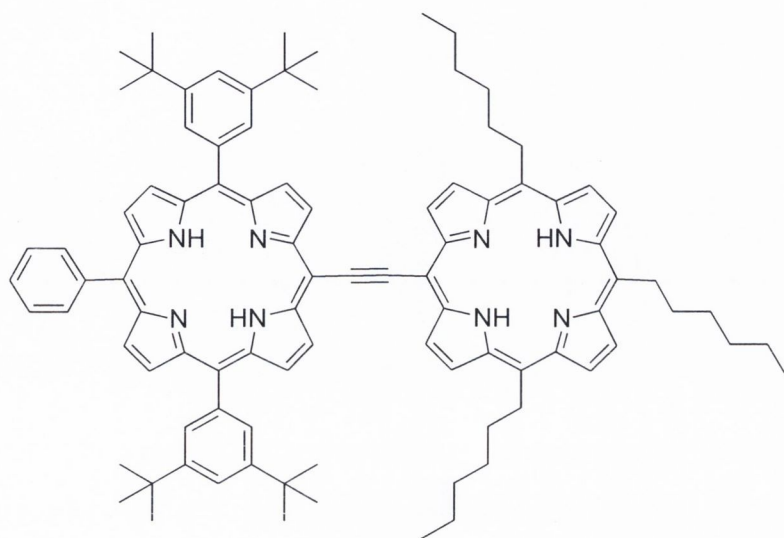
Produced from **151** (10 mg, 0.018 mmol), **90** (13 mg, 0.018 mmol), AsPh_3 (5 mg, 0.020 mmol) and $\text{Pd(PPh}_3)_4$ (2 mg, 0.001 mmol) following procedure I. After purification dark green crystals were isolated (3 mg, 0.002 mmol, 29%). M.p. $>300^\circ\text{C}$; $R_f = 0.30$ (CH_2Cl_2 : n -hexane = 4 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.03$ (s, 2H, NH) -2.01(s, 2H, NH), 3.98 (s, 3H, OCH_3), 4.01 (s, 6H, OCH_3), 7.10 (d, $^3J_{\text{H-H}} = 15.9$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.63 (m, 9H, Ph- H), 7.75 (d, $^3J_{\text{H-H}} = 15.9$ Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.91-7.87 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.24-8.20 (m, 2H, Ph- H), 8.32-8.27 (m, 4H, Ph- H), 8.83-8.81 (m, 2H, H_β), 8.87-8.85 (m, 2H, H_β), 8.95-8.90 (m, 2H, H_β), 9.11-9.08 (m, 2H, H_β), 9.15-9.12 (m, 2H, H_β), 9.35-9.32 (m, 2H, H_β), 10.37-10.32 (m, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.0, 22.5, 22.6, 29.2, 29.7, 29.9, 31.8, 55.5, 125.3, 126.7, 127.5, 127.9, 128.2, 128.8, 130.3, 134.3, 134.4, 136.7, 143.2$ ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 412 (4.91), 473 (4.88), 517 (4.01), 620 (4.09), 713 (4.19) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{81}\text{H}_{56}\text{N}_8\text{O}_3](\text{M}^+)$: 1188.4475, found 1188.4490.

5-{5',10',20'-Tris(4-methoxyphenyl)ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin (165):



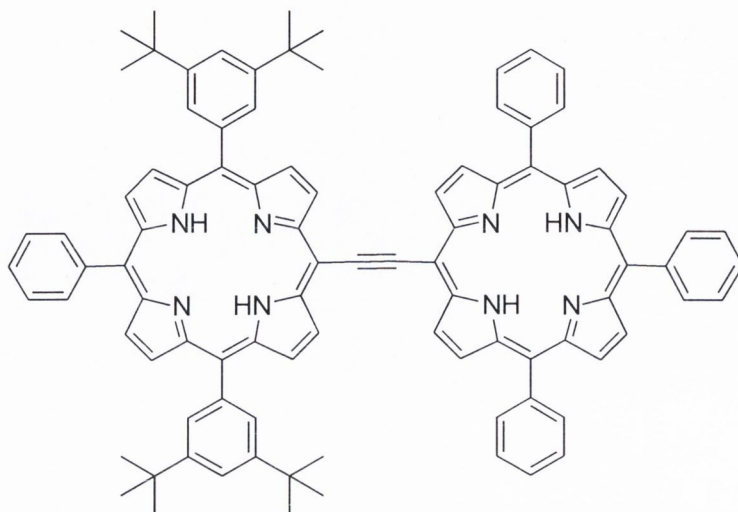
Following procedure I, ethynylporphyrin **156** (20.0 mg, 0.025 mmol), bromoporphyrin **91** (18 mg, 0.025 mmol), AsPh_3 (10 mg, 0.033 mmol) and $\text{Pd}_2(\text{dba})_3$ (2 mg, 0.003 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 14 h at 65 °C. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 4 to 2 : 1, v/v) to yield a red-green solid. Yield: 23 mg (0.016 mmol, 64%). M.p. >300 °C; R_f = 0.33 (CH_2Cl_2 : *n*-hexane : TEA = 2 : 1 : 0.01, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -1.92 (s, 2H, NH), -1.89 (s, 2H, NH), 1.59 (s, 36H, *t*-butyl-*H*), 4.11 (s, 3H, OCH_3), 4.14 (s, 6H, OCH_3), 7.31 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 2H, C_6H_4 -*H*), 7.31 (d, $^3J_{\text{H-H}}$ = 8.8 Hz, 4H, Ar-*H*), 7.74-7.80 (m, 5H, aryl-*H*), 7.85-7.89 (m, 2H, C_6H_4 -*H*), 8.15 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 2H, Ph-*H*), 8.17-8.21 (m, 4H, aryl-*H*), 8.23 (d, $^3J_{\text{H-H}}$ = 8.8 Hz, 4H, Ph-*H*), 8.84-8.93 (m, 8H, H_β), 9.17 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β) 9.20 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β) 10.40 (m, 4H, H_β) ppm; ^{13}C -NMR (150 MHz, CDCl_3): δ = 35.2, 55.6, 55.6, 99.9, 100.2, 100.3, 100.3, 112.3, 112.4, 121.2, 121.3, 121.8, 122.9, 126.7, 129.8, 134.3, 134.3, 135.5, 135.6, 140.8, 149.0, 159.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 409 (4.77), 475 (4.95), 522 (4.05), 623 (4.22), 719 (4.34) nm; HRMS (ESI) m/z calcd. for $(\text{C}_{97}\text{H}_{88}\text{N}_8\text{O}_3)(\text{M}+\text{H})^+$ 1413.7086, found 1413.7058.

5-(5',10',20'-Trihexylporphyrin)ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin (166):



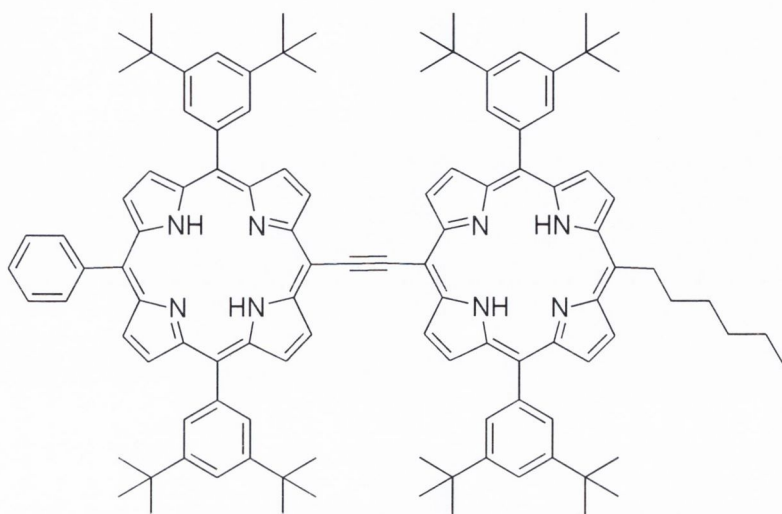
Following procedure I ethynylporphyrin **156** (21 mg, 0.027 mmol), bromoporphyrin **85** (17 mg, 0.027 mmol), AsPh_3 (25 mg, 0.082 mmol) and $\text{Pd}_2(\text{dba})_3$ (16 mg, 0.028 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 4 h at 65 °C and then for 15 h at room temperature. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 4 to 1 : 1, v/v) to yield a red-green solid. Yield: 16 mg (0.012 mmol, 45%). M.p. >300 °C; R_f = 0.32 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = -1.93 (s, 2H, NH), -1.89 (s, 2H, NH), 0.94-1.00 (t, $^3J_{\text{H-H}}$ = 14.7 Hz, 9H, CH_3), 1.38-1.49 (m, 6H, CH_2), 1.51-1.60 (m, 6H, CH_2), 1.59 (s, 36H, *t*-butyl-*H*), 1.81-1.91 (m, 6H, CH_2), 2.51-2.61 (m, 6H, CH_2), 4.91-4.98 (m, 6H, CH_2), 7.72-7.80 (m, 3H, Ph-*H*), 7.83-7.86 (m, 2H, Ph-*H*), 8.13-8.16 (m, 4H, Ar-*H*), 8.21-8.25 (m, 2H, Ar-*H*), 8.81 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 8.88 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.17 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.45 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.49 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.61 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 10.32 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 10.37 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.1, 14.2, 22.7, 22.8, 29.7, 29.8, 30.3, 30.4, 31.8, 31.9, 35.1, 35.4, 36.0, 98.4, 99.4, 100.3, 100.7, 120.8, 121.3, 121.6, 121.8, 122.8, 126.7, 127.8, 128.4, 128.9, 129.9, 133.7, 134.3, 140.9, 142.2, 149.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 410 (4.61), 473 (4.82), 522 (3.85), 623 (4.04), 723 (4.17) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{94}\text{H}_{107}\text{N}_8](\text{M}+\text{H})^+$: 1347.8606, found 1347.8619.

5-(5',10',20'-Triphenylporphyrin)ethynyl-10,20-bis-(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin (167):

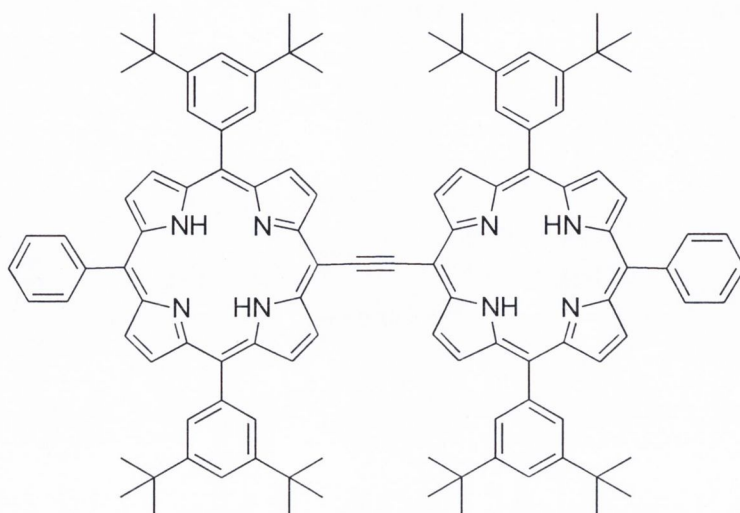


Following procedure I, ethynylporphyrin **156** (20 mg, 0.025 mmol), bromoporphyrin **83** (16 mg, 0.025 mmol), AsPh₃ (10 mg, 0.033 mmol) and Pd₂(dba)₃ (2 mg, 0.002 mmol) were dried *in vacuo* and dissolved in degassed NEt₃ (1 mL) and THF (4 mL). The solution was stirred for 4 h at 65 °C and then for 15 h at room temperature. All solvents were removed and the residue purified by column chromatography (silica, CH₂Cl₂ : *n*-hexane, 1 : 3 to 1 : 1, v/v) to yield a red-green solid. Yield: 15 mg (0.012 mmol, 45%). M.p. >300 °C; *R*_f = 0.29 (CH₂Cl₂ : *n*-hexane = 2 : 1, v/v); ¹H-NMR (600 MHz, CDCl₃, TMS): δ = -2.00 (s, 2H, NH), -1.94 (s, 2H, NH), 1.58 (s, 36H, *t*-butyl-*H*), 7.74-7.85 (m, 12H, Ar/Ph-*H*), 7.83-7.86 (m, 2H, Ar/Ph-*H*), 8.15-8.18 (m, 4H, Ar/Ph-*H*), 8.21-8.26 (m, 4H, Ar/Ph-*H*), 8.28-8.34 (m, 4H, Ar/Ph-*H*), 8.80-8.90 (m, 8H, *H*_β), 9.11 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.15 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 10.36 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 10.37 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 35.1, 53.4, 99.7, 100.1, 100.4, 100.7, 121.3, 121.5, 121.9, 122.0, 123.0, 126.7, 126.8, 126.9, 127.8, 127.9, 129.8, 134.3, 134.4, 134.6, 140.8, 141.8, 142.0, 142.2, 149.0 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 406 (4.80), 474 (4.99), 521 (4.31), 624 (4.37), 719 (4.42) nm; HRMS (ESI) *m/z* calcd. for [C₉₄H₈₂N₈](M+H)⁺: 1323.6749, found 1323.6741.

5-(5',15'-Bis(3,5-di-*tert*-butylphenyl)-10'-phenylporphyrin)ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-hexylporphyrin (168):

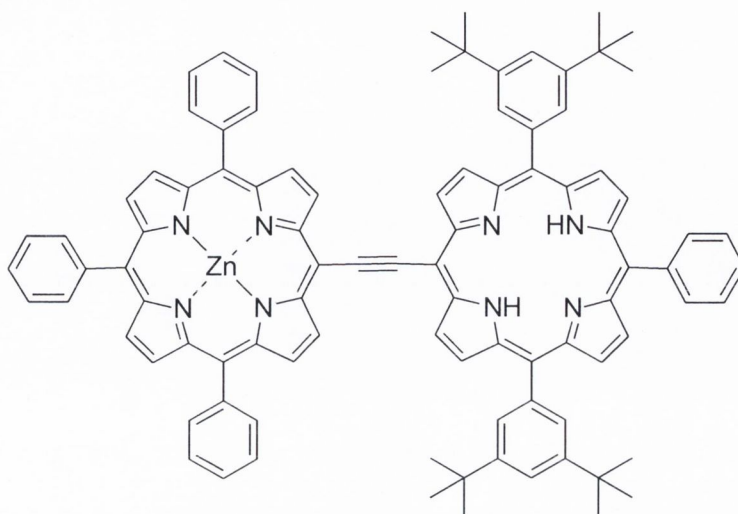


Following procedure I, ethynylporphyrin **158** (30 mg, 0.039 mmol), bromoporphyrin **87** (33 mg, 0.039 mmol), AsPh₃ (10 mg, 0.033 mmol) and Pd₂(dba)₃ (4 mg, 0.004 mmol) were dried *in vacuo* and dissolved in degassed NEt₃ (1 mL) and THF (4 mL). The solution was stirred for 6 h at 65 °C. All solvents were removed and the residue purified by column chromatography (silica, CH₂Cl₂ : *n*-hexane, 1 : 4 to 2 : 1, v/v) to yield a red-green solid. Yield: 20 mg (0.013 mmol, 34%). M.p. >300 °C; *R*_f = 0.32 (CH₂Cl₂ : *n*-hexane = 3 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -1.95 (s, 2H, NH), -1.88 (s, 2H, NH), 0.94-0.98 (t, ³*J*_{H-H} = 15.4 Hz, 3H, CH₃), 1.57 (s, 36H, *t*-butyl-*H*), 1.59 (s, 36H, *t*-butyl-*H*), 1.41-1.47 (m, 2H, CH₂), 1.64-1.70 (m, 2H, CH₂), 1.83-1.90 (m, 2H, CH₂), 2.55-2.60 (m, 2H, CH₂), 4.94-5.02 (m, 2H, CH₂), 7.72-7.80 (m, 3H, Ph-*H*), 7.83-7.87 (m, 2H, Ar/Ph-*H*), 7.83-7.86 (m, 2H, Ar/Ph-*H*), 8.12-8.16 (m, 4H, Ar/Ph-*H*), 8.20-8.24 (m, 2H, Ar/Ph-*H*), 8.79 (d, ³*J*_{H-H} = 5.7 Hz, 2H, Ph-*H*), 8.84 (d, ³*J*_{H-H} = 5.7 Hz, 2H, Ph-*H*), 8.92 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.06 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.11 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.44 (s, 2H, *H*_β), 10.27 (s, 4H, *H*_β), 10.33 (s, 4H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 14.0, 22.6, 25.5, 29.3, 29.4, 29.6, 30.2, 30.3, 34.9, 121.1, 122.2, 122.7, 124.7, 125.4, 126.5, 129.5, 129.6, 134.2, 135.5, 140.7, 140.9 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 408 (4.94), 474 (5.13), 521 (4.24), 622 (4.38), 721 (4.50) nm; HRMS (ESI) *m/z* calcd. for (C₁₁₀H₁₂₂N₈)(M⁺): 1554.9792, found 1554.9810.

Bis{10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin-5-yl}ethynyl (169):

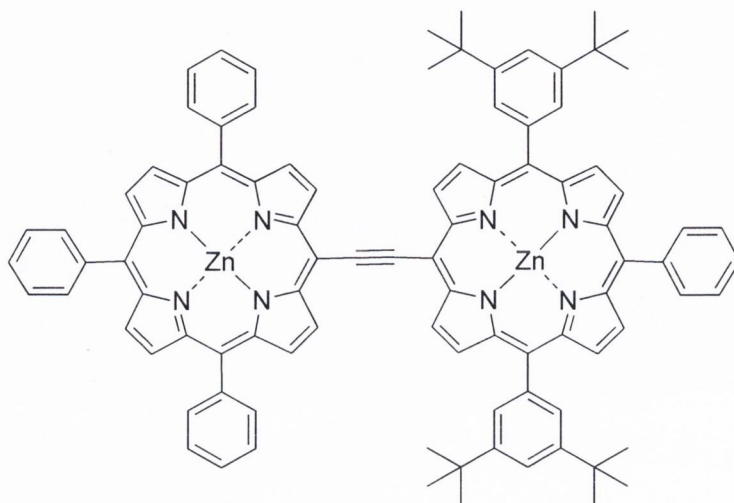
Following procedure I, ethynylporphyrin **156** (18 mg, 0.023 mmol), bromoporphyrin **87** (19 mg, 0.023 mmol), AsPh_3 (10 mg, 0.033 mmol) and $\text{Pd}_2(\text{dba})_3$ (1 mg, 0.002 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 6 h at 65 °C. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 4 to 2 : 1, v/v) to yield a red-green solid. Yield: 15 mg (0.010 mmol, 43%). M.p. >300 °C; R_f = 0.27 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = -1.93 (s, 4H, NH), 1.58 (s, 72H, *t*-butyl-*H*), 7.72-7.81 (m, 6H, Ar-*H*), 7.83-7.87 (m, 4H, Ar-*H*), 8.13-8.18 (m, 8H, Ar/Ph-*H*), 8.21-8.26 (m, 4H, Ph-*H*), 8.79 (s, 4H, H_β), 8.86 (s, 4H, H_β), 9.14 (s, 4H, H_β), 10.36 (s, 4H, H_β) ppm; ^{13}C -NMR (150 MHz, CDCl_3): δ = 35.0, 53.3, 99.8, 100.2, 121.1, 121.6, 122.7, 126.6, 127.6, 129.7, 134.2, 140.7, 142.0, 148.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 413 (4.59), 474 (4.72), 523 (3.87), 622 (3.99), 718 (4.09) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{110}\text{H}_{114}\text{N}_8](\text{M}+\text{H})^+$: 1547.9292, found 1547.9245.

{5-(10',20'-Bis(3,5-di-*tert*-butylphenyl)-15'-phenylporphyrin-5-yl)ethynyl-10,15,20-triphenylporphyrinato}zinc(II) (170):



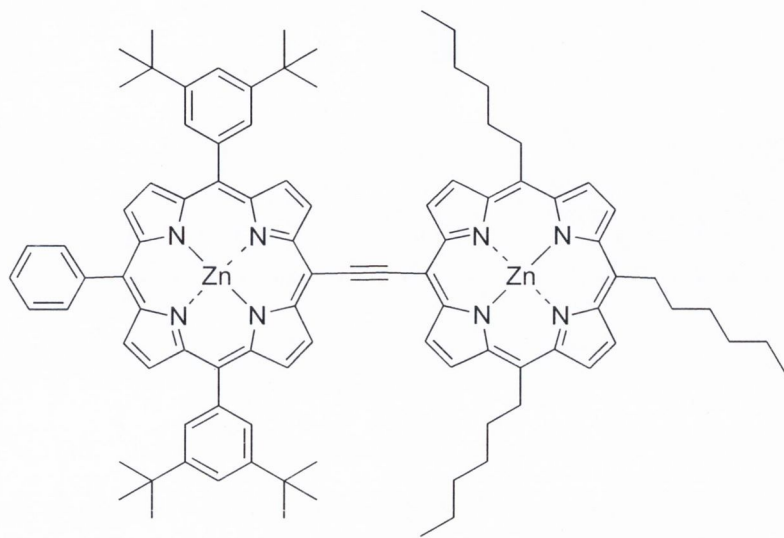
Following procedure I, ethynylporphyrin **156** (32 mg, 0.040 mmol), bromoporphyrin **104** (27 mg, 0.040 mmol), AsPh₃ (20.2 mg, 0.066 mmol) and Pd₂(dba)₃ (9.0 mg, 0.010 mmol) were dried *in vacuo* and dissolved in degassed NEt₃ (1 mL) and THF (4 mL). The solution was stirred for 4 h at 65 °C and then for 15 h at room temperature. All solvents were removed and the residue purified by column chromatography (silica, CH₂Cl₂ : hexane, 1 : 4 to 1 : 1, v/v) to yield a red-green solid. Yield: 30 mg (0.022 mmol, 54%). M.p. >300 °C; *R*_f = 0.26 (CH₂Cl₂ : *n*-hexane : TEA = 1 : 1 : 0.01, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -1.93 (s, 2H, NH), 1.58 (s, 36H, *t*-butyl-*H*), 7.70-7.83 (m, 12H, Ar/Ph-*H*), 7.85-7.87 (m, 4H, Ar/Ph-*H*), 8.15-8.18 (m, 4H, Ar/Ph-*H*), 8.22-8.25 (m, 2H, Ar/Ph-*H*), 8.29-8.32 (m, 4H, Ar/Ph-*H*), 8.80 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 8.87 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 8.88 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 8.92 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.13 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 9.19 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β), 10.33 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β) 10.43 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 31.7, 35.0, 99.7, 100.0, 100.3, 101.8, 121.1, 121.6, 121.9, 122.3, 122.7, 126.4, 126.6, 127.6, 129.7, 130.8, 131.9, 132.2, 133.2, 134.1, 134.2, 134.3, 140.7, 142.4, 148.8, 149.9, 150.1, 150.5, 152.8 ppm; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 406 (4.86), 473 (4.99), 521 (4.31), 624 (4.37), 716 (4.42) nm; HRMS (ESI) *m/z* calcd. for [C₉₄H₈₁N₈Zn](M+H)⁺: 1385.5930, found 1385.5876.

{5-[(10',20'-Bis(3,5-di-*tert*-butylphenyl)-15'-phenylporphyrinato-5-yl]zinc(II)}ethynyl-10,15,20-triphenylporphyrinato}zinc(II) (171):



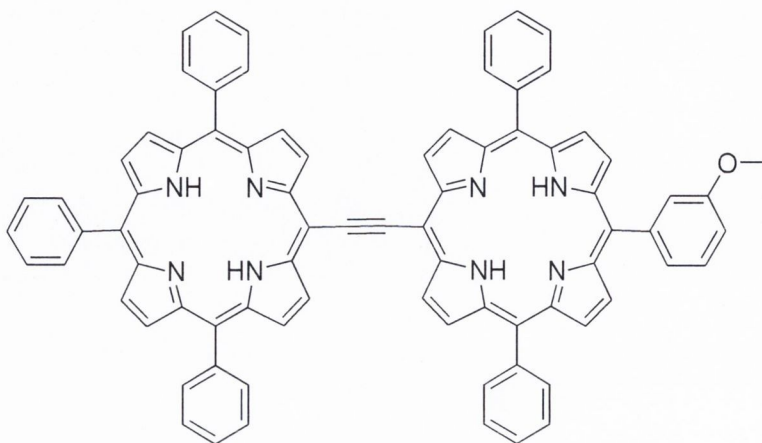
Following procedure I, ethynylporphyrin **157** (28 mg, 0.033 mmol), bromoporphyrin **104** (22 mg, 0.033 mmol), AsPh_3 (15 mg, 0.049 mmol) and $\text{Pd}_2(\text{dba})_3$ (5 mg, 0.005 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred at 65 °C for 16 h. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 4 to 1 : 1, v/v) to yield a red-brown solid. Yield: 25 mg (0.017 mmol, 52%). M.p. >300 °C; R_f = 0.29 (CH_2Cl_2 : *n*-hexane : TEA = 1 : 1 : 0.01, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = 1.59 (s, 36H, *t*-butyl-*H*), 7.70-7.83 (m, 14H, Ar/Ph-*H*), 8.15-8.22 (m, 8H, Ar/Ph-*H*), 8.29-8.32 (m, 4H, Ar/Ph-*H*), 8.89 (s, 2H, H_β), 8.92 (s, 4H, H_β), 8.97 (s, 2H, H_β), 9.18 (s, 2H, H_β), 9.23 (s, 2H, H_β), 10.43 (s, 4H, H_β) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 31.8, 35.1, 121.0, 122.4, 122.8, 123.9, 126.6, 126.7, 127.7, 129.7, 130.7, 131.0, 132.0, 132.3, 132.3, 133.3, 133.6, 134.2, 134.3, 134.4, 141.5, 142.5, 148.8, 150.0, 150.1, 150.3, 150.3, 150.6, 150.9, 152.8, 152.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 413 (4.63), 480 (4.92), 559 (4.22), 690 (4.35) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{94}\text{H}_{78}\text{N}_8\text{Zn}_2](\text{M}+\text{H})^+$: 1447.4935, found 1447.5011.

{5-[(5',10',20'-Trihexylporphyrinato-5-yl)zinc(II)ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrinato}zinc(II) (172):



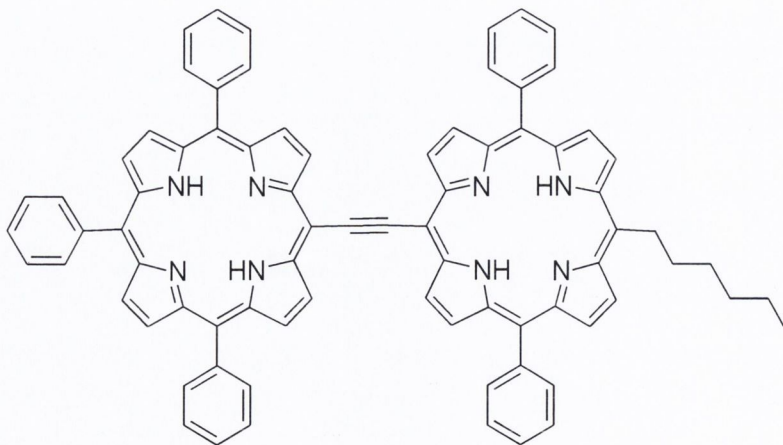
Dimer **166** (11 mg, 0.008 mmol) was dissolved in CHCl_3 (10 mL) and heated to reflux for 10 min. Zinc(II)acetate (100 mg, 0.406 mmol) was dissolved in methanol (2 mL) and both solutions were combined. The mixture was heated to reflux for 30 min. All solvents were removed *in vacuo*, the residue dissolved in CH_2Cl_2 (5 mL) and filtered through a plug of silica. All solvents were removed to yield a red/brown solid. Yield: 8 mg (0.006 mmol, 68%). M.p. $>300^\circ\text{C}$; $R_f = 0.32$ (CH_2Cl_2 : *n*-hexane : TEA = 1 : 1 : 0.01, v/v); ^1H NMR (600 MHz, THF-d_8 , TMS): $\delta = 0.94\text{--}0.99$ (m, 9H, CH_3), $1.42\text{--}1.48$ (m, 6H, CH_2), $1.54\text{--}1.60$ (m, 6H, CH_2), 1.61 (s, 36H, *t*-Bu-*H*), $1.86\text{--}1.94$ (m, 6H, CH_2), $2.54\text{--}2.65$ (m, 6H, CH_2), $5.03\text{--}5.12$ (m, 6H, CH_2), $7.74\text{--}7.78$ (m, 3H, Ar/Ph-*H*), $7.93\text{--}7.95$ (m, 2H, Ar/Ph-*H*), $8.19\text{--}8.25$ (m, 6H, Ar/Ph-*H*), 8.78 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 8.84 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.16 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.57 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.59 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.77 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 10.43 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 10.49 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, THF-d_8): $\delta = 14.5, 23.7, 30.7, 31.2, 32.1, 33.0, 35.8, 40.0, 121.7, 122.0, 122.8, 124.0, 125.9, 127.2, 129.4, 130.6, 130.7, 131.3, 132.5, 133.6, 135.2, 138.2, 143.5, 149.5, 150.2, 150.5, 151.1, 151.2, 151.6, 153.2, 153.7$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 432 (4.45), 479 (4.78), 557 (4.21), 696 (4.38) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{94}\text{H}_{103}\text{N}_8\text{Zn}_2](\text{M}+\text{H})^+$: 1471.6903, found 1471.6889.

5-(5',10',20'-Triphenylporphyrin-5-yl)ethynyl-15-(3-methoxyphenyl)-10,20-diphenylporphyrin (173):^[331]



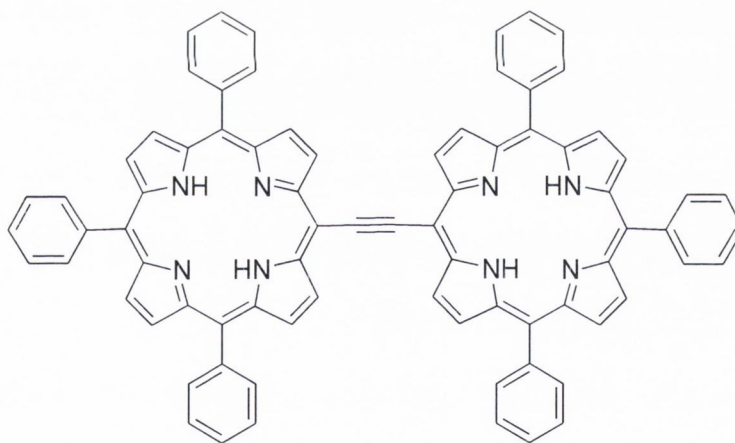
Obtained from ethynylporphyrin **159** (25 mg, 0.042 mmol), bromoporphyrin **83** (26 mg, 0.042 mmol), AsPh₃ (27 mg, 0.089 mmol) and Pd₂(dba)₃ (3.8 mg, 0.004 mmol) using general procedure I to yield a dark green solid following column chromatography CH₂Cl₂ : *n*-hexane (1 : 3, v/v). Yield (18 mg, 0.016 mmol, 38%). M.p. >300 °C; *R*_f = 0.37 (CH₂Cl₂ : *n*-hexane = 3 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.09 (s, 2H, NH), -1.99 (s, 2H, NH), 4.02 (s, 3H, OCH₃), 7.54 (m, 4H, aryl-*H*), 7.84 (m, 16H, aryl-*H*), 8.27 (m, 8H, Ph-*H*), 8.82 (m, 8H, *H*_β), 9.03-9.04 (d, ³*J*_{H-H} = 4.5 Hz, 2H, *H*_β), 9.11-9.12 (d, ³*J*_{H-H} = 4.5 Hz, 2H, *H*_β), 9.95-9.96 (d, ³*J*_{H-H} = 4.8 Hz, 2H, *H*_β), 10.36-10.37 (d, ³*J*_{H-H} = 4.7 Hz, 2H, *H*_β) ppm; UV/vis (THF): λ_{max} (log ε) = 407 (4.89), 471 (5.13), 520 (4.22), 625 (4.40), 712 (4.48) nm; HRMS (ESI) *m/z* calcd. for (C₇₉H₅₂N₈O)(M)⁺: 1128.4264, found 1128.4277.

5-(5'-Hexyl-10',20'-diphenyl-5-yl)ethynyl-10,15,20-triphenylporphyrin (174):



Produced from ethynylporphyrin **151** (30 mg, 0.053 mmol), bromoporphyrin **84** (33 mg, 0.053 mmol), AsPh_3 (34 mg, 0.111 mmol) and $\text{Pd}_2(\text{dba})_3$ (5 mg, 0.004 mmol) using general procedure I to yield a dark solid following column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1 : 3, v/v) (23 mg, 0.340 mmol, 39%). M.p. $>300^\circ\text{C}$; $R_f = 0.29$ (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -1.99$ (s, 2H, NH) -1.93 (s, 2H, NH) 0.91 (t, $^3J_{\text{H-H}} = 15.3$ Hz, 3H, CH_3), 1.76-1.81 (m, 4H, CH_2), 1.84-1.88 (m, 2H, CH_2), 2.58 (m, 2H, CH_2), 5.00 (m, 2H, CH_2), 7.82 (m, 16H, Ph-*H*), 8.30 (m, 12H, Ph-*H*), 8.23-8.36 (m, 4H, H_β), 8.90-8.91 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.05-9.06 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.09-9.11 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.46-9.48 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 10.27-10.29 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 10.33-10.34 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.2, 22.8, 29.4, 29.7, 31.9, 36.0, 126.8, 126.9, 127.9, 134.4, 134.5, 134.6, 141.9$ ppm; UV/Vis (THF): λ_{max} (log ϵ) = 427 (4.79), 472 (5.02), 519 (4.11), 620 (4.24), 714 (4.34) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{78}\text{H}_{59}\text{N}_8](\text{M}+\text{H})^+$ 1107.4904, found 1107.4863.

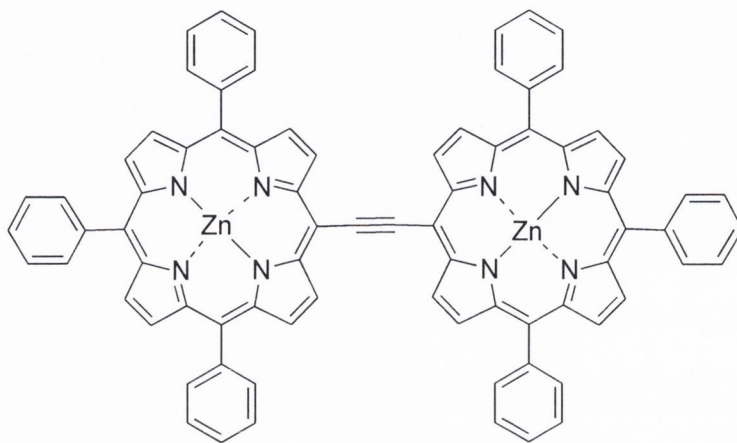
1,2-Bis(5,10,15-triphenylporphyrin-20-yl)ethine (**175**):



Produced from ethynylporphyrin **151** (80 mg, 0.142 mmol), bromoporphyrin **83** (76 mg, 0.142 mmol), AsPh_3 (48 mg, 0.156 mmol) and $\text{Pd}_2(\text{dba})_3$ (13 mg, 0.014 mmol) using general procedure I. The solvent was removed *in vacuo* and the residue filtered through a plug of silica using CH_2Cl_2 : TEA as eluent (99 : 1, v/v), giving a green fraction. After removal of the solvent and recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ a dark powder was obtained (75 mg, 0.068 mmol, 48%). M.p. $>300^\circ\text{C}$; $R_f = 0.37$ (CH_2Cl_2 : *n*-hexane = 5 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -1.96$ (s, 4H, NH) 7.81 (m, 18H, Ph-*H*), 8.23 (m, 6H, Ph-*H*), 8.32 (m, 8H, Ph-*H*), 8.84 (m, 8H, H_β), 9.11-9.13 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 4H, H_β), 10.36-10.38 (d, $^3J_{\text{H-H}} = 4.8$ Hz 4H, H_β) ppm; ^{13}C NMR (150

MHz, THF- d_8): δ = 29.5, 53.3, 126.6, 126.9, 128.0, 134.2, 134.5, 141.6 ppm; UV/vis (THF): λ_{max} ($\log \epsilon$) = 407 (5.04), 472 (5.24), 519 (5.29), 619 (4.44), 712 (4.53) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{78}\text{H}_{51}\text{N}_8](\text{M}+\text{H})^+$: 1099.4255, found 1099.4237.

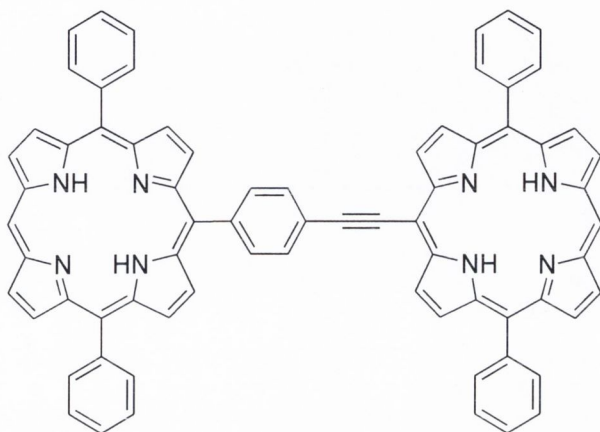
1,2-Bis[5,10,15-triphenylporphyrin-20-ylato}zinc(II)]ethine (176):



Produced from ethynylporphyrin **152** (70 mg, 0.112 mmol), bromoporphyrin **104** (67 mg, 0.112 mmol), AsPh_3 (38 mg, 0.123 mmol) and $\text{Pd}_2(\text{dba})_3$ (10 mg, 0.011 mmol) using general procedure I. The solvent was removed *in vacuo* and the residue filtered through a plug of silica using CH_2Cl_2 : TEA as eluent (99 : 1, v/v), to yield a green fraction. Recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave a dark powder (75 mg, 0.068 mmol, 47%). M.p. > 300 °C; R_f = 0.22 (CH_2Cl_2 : *n*-hexane : TEA = 1 : 1 : 0.01, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 7.83 (m, 20H, Ph-*H*), 8.26 (m, 4H, Ph-*H*), 8.33 (m, 6H, Ph-*H*), 8.95-8.96 (d, $^3J_{\text{H-H}}$ = 4.8 Hz 8H, H_β), 9.23-9.24 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 4H, H_β), 10.51-10.52 (d, $^3J_{\text{H-H}}$ = 4.6 Hz 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 98.8, 99.2, 120.3, 120.7, 124.6, 124.6, 125.7, 128.5, 129.6, 129.8, 130.8, 132.6, 132.8, 141.6, 141.7, 148.1, 148.4, 148.8, 151.1 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 412 (5.18), 479 (5.44), 548 (4.36), 685 (4.74) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{78}\text{H}_{46}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1222.2428, found 1222.2468.

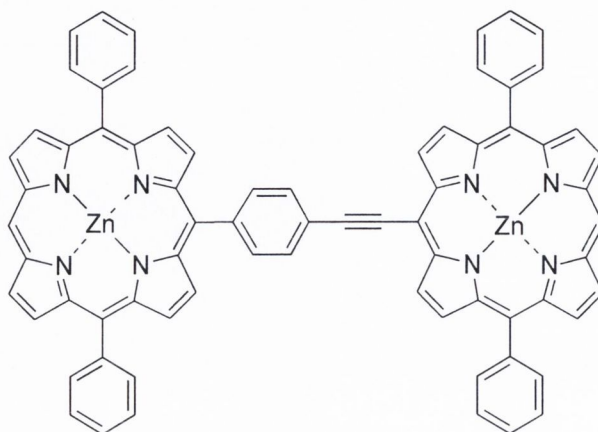
7.3.3 Phenylacetylene linked dimers

4-(10,20-Diphenylporphyrin-5-yl)-phenylethynyl-(10,20-diphenylporphyrin-5-yl) (177):



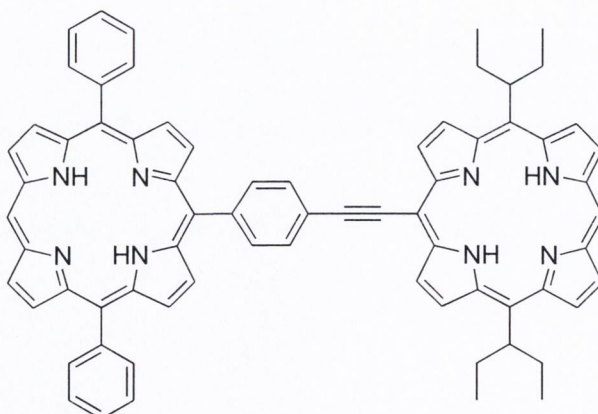
Following the general procedure I, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **62** (30 mg, 0.0533 mmol), 5-bromo-10,20-diphenylporphyrin **94** (32 mg, 0.059 mmol), AsPh₃ (33 mg, 0.106 mmol) and Pd₂(dba)₃ (12 mg, 0.013 mmol) in a mixture of THF (15 mL) and NEt₃ (5 mL) were used. Purification via column chromatography on silica gel (CH₂Cl₂ : *n*-hexane = 1 : 1, v/v) followed by recrystallisation from CH₂Cl₂/CH₃OH gave purple crystals (25 mg, 0.0244 mmol, 46 %). M.p. >300 °C; *R*_f = 0.25 (*n*-hexane : CH₂Cl₂ = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.91 (s, 2H, NH), -2.44 (s, 2H, NH), 7.85 (m, 12H, C₆H₄/Ph-*H*), 8.31 (m, 8H, Ph-*H*), 8.47 (s, 4H, Ph-*H*), 9.01 (m, 4H, *H*_β), 9.08 (m, 6H, *H*_β), 9.33 (d, ³*J*_{H-H} = 4.4 Hz, 2H, *H*_β), 9.39 (d, ³*J*_{H-H} = 4.4 Hz, 2H, *H*_β), 10.05 (d, ³*J*_{H-H} = 4.4 Hz, 2H, *H*_β), 10.22 (s, 1H, *H*_{meso}), 10.28 ppm (s, 1H, *H*_{meso}) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 93.5, 96.6, 96.7, 104.8, 106.4, 119.5, 120.5, 123.4, 126.7, 127.6, 127.7, 128.6, 129.7, 131.1, 134.5, 134.8 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 413 (4.87), 433 (4.92), 511 (3.76), 571 (3.92), 571 (3.92), 602 (3.43), 662 (3.59) nm; HRMS (ESI) *m/z* calcd. for [C₇₂H₄₇N₈](M+H⁺): 1023.3910, found 1023.3924.

5-[(10',20'-Diphenylporphyrinato-5-yl)zinc(II)]-4-phenylethynyl-10,20-diphenylporphyrinato}zinc(II) (178)



Following general procedure I, **178** was produced from phenylethynyl porphyrin **117** (20 mg, 0.032 mmol) and bromoporphyrin **105** (19 mg, 0.032 mmol) to yield a purple product (16 mg, 0.014 mmol, 44%). M.p. >300 °C; R_f = 0.27 (CH_2Cl_2 : n -hexane = 2 : 1, v/v); ^1H NMR (400 MHz $\text{CDCl}_3/\text{pyridine-}d_5$ 10:1, TMS): δ = 7.02 (d, $^3J_{\text{H-H}}$ = 7.3 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.54 (d, $^3J_{\text{H-H}}$ = 7.3 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.25 (m, 2H, Ph- H), 7.86 (10H, m, Ph- H), 8.32 (8H, m, Ph- H), 8.48 (s, 2H, H_β), 9.10 (m, 4H, H_β), 9.17 (m, 4H, H_β), 9.41-9.42 (d, $^3J_{\text{H-H}}$ = 4.3 Hz, 2H, H_β), 9.47-9.48 (d, $^3J_{\text{H-H}}$ = 4.3 Hz, 2H, H_β), 10.11-10.12 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 10.28 (s, 1H, H_{meso}), 10.35 (s, 1H, H_{meso}) ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 419 (4.89), 440 (4.62), 552 (3.75), 617 (3.61) nm; HRMS (Maldi) m/z calcd. for $[\text{C}_{72}\text{H}_{43}\text{N}_8\text{Zn}_2](\text{M}+\text{H})^+$ 1147.2147, found 1147.2135.

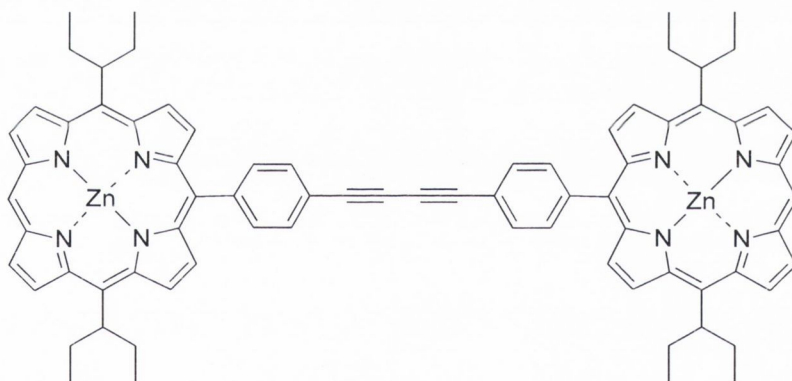
5-[4-(10',20'-Diphenylporphyrin-5-yl)phenylethynyl]-10,20-bis(1-ethylpropyl)porphyrin 179.



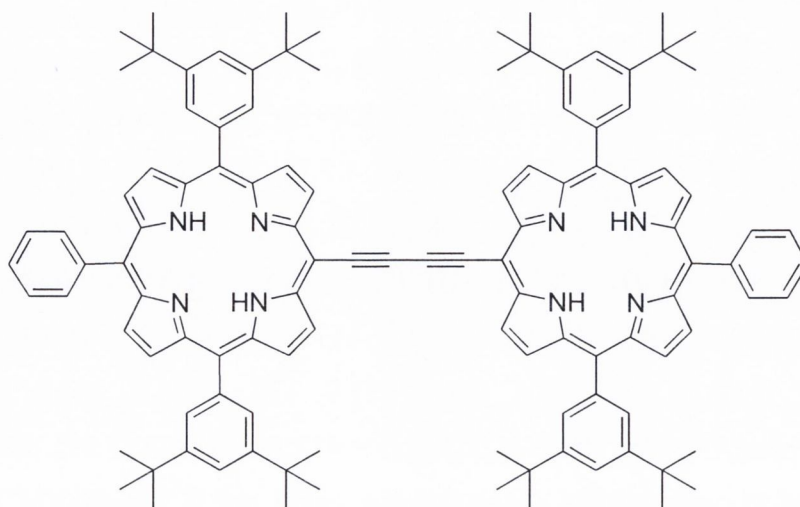
Produced from porphyrin **62** (23 mg, 0.041 mmol) and bromoporphyrin **95** (25 mg, 0.041 mmol), following general procedure I to yield a purple powder (green in solution)

(19 mg, 0.018 mmol, 45%). M.p. >300 °C; R_f = 0.32 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = -2.87 (s, 2H, *NH*), -1.89 (s, 2H, *NH*), 1.03 (t, $^3J_{\text{H-H}}$ = 14.7 Hz, 12H, CH_3), 2.88 (m, 4H, CH_2), 3.02 (m, 4H, CH_2), 5.05 (m, 2H, *CH*), 7.85 (m, 6H, *Ph-H*), 8.31-8.34 (m, 4H, *Ph-H*), 8.49 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 9.04-9.05 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.09-9.12 (dd, $^3J_{\text{H-H}}$ = 13.2, 4.7 Hz, 4H, H_β), 9.36 (m, 2H, H_β), 9.41-9.42 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.67-9.68 (m, 2H, H_β), 9.78-9.79 (m, 2H, H_β), 10.14 (s, 1H, H_{meso}), 10.15 (s, 2H, H_β), 10.30 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 13.9, 29.2, 29.3, 29.5, 30.2, 31.8, 34.1, 45.6, 119.7, 122.3, 123.6, 123.0, 125.4, 126.7, 127.4, 127.6, 128.3, 129.3, 129.6, 131.2, 131.9, 132.1, 134.6, 134.8, 138.5, 139.5, 139.7, 141.6 ppm; UV/vis (THF): λ_{max} (log ϵ) = 412 (6.05), 434 (5.99), 508 (4.97), 572 (5.07), 666 (4.71) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{70}\text{H}_{58}\text{N}_8](\text{M}^+)$ 1010.4784, found 1010.4736.

4,4'-Bis[{10,15-bis(1-ethylpropyl)porphyrinato}zinc(II)]phenyl]-but-1,3-diyne (180):



Homocoupled side product obtained as a purple powder from the synthesis of **189** (11 mg, 0.009 mmol, 21%). M.p. >300 °C; R_f = 0.37 (CH_2Cl_2 : *n*-hexane : MeOH = 2 : 1 : 0.1, v/v); ^1H NMR (400 MHz, CDCl_3): δ = 1.02 (t, $^3J_{\text{H-H}}$ = 14.3 Hz, 24H, CH_3), 2.88 (m, 8H, CH_2), 3.06 (m, 8H, CH_2), 5.09 (m, 4H, *CH*), 8.05-8.07 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.28-8.30 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 9.13-9.14 (d, $^3J_{\text{H-H}}$ = 9.1 Hz, 4H, H_β), 9.47-9.48 (m, 4H, H_β), 9.86 (m, 8H, H_β), 10.19 (s, 2H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.1, 22.5, 29.5, 123.8, 128.5, 130.8, 130.9, 134.4 ppm; UV/vis: λ_{max} (log ϵ) = 420 (5.63), 456 (4.75), 552 (4.40), 592 (3.86), 668 (4.00) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{76}\text{H}_{70}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1222.4306, found 1222.4417.

Bis[5,5']-[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl]porphyrin-but-1,3-diyne (182):

Using the original Sonogashira conditions, 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin **157** (20 mg, 0.025 mmol), 5-bromo-10,15,20-tris(4-methoxyphenyl)porphyrin **90** (16 mg, 0.025 mmol), CuI (4 mg, 0.020 mmol) and PdCl₂(PPh₃)₂ (20 mg, 0.011 mmol) were dried *in vacuo* and then dissolved in degassed NEt₃ (1 mL) and THF (4 mL). After stirring the solution for 15 h at rt all solvents were removed *in vacuo* and the residue purified by column chromatography (silica, CH₂Cl₂: *n*-hexane, 1 : 1, v/v) to yield a green solid. NMR showed that not the desired product was formed, but **157** had undergone reductive coupling to give **182**. Yield: 9 mg (0.006 mmol, 22%). M.p. >300 °C; *R*_f = 0.38 (CH₂Cl₂ : *n*-hexane : TEA = 1 : 1 : 0.05, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -2.00 (s, 4H, NH), 1.59 (s, 72H, *t*-butyl-*H*), 7.73-7.81 (m, 6H, Ph-*H*), 7.85-7.87 (m, 4H, Ph-*H*), 8.13-8.16 (m, 8H, Ph-*H*), 8.21-8.24 (m, 4H, Ph-*H*), 8.79 (d, ³*J*_{H-H} = 4.7 Hz, 4H, *H*_β), 8.84 (d, ³*J*_{H-H} = 4.7 Hz, 4H, *H*_β), 9.07 (d, ³*J*_{H-H} = 4.7 Hz, 4H, *H*_β), 9.96 (d, ³*J*_{H-H} = 4.7 Hz, 4H, *H*_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 31.7, 35.0, 83.6, 85.7, 121.2, 123.0, 126.5, 128.3, 128.5, 129.8, 133.6, 134.2, 139.5, 140.5, 188.9 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 446 (4.79), 476 (4.65), 526 (3.76), 610 (4.08), 708 (4.19) nm; HRMS (ESI) *m/z* calcd. for [C₁₁₂H₁₁₄N₈](M+H)⁺: 1571.9406, found 1571.9456.

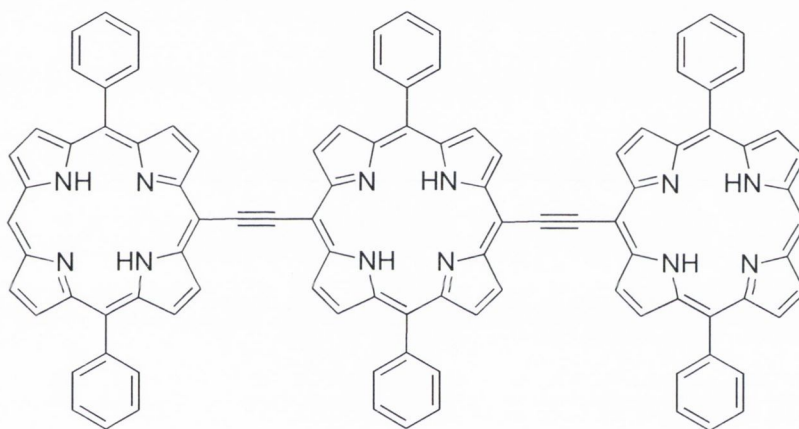
7.3.5 Trimers

General procedure J – Copper-free Sonogashira coupling for porphyrin arrays:

This procedure was adapted from a method by Wagner *et al.*^[126] For the trimers **184-190** monofunctionalised porphyrin (2.1 equiv.) and difunctionalised porphyrin (1

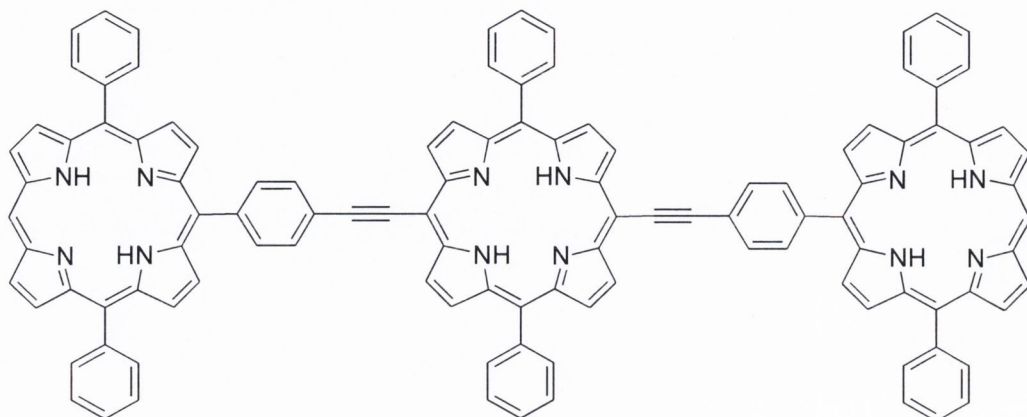
equiv.) were added to a Schlenk tube. To this AsPh_3 (2.1 equiv.) and $\text{Pd}_2(\text{dba})_3$ were added and the contents dried under high vacuum for 30 minutes and the flask was purged with argon. Dry THF (12 mL) and dry TEA (4 mL) were added and the solution was degassed *via* three freeze-pump-thaw cycles. The flask was then purged with argon, stirred, sealed and heated to 67 °C and left to stir overnight. The reaction was monitored by TLC analysis using CH_2Cl_2 : *n*-hexane (1 : 1, v/v) as eluent. On consumption of starting materials the heat source was removed and the solvents removed *in vacuo*. The crude mixture was passed through a silica plug and solvents removed *in vacuo*. Column chromatography was then carried out using different eluents to yield the desired oligomer.

5,15-Bis{10,20-diphenylporphyrin-5-yl}ethynyl}-10,20-diphenylporphyrin (184):



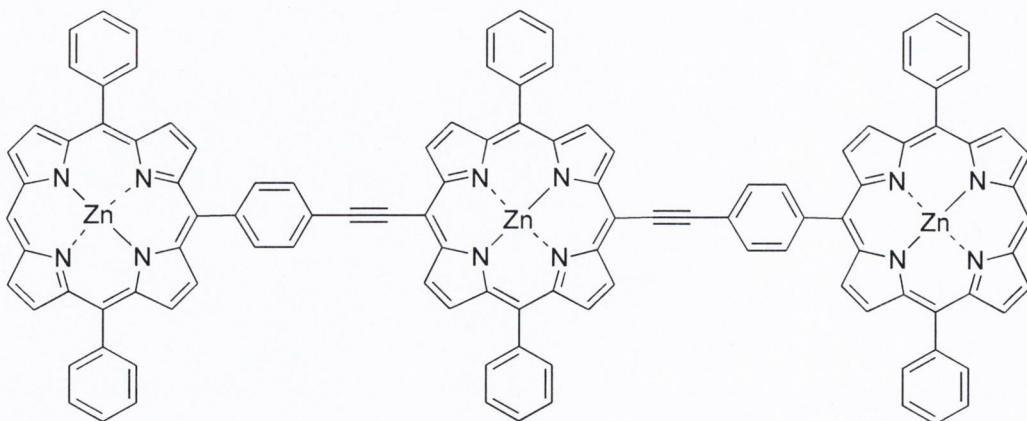
Trimer **130** was generated from bromoporphyrin **94** (40 mg, 0.074 mmol) and ethynylporphyrin **155** (18.0 mg, 0.035 mmol), following general procedure J to yield a purple/brown powder (20 mg, 0.014 mmol, 40%). M.p. >300 °C; R_f = 0.17 (CH_2Cl_2 : *n*-hexane = 10 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 / CF_3COOD 10:1, TMS): δ = 8.16 (m, 12H, Ph-*H*), 8.21 (m, 8H, Ph-*H*), 8.60 (m, 6H, Ph-*H*), 8.71 (m, 4H, Ph-*H*), 9.09-9.10 (dd, $^3J_{\text{H-H}}$ = 4.7, 2.0 Hz, 8H, H_β), 9.17-9.18 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 4H, H_β), 9.54-9.55 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 4H, H_β), 10.11-10.12 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 4H, H_β), 10.20-10.22 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 4H, H_β), 10.89 (s, 2H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3 / CF_3COOD 10:1): δ = 124.6, 125.1, 127.4, 127.6, 128.4, 130.7, 131.2, 137.8, 138.1, 145.9, 146.3 ppm; UV/vis: λ_{max} (log ϵ) = 410 (4.96), 479 (4.96), 634 (4.57), 673 (4.53), 787 (4.45) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{100}\text{H}_{63}\text{N}_{12}](\text{M}+\text{H})^+$: 1431.5236, found 1431.5240.

5,15-Bis{4-(10',20'-diphenylporphyrin-5-yl)phenylethyne}-10,20-diphenylporphyrin (185):



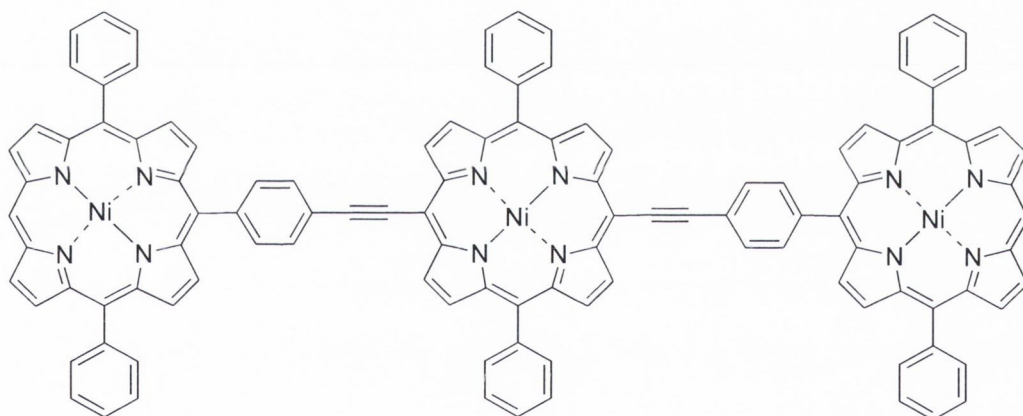
Trimer **185** was obtained from phenylethynylporphyrin **62** (48 mg, 0.086 mmol) and bromoporphyrin **98** (25 mg, 0.040 mmol), following general procedure J to yield a purple powdered product (24 mg, 0.015 mmol, 38%). M.p. >300 °C; R_f = 0.20 (CH₂Cl₂ : *n*-hexane : MeOH = 2 : 1 : 0.1, v/v); ¹H NMR (600 MHz, CDCl₃/CF₃COOD, 10:1, TMS): δ = 8.10 (m, 18H, Ph-*H*), 8.60 (m, 12H, Ph-*H*), 8.79-8.80 (d, ³ J_{H-H} = 7.6 Hz, 4H, C₆H₄-*H*), 8.83-8.85 (d, ³ J_{H-H} = 7.6 Hz, 4H, C₆H₄-*H*), 8.88-8.90 (d, ³ J_{H-H} = 4.7 Hz, 4H, *H* _{β}), 8.93-8.95 (m, 8H, *H* _{β}), 9.10-9.11 (d, ³ J_{H-H} = 4.7 Hz, 4H, *H* _{β}), 9.50-9.51 (d, ³ J_{H-H} = 4.5 Hz, 4H, *H* _{β}), 9.71-9.72 (d, ³ J_{H-H} = 4.5 Hz, 4H, *H* _{β}), 10.75 (s, 2H, *H*_{meso}) ppm; ¹³C NMR (150 MHz, CDCl₃/CF₃COOD 10:1): δ = 128.2, 128.5, 128.6, 129.2, 130.3, 130.4, 130.6, 130.8, 132.3, 138.1, 138.3, 138.9 ppm; UV/vis: λ_{max} (log ϵ) = 412 (5.10), 446 (5.02), 508 (4.70), 602 (4.60), 634 (4.56), 710 (4.51) nm; HRMS (MALDI) *m/z* calcd. for [C₁₁₂H₇₀N₁₂](M⁺) 1582.5846, found 1582.5859.

{5,15-Bis[4-(10',20'-diphenylporphyrinato-5-yl)zinc(II)}phenylethyne]-10,20-di[phenylporphyrin-5-ylato}zinc(II) (186):



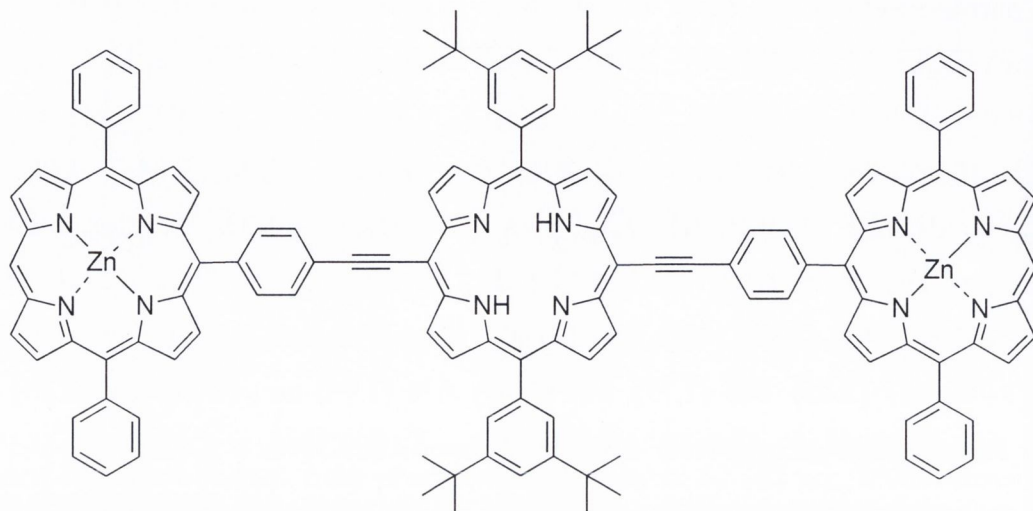
Synthesized from phenylethynylporphyrin **117** (39 mg, 0.061 mmol) and bromoporphyrin **107** (20 mg, 0.029 mmol), following general procedure J to yield a dark purple solid (14 mg, 0.007 mmol, 26%). M.p. >300 °C; R_f = 0.27 (CH₂Cl₂ : *n*-hexane : TEA = 1 : 1, 0.05 v/v); ¹H NMR (400 MHz, CDCl₃/pyridine-*d*₅ 10:1, TMS): δ = 7.78 (m, 18H, Ph-*H*), 8.28 (d, ³*J*_{H-H} = 7.3 Hz, 12H, Ph-*H*), 8.41 (m, 8H, C₆H₄-*H*), 8.98 (m, 8H, *H* _{β}), 9.07 (m, 8H, *H* _{β}), 9.36-9.37 (d, ³*J*_{H-H} = 8.1 Hz, 4H, *H* _{β}), 9.94-9.95 (d, ³*J*_{H-H} = 4.6 Hz, 4H, *H* _{β}), 10.19 (s, 2H, *H*_{meso}) ppm; ¹³C NMR (150 MHz, CDCl₃/pyridine-*d*₅ 10:1): δ = 45.6, 52.8, 63.2, 123.3, 127.0, 127.1, 129.3, 131.4, 131.6, 131.7, 132.1, 132.2, 132.5, 134.4, 134.6, 143.3, 149.3, 149.6 ppm; UV/vis: $\lambda_{\max}$ (log ϵ) = 418 (4.05), 451 (3.79), 551 (2.95), 605 (2.75), 659 (2.97), 698 (1.94) nm; HRMS (MALDI) *m/z* calcd. for [C₁₁₂H₆₅N₁₂Zn₃](M+H)⁺ 1769.3372, found 1769.3369.

{5,15-Bis[4-(10',20'-diphenylporphyrinato-5-yl)nickel(II)]phenylethynyl}-{10,20-diphenylporphyrinato}nickel(II) (187):^[332]



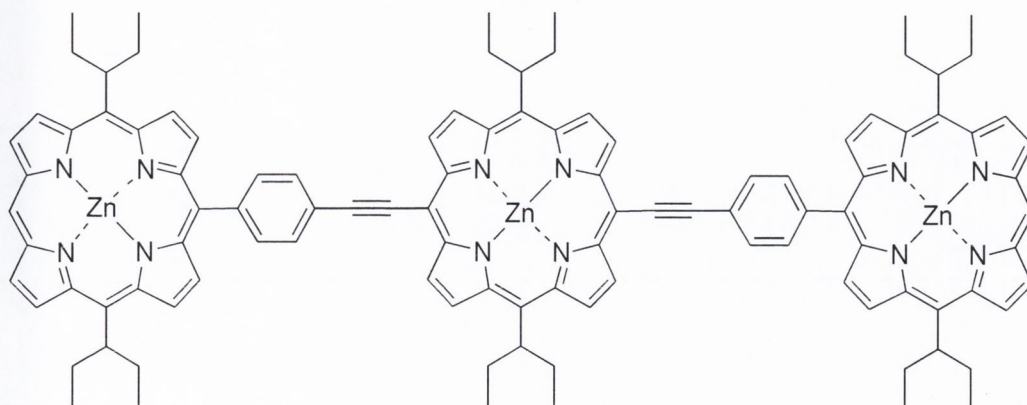
Synthesised from phenylethynylporphyrin **125** (20 mg, 0.032 mmol) and bromoporphyrin **126** (10 mg, 0.015 mmol), following general procedure J to yield an impure dark solid containing **187**. HRMS (MALDI) *m/z* calcd. for [C₁₁₂H₆₄N₁₂Ni₃](M⁺) 1750.3437, found 1750.3448.

{5,15-Bis[4-[(10',20'-diphenylporphyrinato)zinc(II)]phenylethynyl]-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (188):



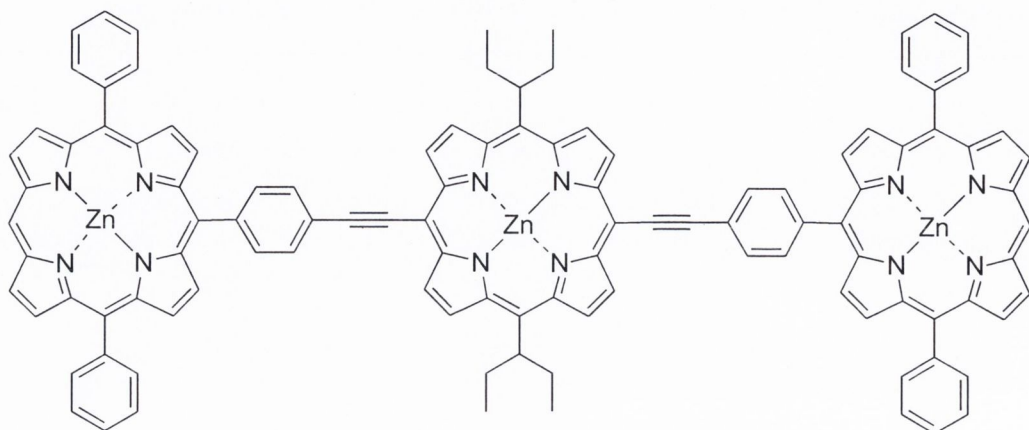
Produced from phenylethynylporphyrin **117** (31 mg, 0.050 mmol) and bromoporphyrin **100** (20 mg, 0.024 mmol), according to general procedure J, to yield a dark green solid (13 mg, 0.006 mmol, 28%). M.p. >300 °C; R_f = 0.33 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$ 10:1, TMS): δ = -1.73 (s, 2H, NH), 1.56 (s, 36H, *t*-butyl-*H*) 7.73 (m, 12H, Ph-*H*), 7.84 (m, 4H, C_6H_4 -*H*), 8.12-8.13 (m, 4H, C_6H_4 -*H*), 8.23 (m, 8H, Ar/Ph-*H*), 8.38 (m, 6H, Ar/Ph-*H*), 8.97 (m, 8H, H_β), 9.01-9.02 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 4H, H_β), 9.04-9.05 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 4H, H_β), 9.31-9.32 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 4H, H_β), 9.90-9.91 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 4H, H_β), 10.14 (s, 2H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$, 10:1): δ = 13.9, 22.4, 31.4, 34.9, 120.0, 126.2, 127.0, 129.4, 129.8, 131.2, 131.4, 131.6, 132.1, 134.5, 134.9, 143.2 ppm; UV/vis: λ_{max} (log ϵ) = 418 (4.55), 447 (4.39), 551 (3.32), 610 (3.57), 698 (3.35) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{128}\text{H}_{99}\text{N}_{12}\text{Zn}_3](\text{M}+\text{H})^+$ 1931.6620, found 1931.662.

{5,15-Bis[4-(10',20'-bis(1-ethylpropyl)porphyrinato-5-yl)zinc(II)]phenylethynyl-10,20-bis(1-ethylpropyl)porphyrinato}zinc(II) (189):



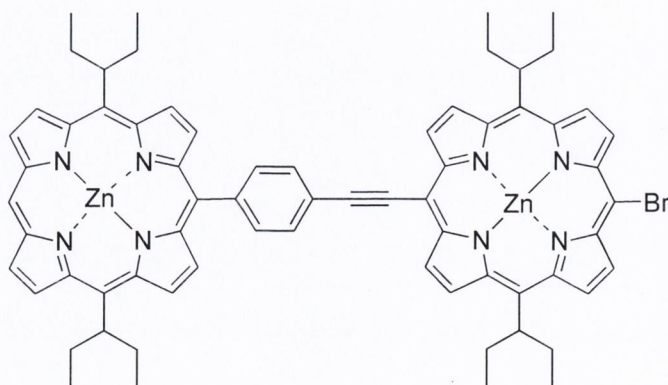
Produced from phenylethynylporphyrin **121** (58 mg, 0.094 mmol) and bromoporphyrin **114** (30 mg, 0.045 mmol) following general procedure J. Column chromatography gave two main fractions, the first of which was the homocoupled side product **181** and the second of which was **189**. Solvents removed to give a purple product (green in solution). Yield (34 mg, 0.020 mmol, 44%). M.p. >300 °C; R_f = 0.40 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (600 MHz, THF-d_8 , TMS): δ = 1.02 (t, $^3J_{\text{H-H}}$ = 14.6 Hz, 36H, CH_3), 2.93 (m, 12H, CH_2), 3.16 (m, 12H, CH_2), 5.35 (m, 6H, CH), 8.50-8.51 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.54-8.55 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 9.12-9.14 (d, $^3J_{\text{H-H}}$ = 9.2 Hz, 4H, H_β), 9.44 (m, 4H, H_β), 9.88-9.90 (m, 12H, H_β), 10.10 (m, 4H, H_β), 10.13 (s, 2H, H_β) ppm; ^{13}C NMR (150 MHz, THF-d_8): δ = 13.3, 20.2, 28.8, 29.6, 34.7, 45.1, 50.2, 124.9, 129.4, 129.9, 130.2, 130.5, 130.8, 131.1, 131.3, 134.8, 142.1, 144.5, 146.7, 147.7, 148.0, 148.8, 149.1, 149.3, 149.7, 151.6, 152.2, 152.4 ppm; UV/vis: λ_{max} (log ϵ) = 418 (5.41), 454 (5.32), 554 (4.22), 668 (4.59) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{128}\text{H}_{98}\text{N}_{12}\text{Zn}_3](\text{M}^+)$: 1732.6068, found 1732.6035.

{5,15-Bis[4-(10',20'-diphenylporphyrinato-5-yl)zinc(II)]phenylethynyl-10,20-bis(1-ethylpropyl)porphyrinato}zinc(II) (190):



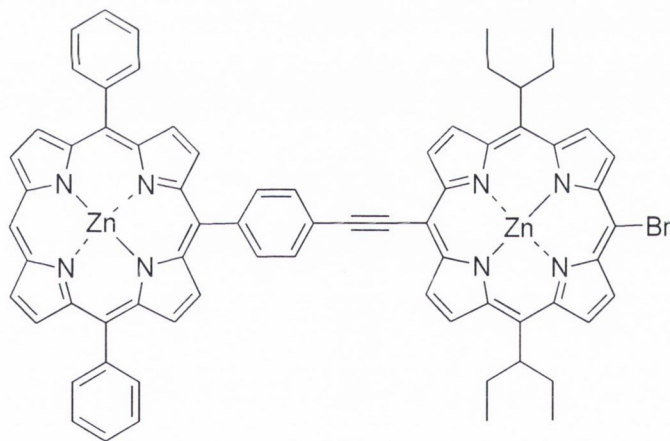
Produced from phenylethynylporphyrin **117** (20 mg, 0.032 mmol) and bromoporphyrin **114** (10 mg, 0.015 mmol) following general procedure J to yield a dark green product (bright green in solution). Yield (6 mg, 0.003 mmol, 21%). M.p. >300 °C; R_f = 0.35 (CH_2Cl_2 : n -hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.98 (t, 12H, $^3J_{\text{H-H}}$ = 14.6 Hz, CH_3), 2.89 (m, 4H, CH_2), 3.07 (m, 4H, CH_2), 5.16 (m, 2H, CH), 7.67 (s, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.80 (m, 12H, Ph-H), 8.29 (m, 8H, Ph-H), 8.43-8.44 (d, $^3J_{\text{H-H}}$ = 3.5 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 9.03-9.04 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 4H, H_β), 9.07-9.08 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 4H, H_β), 9.11-9.13 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 4H, H_β), 9.38-9.39 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 4H, H_β), 9.79 (m, 4H, H_β), 10.00 (m, 4H, H_β), 10.20 (s, 2H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.6, 35.1, 50.8, 106.0, 126.5, 127.3, 129.7, 131.2, 132.0, 132.8, 134.0, 134.8, 135.2 ppm; UV/vis (THF): λ_{max} ($\log \epsilon$) = 422 (5.63), 457 (5.20), 554 (4.14), 673 (4.20) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{110}\text{H}_{76}\text{N}_{12}\text{Zn}_3](\text{M}^+)$: 1756.4190, found 1756.4214.

{5-Bromo-10,20-bis(1-ethylpropyl)-15-{4-[(10',20'-bis(1-ethylpropyl)porphyrinato)zinc(II)]phenylethynyl}porphyrinato}zinc(II) (192):



Produced as a side product from the synthesis of **189**, via Sonogashira conditions (general procedure F) using phenylethynylporphyrin **121** (48 mg, 0.078 mmol) and bromoporphyrin **114** (25 mg, 0.037 mmol) to yield a purple solid (18 mg, 0.015 mmol, 40%). M.p. >300 °C; $R_f = 0.35$ (CH_2Cl_2 : n -hexane = 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): $\delta = 1.02$ (t, $^3J_{\text{H-H}} = 14.5$ Hz, 24H, CH_3), 2.88 (m, 8H, CH_2), 3.06 (m, 8H, CH_2), 5.21 (m, 2H, CH), 5.23 (m, 2H, CH), 7.55 (s, 1H, C_6H_4 -H), 7.72 (s, 1H, C_6H_4 -H), 8.04-8.06 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 1H, C_6H_4 -H), 8.28-8.30 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 1H, C_6H_4 -H), 9.18-9.20 (m, 2H, H_β), 9.47-9.48 (m, 2H, H_β), 9.69-9.93 (m, 10H, H_β), 10.07 (m, 2H, H_β), 10.18 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.1, 14.2, 22.5, 22.8, 29.5, 34.7, 50.4, 123.4, 123.6, 125.8, 128.7, 129.4, 130.7, 131.3, 131.6, 132.8, 134.3, 134.6, 143.7, 149.4, 152.3$ ppm; UV/vis: λ_{max} (log ϵ) = 418 (5.19), 444 (5.21), 554 (4.03), 640 (4.29) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{68}\text{H}_{65}\text{N}_8\text{Zn}_2\text{Br}](\text{M}^+)$: 1200.3098, found 1200.3135.

{5-Bromo-10,20-bis(1-ethylpropyl)-15-[4-[10',20'-diphenylporphyrinato-5-yl]zinc(II)]phenylethynyl}porphyrinato}zinc(II) (193**):**



Produced from phenylethynylporphyrin **117** (39 mg, 0.063 mmol) and bromoporphyrin **114** (20 mg, 0.030 mmol) using Sonogashira conditions (procedure F) to yield a purple solid (15 mg, 0.013 mmol, 42%). M.p. >300 °C; $R_f = 0.41$ (CH_2Cl_2 : n -hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 0.97$ (t, $^3J_{\text{H-H}} = 14.8$ Hz, 12H, CH_3), 2.86 (m, 4H, CH_2), 3.02 (m, 4H, CH_2), 5.12 (m, 2H, CH), 7.82 (m, 6H, Ph-H), 8.32 (m, 4H, Ph-H), 8.45 (m, 4H, C_6H_4 -H), 9.02-9.04 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.07-9.08 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 9.11-9.12 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.37-9.38 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 9.71 (m, 6H, H_β), 9.99 (s, 2H, H_β), 10.20 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.0, 29.5, 34.7, 50.3, 120.2, 126.2, 127.1, 129.3, 130.7, 131.5,$

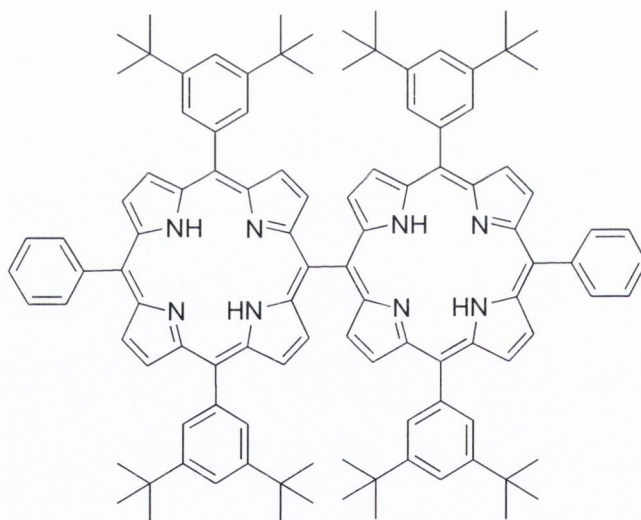
131.7, 132.3, 134.5, 134.8, 143.1, 145.8, 149.1, 149.4, 149.7, 149.9, 150.1 ppm; UV/vis: λ_{max} ($\log \epsilon$) = 420 (5.49), 444 (5.46), 552 (4.33), 640 (4.54) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{70}\text{H}_{53}\text{N}_8\text{Zn}_2\text{Br}](\text{M})^+$: 1212.2159, found 1212.2184.

7.4 Fused arrays

7.4.1 Directly linked arrays via organolithium, PIFA oxidation and Suzuki coupling

Porphyrins **194**^[207] and **195**^[207] were synthesised via organolithium methods and spectroscopic data was in agreement with those in the literature. Dimer **201**^[157] was synthesised via oxidative methods using PIFA and spectroscopic data agreed with literature data.

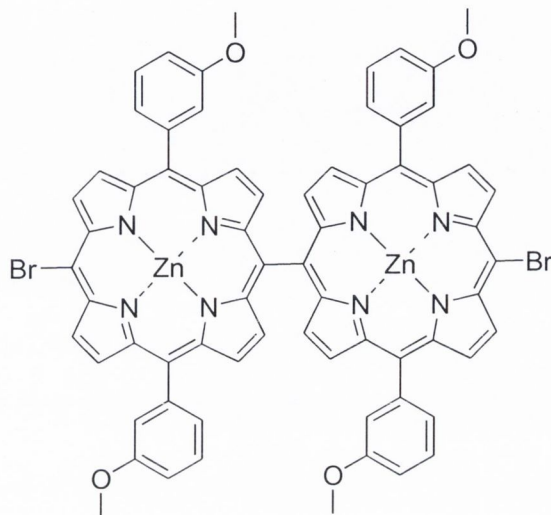
Bis{(5-phenyl-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin-15-yl) (196):



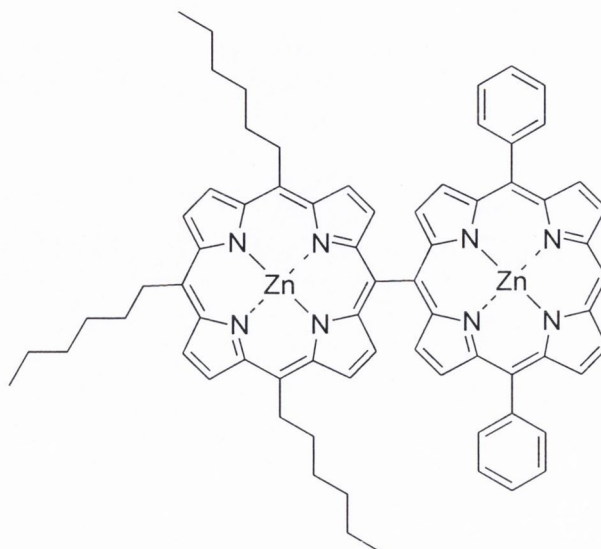
Synthesised from 5,15-di(3,5-di-*tert*-butyl)phenylporphyrin **74** (60 mg, 0.010 mmol), PhLi **52**. DDQ (113 mg, 0.498 mmol) in THF (15 mL) added and reaction stirred for a further 1 h at room temperature. Reaction mixture filtered through a short plug of silica using CH_2Cl_2 as eluent. Solvents were removed and residue recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to yield **196** a dark solid (48 mg, 0.040 mmol, 79%). M.p. $>300^\circ\text{C}$; R_f = 0.39 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = -2.13 (s, 4H, NH), 1.46 (s, 72H, *t*-butyl-*H*), 7.72 (s, 4H, C_6H_3 -*H*), 7.83 (m, 6H, Ph-*H*) 8.09 (m, 12 H, C_6H_3 -*H/H}_\beta*), 8.32-8.34 (d, $^3J_{\text{H-H}}$ = 6.4 Hz, 4H, Ph-*H*), 8.74 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 4H, H_β), 8.94 (s, 8H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 31.5, 102.6, 117.5, 120.6, 120.9, 122.2, 126.5, 127.6, 129.5, 129.8, 134.3, 140.8, 142.3, 148.5 ppm; UV/vis

(CH₂Cl₂): $\lambda_{\max}$ (log ϵ) = 420 (5.24), 452 (5.17), 526 (4.54), 596 (4.14), 654 (3.94) nm; HRMS (MALDI) m/z calcd. for [C₁₀₈H₁₁₄N₈](M⁺): 1522.9166, found 1522.9108.

Bis{5-bromo-10,20-bis(3-methoxyphenyl)porphyrin-15-ylato}zinc(II)} (202):

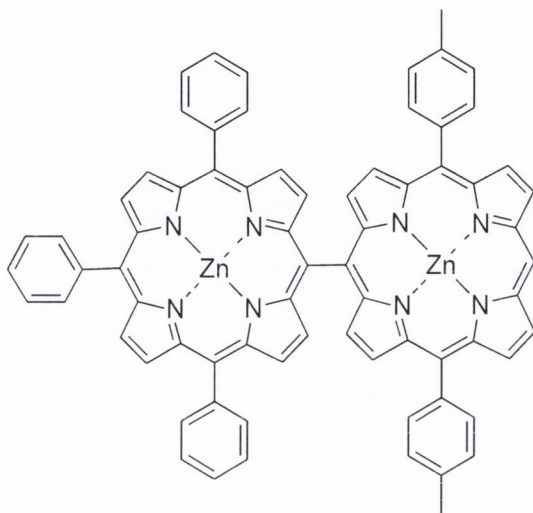


Synthesised from 5-bromo-10,20-(3-methoxyphenyl)porphyrinatozinc(II) **110** (50 mg, 0.075 mmol) in CH₂Cl₂ (120 mL). PIFA (26 mg, 0.06 mmol) was added at -78 °C, the reaction mixture was warmed to rt and stirred at this temperature for 45 min. NaBH₄ (14 mg, 0.375 mmol) in MeOH (5 mL) was added and the reaction stirred for a further 0.75 h. Reaction mixture added to H₂O (100 mL) and organic layer extracted using CH₂Cl₂. Organic layer then washed with NaHCO₃ (2 × 50 mL), H₂O (30 mL) and dried over Na₂SO₄, which was then filtered and solvents removed *in vacuo*. The red residue was recrystallised from CH₂Cl₂/*n*-hexane to give a purple solid (43 mg, 0.032 mmol, 86%). M.p. >300 °C; R_f = 0.40 (CH₂Cl₂ : *n*-hexane = 3 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.89 (s, 12H, OCH₃), 7.22-7.24 (d, ³ $J_{\text{H-H}}$ = 8.6 Hz, 4H, C₆H₄-H), 7.55-7.56 (t, ³ $J_{\text{H-H}}$ = 15.9 Hz, 4H, C₆H₄-H), 7.73 (m, 4H, C₆H₄-H), 7.79-7.80 (d, ³ $J_{\text{H-H}}$ = 7.8 Hz, 4H, C₆H₄-H), 8.07-8.08 (d, ³ $J_{\text{H-H}}$ = 4.7 Hz, 4H, H_β), 8.66-8.67 (d, ³ $J_{\text{H-H}}$ = 4.7 Hz, 4H, H_β), 9.09-9.10 (d, ³ $J_{\text{H-H}}$ = 4.7 Hz, 4H, H_β), 9.86-9.87 (d, ³ $J_{\text{H-H}}$ = 4.7 Hz, 4H, H_β) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 55.4, 105.4, 113.5, 120.3, 122.3, 127.4, 127.5, 132.3, 133.2, 134.2, 143.5, 149.7, 150.0, 151.0, 155.2, 157.8 ppm; UV/vis (CH₂Cl₂): $\lambda_{\max}$ (log ϵ) = 421 (5.26), 455 (5.16), 562 (4.52) nm; HRMS (MALDI) m/z calcd. for [C₆₈H₄₄Br₂N₈O₄Zn₂](M⁺): 1322.0435, found 1322.0432.

{5,10,15-Trihexyl-20-(10',20'-diphenylporphyrin-5'-yl)porphyrinato}zinc(II) (203):

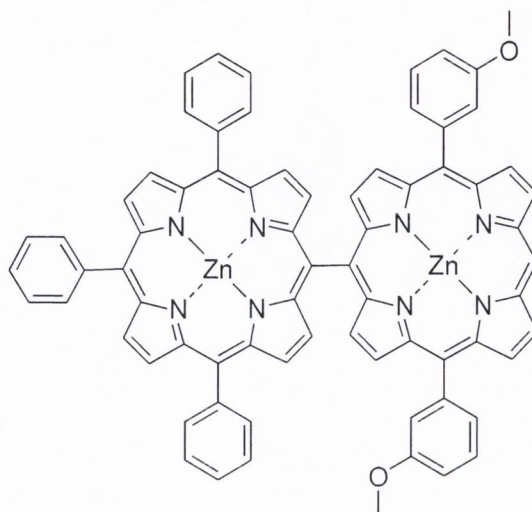
Produced from **133** (50 mg, 0.066 mmol), **103** (40 mg, 0.066 mmol), Cs_2CO_3 (45 mg, 0.139 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 0.007 mmol), DMF (3 mL) and toluene (7 mL) following general procedure H to give a purple solid. Yield = 39 mg (0.034 mmol, 52%). M.p. >300 °C; R_f = 0.53 (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^1H NMR (400 MHz, CDCl_3): δ = 0.88-0.93 (t, $^3J_{\text{H-H}}$ = 14.6 Hz, 9H, CH_3), 1.38 (m, 6H, CH_2), 1.59 (m, 6H, CH_2), 1.85 (m, 6H, CH_2), 2.57 (m, 6H, CH_2), 4.81-4.85 (t, $^3J_{\text{H-H}}$ = 16.4 Hz, 2H, CH_2), 4.88-4.92 (t, $^3J_{\text{H-H}}$ = 15.7 Hz, 4H, CH_2), 7.72 (m, 6H, Ph-*H*), 8.08-8.09 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 8.21-8.23 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 8.30 (m, 4H, Ph-*H*), 8.75-8.76 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.17-9.18 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.21-9.23 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.43-9.44 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.51 (m, 4H, H_β), 10.38 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.1, 14.2, 22.7, 22.8, 28.7, 30.4, 31.9, 32.0, 35.5, 35.8, 38.9, 39.1, 117.6, 119.4, 121.1, 121.4, 126.6, 127.4, 128.5, 128.6, 128.7, 128.8, 129.1, 129.2, 131.4, 131.8, 132.5, 134.0, 134.1, 134.5, 142.6, 148.5, 148.9, 149.4, 149.8, 150.1, 150.6, 154.4, 154.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 413 (5.33), 450 (5.10), 559 (4.37) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{70}\text{H}_{66}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1146.3993, found 1146.4038.

{5-(10',15',20'-Triphenylporphyrin-5'-ylato)-10,20-di(4-methylphenyl)porphyrinato}zinc(II) (204**):**



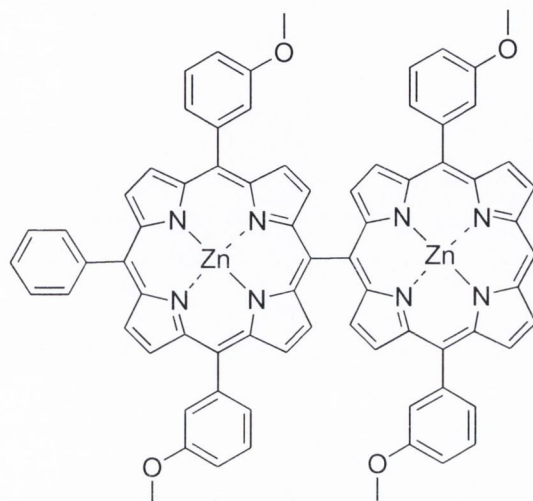
Synthesised from bromo-porphyrin **108** (70 mg, 0.110 mmol), borylated porphyrin **129** (80 mg, 0.110 mmol), Cs_2CO_3 (90 mg, 0.275 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (19 mg, 0.017 mmol), DMF (4 mL) and toluene (10 mL) following general procedure H. The residue was subjected to column chromatography (silica gel, CH_2Cl_2 : *n*-hexane, 2 : 3, v/v) to give two fractions. The first fraction contained a mixture of debrominated **108** and deborylated **129**, the second (red fraction) was dimer **204**. Solvents were removed to give a purple solid. Yield = 97 mg (0.084 mmol, 76%). M.p. >300 °C; R_f = 0.58 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$ 10:1): δ = 2.64 (s, 6H, tolyl- CH_3), 7.47-7.49 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.64 (m, 9H, Ph- H), 7.80-7.81 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 7.86-7.87 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 8.12-8.14 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 8.21 (m, 6H, Ph- H), 8.49-8.51 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 8.60-8.61 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 8.92-8.93 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 8.95-8.96 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.10-9.11 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 2H, H_β), 9.41-9.42 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 2H, H_β), 10.24 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$ 10:1): δ = 22.7, 105.9, 119.9, 120.8, 121.1, 121.3, 126.2, 126.3, 127.0, 127.2, 131.2, 131.4, 131.6, 132.0, 133.5, 133.6, 134.5, 134.6, 136.6, 140.4, 143.5, 143.7, 149.5, 149.6, 149.7, 150.0, 150.4, 150.6, 154.5, 154.9, 155.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 413 (5.16), 449 (5.18), 555 (4.53) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{72}\text{H}_{46}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1150.2428, found 1150.2389.

{5-(10',20'-Bis(3-methoxyphenyl)porphyrin-5'-ylato)-10,15,20-triphenylporphyrinato}zinc(II) (205):



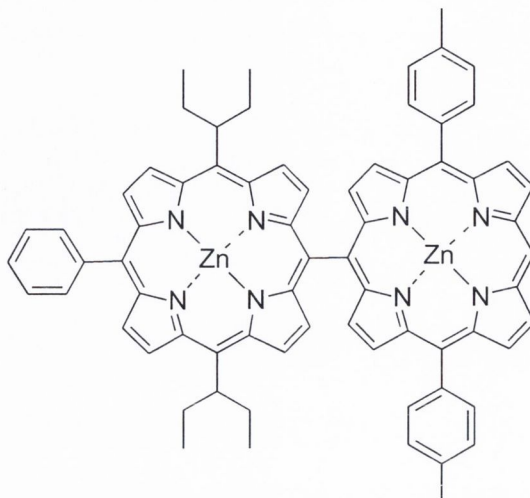
Produced from bromoporphyrin **110** (73 mg, 0.110 mmol), borylated porphyrin **129** (80 mg, 0.110 mmol), Cs_2CO_3 (90 mg, 0.275 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (19 mg, 0.017 mmol), DMF (3 mL) and toluene (10 mL) following general procedure H. The residue was subjected to column chromatography to give four fractions. Fraction one was borylated starting material **129**, fraction two was dimer **210** (19%), fraction three contained debrominated **110** and fraction four yielded the desired dimer. Solvents were removed *in vacuo* to give a purple solid (78 mg, 0.066 mmol, 60%). M.p. $>300^\circ\text{C}$; $R_f = 0.46$ (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.91$ (d, $^3J_{\text{H-H}} = 1.8$ Hz, 6H, OCH_3), 7.23-7.26 (dd, $^3J_{\text{H-H}} = 8.2, 2.4$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.58-7.62 (t, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.83 (m, 11H, Ph/ $\text{C}_6\text{H}_4\text{-H}$), 8.12-8.15 (q, $^3J_{\text{H-H}} = 12.1$ Hz, 2H, H_β), 8.18-8.19 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 8.25 (m, 6H, Ph-*H*), 8.35 (m, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.78-8.80 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.03-9.04 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.06-9.07 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.21-9.22 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.50-9.51 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.96-9.97 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 10.40 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.4, 106.7, 113.4, 119.9, 120.3, 121.2, 121.9, 126.5, 126.6, 127.3, 127.6, 131.9, 132.0, 132.2, 132.9, 134.0, 134.4, 134.5, 142.7, 142.9, 143.9, 149.7, 149.8, 149.9, 150.2, 150.6, 150.7, 154.7, 155.0, 157.8$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 417 (5.57), 450 (4.87), 549 (4.41) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{72}\text{H}_{46}\text{N}_8\text{O}_2\text{Zn}_2](\text{M}^+)$: 1182.2327, found 1182.2358.

{5-(10',20'-Bis(3-methoxyphenyl)porphyrin-15'-ylato)-10,20-bis(3-methoxyphenyl)-15-phenylporphyrinato}zinc(II) (206**):**



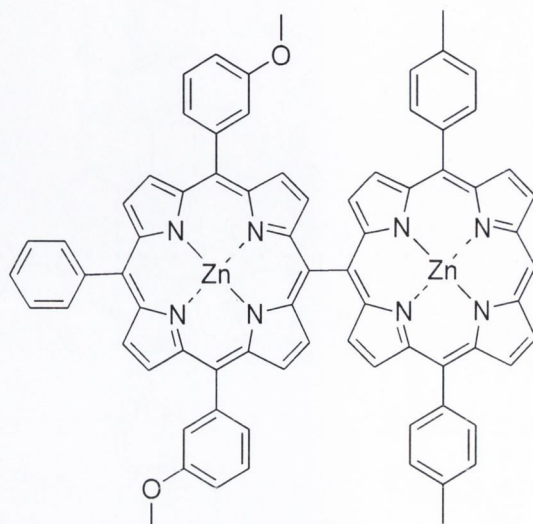
Produced from bromoporphyrin **110** (71 mg, 0.097 mmol), borylated porphyrin **131** (80 mg, 0.102 mmol), Cs_2CO_3 (70 mg, 0.214 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (12 mg, 0.010 mmol), DMF (3 mL) and toluene (10 mL) following general procedure H. The residue was subjected to column chromatography (silica, CH_2Cl_2 : *n*-hexane, 2 : 1, v/v) to give two fractions. Fraction one consisted of debrominated and deborylated starting materials. The red second fraction yielded dimer **206**. Solvents were removed *in vacuo* to give a purple solid (71 mg, 0.057 mmol, 56%). M.p. >300 °C; R_f = 0.39 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): δ = 3.92 (s, 8H, OCH_3), 3.95 (s, 4H, OCH_3) 7.23 (m, 2H, C_6H_4 -*H*), 7.25 (m, 2H, C_6H_4 -*H*), 7.58 (m, 4H, C_6H_4 -*H*), 7.84 (m, 11H, $\text{Ph}/\text{C}_6\text{H}_4$ -*H*), 8.12 (m, 4H, H_β), 8.33 (m, 2H, Ph -*H*), 8.72 (m, 2H, H_β), 8.78 (m, 2H, H_β), 9.06 (m, 4H, H_β), 9.22-9.23 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 2H, H_β), 9.52-9.53 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 10.42 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 55.5, 106.7, 113.4, 113.5, 119.6, 120.1, 120.3, 121.2, 121.7, 121.9, 126.6, 127.3, 127.4, 127.5, 127.6, 131.9, 132.0, 132.5, 133.9, 134.5, 142.9, 143.9, 144.0, 149.7, 149.9, 150.2, 150.6, 154.6, 155.0, 157.8, 157.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 420 (5.32), 455 (5.14), 558 (4.36) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{74}\text{H}_{50}\text{N}_8\text{O}_4\text{Zn}_2](\text{M}^+)$: 1242.2538, found 1242.2524.

{5-(10',20'-Bis(4-methylphenyl)porphyrin-15'-ylato)-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (207**):**



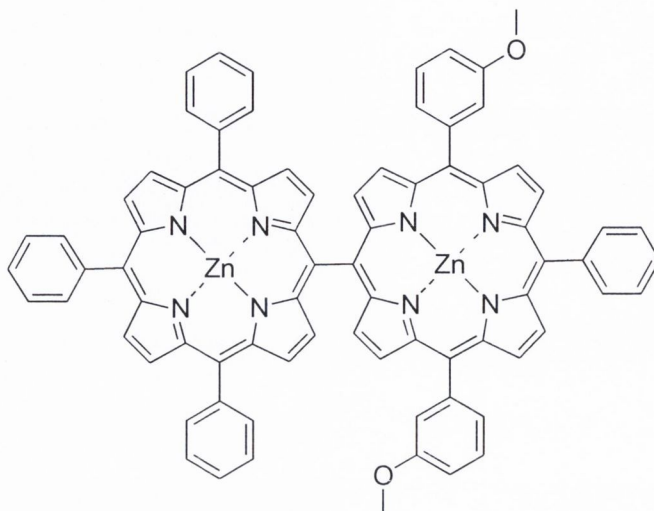
Produced from bromoporphyrin **113** (76 mg, 0.114 mmol), borylated porphyrin **130** (78 mg, 0.114 mmol), Cs_2CO_3 (78 mg, 0.239 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (13 mg, 0.011 mmol), DMF (3 mL) and toluene (10 mL) following general procedure H. After 20 h at 90 °C, the solvents were removed and the residue was filtered through short plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* and the residue was subjected to column chromatography (silica, CH_2Cl_2 : *n*-hexane, 1:2, v/v) to give three fractions. Fraction three yielded the desired dimer. Solvents were removed *in vacuo* to give a purple solid **207** (69 mg, 0.060 mmol, 53%). M.p. >300 °C; R_f = 0.45 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): δ = 0.89-0.93 (t, $^3J_{\text{H-H}}$ = 14.7 Hz, 12H, CH_3), 2.66 (s, 6H, tolyl- CH_3), 2.80 (m, 8H, CH_2), 5.03 (m, 1H, CH), 5.14 (m, 1H, CH), 7.51-7.53 (d, $^3J_{\text{H-H}}$ = 7.9 Hz, 4H, C_6H_4 -H), 7.84 (m, 3H, Ph-H), 8.10 (m, 2H, H_β), 8.17-8.18 (d, $^3J_{\text{H-H}}$ = 7.7 Hz, 6H, Ph/ C_6H_4 -H), 8.31-8.33 (d, $^3J_{\text{H-H}}$ = 7.3 Hz, 2H, H_β), 8.77-8.78 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 2H, H_β), 9.03-9.05 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 2H, H_β), 9.22-9.23 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.39-9.43 (d, $^3J_{\text{H-H}}$ = 17.0 Hz, 2H, H_β), 9.52-9.54 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 2H, H_β), 9.76-9.79 (d, $^3J_{\text{H-H}}$ = 15.1 Hz, 2H, H_β), 10.60 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 14.4, 21.5, 22.7, 29.7, 31.6, 34.7, 50.6, 106.5, 121.5, 125.0, 126.5, 127.3, 127.5, 130.0, 131.8, 131.9, 132.5, 134.0, 134.4, 137.1, 139.7, 143.5, 139.8, 150.0, 150.8, 154.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 416 (5.42), 454 (5.37), 560 (4.64) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{70}\text{H}_{58}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1138.3367, found 1138.3351.

{5-(10',20'-Bis(4-methylphenyl)porphyrin-5'-ylato)-10,20-bis(3-methoxyphenyl)-15-phenyl}porphyrinato}zinc(II) (208**):**

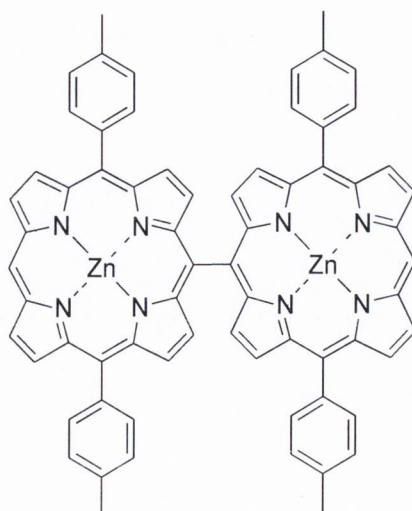


Produced from bromoporphyrin **111** (98 mg, 0.132 mmol), borylated porphyrin **130** (90 mg, 0.132 mmol), Cs_2CO_3 (107 mg, 0.330 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.020 mmol), DMF (3 mL) and toluene (12 mL) following general procedure H. The residue was subjected to column chromatography to give three fractions. Fraction one was starting material **111**, fraction two was dimer **211** (20%) and fraction three yielded the desired dimer. Solvents were removed *in vacuo* to give a purple solid **208** (97 mg, 0.080 mmol, 61%). M.p. $>300^\circ\text{C}$; $R_f = 0.54$ (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 2.65$ (s, 6H, tolyl- CH_3), 3.88 (s, 6H, OCH_3), 7.21-7.23 (dd, $^3J_{\text{H-H}} = 8.6$, 2.1 Hz, 2H, C_6H_4 -*H*), 7.51-7.53 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, C_6H_4 (tolyl)-*H*), 7.54-7.58 (t, $^3J_{\text{H-H}} = 16.0$ Hz, 2H, C_6H_4 -*H*), 7.78 (m, 7H, Ph/ C_6H_4 -*H*), 8.11-8.12 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 8.14-8.16 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 6H, C_6H_4 (tolyl)/ H_β), 8.32-8.34 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 2H, Ph-*H*), 8.71-8.72 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 8.77-8.78 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 9.05 (m, 4H, H_β), 9.19-9.20 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, H_β), 9.48-9.50 (d, $^3J_{\text{H-H}} = 4.3$ Hz, 2H, H_β), 10.37 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$): $\delta = 21.5$, 55.4, 106.6, 113.4, 120.2, 120.4, 126.5, 127.3, 127.5, 127.6, 131.8, 133.8, 134.0, 134.3, 134.5, 137.1, 139.6, 143.7, 144.0, 149.7, 149.8, 149.9, 150.3, 150.5, 150.7, 150.8, 154.5, 155.0, 157.8, 157.9, 127.6, 131.9, 132.0, 132.2, 132.9, 134.0, 134.4, 134.5, 142.7, 142.9, 143.9, 149.7, 149.8, 149.9, 150.2, 150.6, 150.7, 154.7, 155.0, 157.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 415 (5.54), 454 (5.32), 550 (4.68) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{74}\text{H}_{50}\text{N}_8\text{O}_2\text{Zn}_2](\text{M}^+)$: 1210.2640, found 1210.2672.

{5-(10',20'-Bis(3-methoxyphenyl)porphyrin-15-phenyl-5'-ylato)-10,15,20-triphenylporphyrinato}zinc(II) (209**)**



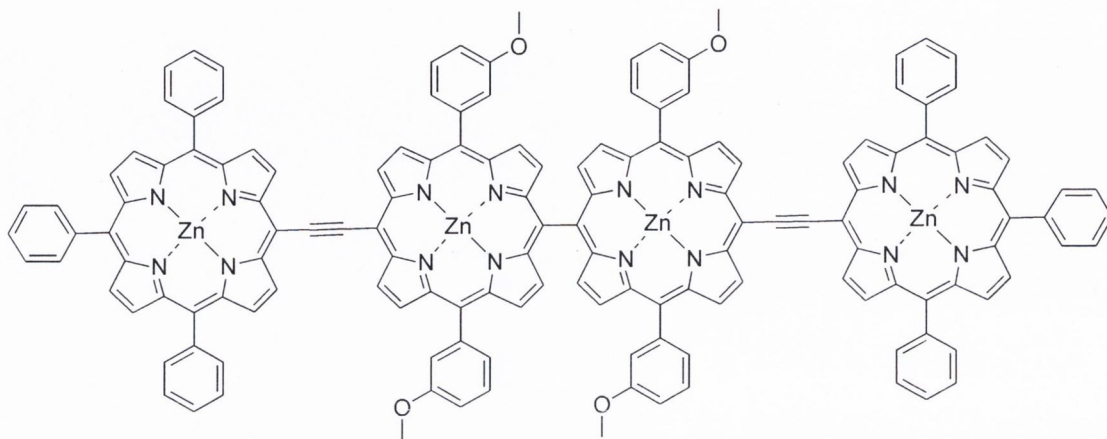
Produced from bromoporphyrin **111** (102 mg, 0.137 mmol), borylated porphyrin **129** (100 mg, 0.137 mmol), Cs_2CO_3 (98 mg, 0.301 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (24 mg, 0.021 mmol), DMF (3 mL) and toluene (12 mL) following general procedure H. The residue was subjected to column chromatography (silica, CH_2Cl_2 : *n*-hexane, 5 : 4, v/v) to give two fractions. Fraction one consisted of debrominated starting material **111** and homocoupled dimer **210** (18%). The red second fraction yielded dimer **209**. Solvents were removed *in vacuo* to give a purple solid (120 mg, 0.095 mmol, 69%). M.p. >300 °C; R_f = 0.36 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^1H NMR (400 MHz, CDCl_3): δ = 3.89 (d, $^3J_{\text{H-H}}$ = 1.8 Hz, 6H, OCH_3), 7.23-7.25 (dd, $^3J_{\text{H-H}}$ = 11.2 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.52-7.56 (t, $^3J_{\text{H-H}}$ = 15.2 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.70-7.85 (m, 16H, $\text{Ph/C}_6\text{H}_4\text{-H}$), 8.22-8.23 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 2H, H_β), 8.28-8.29 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 8.25 (m, 6H, Ph-H), 8.35 (m, 2H, $\text{C}_6\text{H}_4\text{-H}$), 8.73-8.74 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.02-9.03 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.08-9.10 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 2H, H_β), 9.21-9.22 (d, $^3J_{\text{H-H}}$ = 4.6 Hz, 2H, H_β), 9.50-9.51 (d, $^3J_{\text{H-H}}$ = 4.7 Hz, 2H, H_β), 9.75-9.77 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 55.4, 113.4, 113.5, 120.2, 120.4, 126.5, 126.6, 127.4, 128.3, 131.0, 131.9, 132.0, 133.9, 134.4, 142.7, 142.9, 143.8, 144.0, 149.7, 150.2, 150.3, 150.6, 150.7, 154.9, 155.0, 157.8, 157.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 420 (5.20), 455 (5.02), 559 (4.41) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{78}\text{H}_{50}\text{N}_8\text{O}_2\text{Zn}_2](\text{M}^+)$: 1258.2640, found 1258.2618.

Bis{5,15-bis(4-methylphenyl)porphyrin-15-ylato}zinc(II)} (211):

Produced as side product in the synthesis of **207**. Dimer **211** was isolated following column chromatography (silica, CH_2Cl_2 : *n*-hexane, 2 : 3, v/v) as the second fraction. Solvents removed to give red solid **211** (31 mg, 0.028 mmol, 20%). M.p. $>300^\circ\text{C}$; $R_f = 0.45$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, $\text{CDCl}_3/\text{pyridine-}d_5$, 20:1): $\delta = 2.58$ (s, 12H, tolyl- CH_3), 7.42–7.44 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 8H, $\text{C}_6\text{H}_4\text{-}H$), 7.79–7.80 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 4H, H_β), 8.07–8.09 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 8H, $\text{C}_6\text{H}_4\text{-}H$), 8.54–8.55 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 4H, H_β), 9.06–9.07 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 4H, H_β), 9.36–9.37 (d, $^3J_{\text{H-H}} = 4.3$ Hz, 4H, H_β), 10.2 (s, 2H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $\text{CDCl}_3/\text{pyridine-}d_5$): $\delta = 22.7$, 105.8, 120.2, 120.8, 127.0, 131.2, 131.3, 132.0, 133.5, 134.5, 136.5, 140.5, 149.5, 149.6, 150.6, 154.6 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 415 (5.29), 446 (5.32), 552 (4.69) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{68}\text{H}_{46}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1102.2428, found 1102.2433.

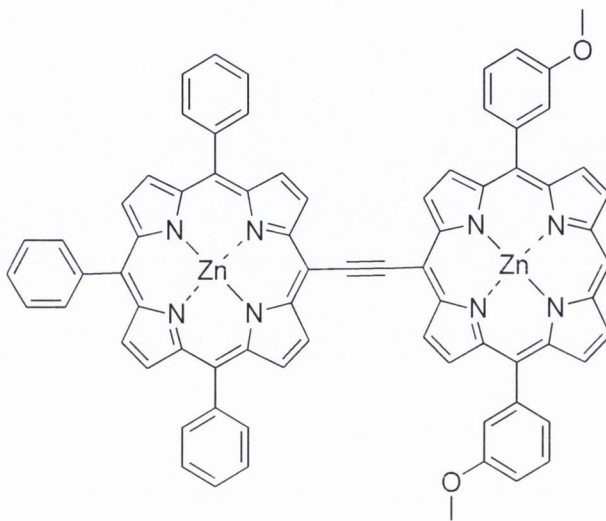
7.4.2. Sonogashira coupling for the synthesis of tetramer **212** and dimer **213**

Bis{5-[(10',20'-bis(3-methoxyphenyl)porphyrinato-15'-yl)zinc(II)ethynyl-10,15,20-triphenyl}porphyrin-15'-ylato}zinc(II) (212**):**



Produced from alkynyl porphyrin **152** (65 mg, 0.104 mmol), bromoporphyrin dimer **202** (66 mg, 0.049 mmol), AsPh₃ (32 mg, 0.104 mmol) and Pd₂(dba)₃ (7 mg, 0.007 mmol) following procedure J. After 48 h reaction time, solvents were removed, the residue was redissolved in CH₂Cl₂ and filtered through plug of silica using CH₂Cl₂ : ethyl acetate (9 : 1, v/v) as eluent. Solvents were removed and the residue was subjected to column chromatography (silica, *n*-hexane : ethyl acetate, 6 : 1, v/v) to give four fractions, the first three containing undesirable dimeric and trimeric products and the fourth of which contained the desired tetramer **212**. Solvents were removed *in vacuo* to give dark green solid **212** (34 mg, 0.011 mmol, 27%). M.p. >300 °C; *R*_f = 0.27 (hexane : ethyl acetate = 3 : 2, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = 3.93 (m, 12H, OCH₃), 7.26 (m, 4H, C₆H₄-H), 7.62 (m, 4H, C₆H₄-H), 7.84 (m, 22H, Ph/C₆H₄-H), 8.19 (m, 4H, H_β) 8.25-8.27 (d, ³J_{H-H} = 6.4 Hz, 8H, C₆H₄-H), 8.32 (m, 8H, Ph-H), 8.73 (m, 4H, H_β), 8.95-8.96 (d, ³J_{H-H} = 6.5 Hz, 8H, H_β), 9.24-9.25 (d, ³J_{H-H} = 4.1 Hz, 4H, H_β), 9.28 (m, 4H, H_β), 10.55-10.56 (d, ³J_{H-H} = 4.3 Hz, 8H, H_β) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 55.4, 55.5, 101.0, 102.4, 113.6, 120.3, 122.5, 123.0, 126.7, 126.8, 127.4, 127.6, 127.7, 131.0, 132.1, 132.3, 133.2, 133.4, 134.2, 134.3, 134.5, 142.5, 142.6, 143.6, 150.1, 150.3, 150.4, 150.7, 152.9, 153.0, 155.0, 157.9 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 411 (5.31), 498 (5.54), 564 (4.61), 700 (5.07) nm; HRMS (MALDI) *m/z* calcd. for [C₁₄₈H₉₀N₁₆O₄Zn₄](M⁺): 2410.4497, found 2410.4441.

{5-[(10',20'-bis(3-methoxyphenyl)porphyrinato-5-yl)zinc(II)ethynyl-10,15,20-triphenylporphyrinato}zinc(II) (213):



Produced from alkynyl porphyrin **152** (56 mg, 0.089 mmol), bromoporphyrin **110** (60 mg, 0.089 mmol), AsPh₃ (57 mg, 0.185 mmol) and Pd₂(dba)₃ (8 mg, 0.008 mmol) following procedure I. After 22 h, solvents were removed, the residue was redissolved in CH₂Cl₂ and filtered through plug of silica using CH₂Cl₂ as eluent. Solvents were removed and the residue was subjected to column chromatography (silica, *n*-hexane : ethyl acetate, 4 : 1, v/v) to give four fractions, fraction one being monomer **152** with fractions two and three containing mixtures of undersired oligomers. The fourth fraction contained the desired dimer **213**. Solvents were removed *in vacuo* to give dark green solid **213** (46 mg, 0.038 mmol, 43%). M.p. >300 °C; *R*_f = 0.35 (*n*-hexane: EtOAc, 3 : 2, v/v); ¹H NMR (400 MHz, CDCl₃/pyridine-d₅, 20 : 1, TMS): δ = 4.07 (s, 6H, OCH₃), 7.37-7.40 (dd, ³*J*_{H-H} = 7.3, 2.4 Hz, 2H, C₆H₄-*H*), 7.78 (m, 11H, Ph/C₆H₄-*H*), 7.89 (m, 2H, C₆H₄-*H*), 8.23 (m, 6H, Ph-*H*), 8.30 (m, 2H, C₆H₄-*H*), 9.01-9.02 (d, ³*J*_{H-H} = 4.6 Hz, 2H, *H*_β), 9.04-9.05 (d, ³*J*_{H-H} = 4.4 Hz, 2H, *H*_β), 9.11-9.12 (d, ³*J*_{H-H} = 4.5 Hz, 2H, *H*_β), 9.20-9.22 (d, ³*J*_{H-H} = 4.5 Hz, 2H, *H*_β), 9.30-9.31 (d, ³*J*_{H-H} = 4.4 Hz, 2H, *H*_β), 9.96-9.97 (d, ³*J*_{H-H} = 4.6 Hz, 2H, *H*_β), 10.11 (s, 1H, *H*_{meso}), 10.46-10.47 (d, ³*J*_{H-H} = 4.6 Hz, 2H, *H*_β), 10.49-10.50 (d, ³*J*_{H-H} = 4.6 Hz, 2H, *H*_β) ppm; ¹³C NMR (100 MHz, CDCl₃/pyridine-D₅ 20:1): δ = 55.6, 100.7, 107.2, 113.1, 120.1, 120.8, 121.1, 122.0, 122.1, 122.4, 126.3, 126.4, 127.3, 127.4, 128.0, 120.6, 131.5, 131.6, 131.8, 132.0, 132.2, 132.7, 132.8, 133.1, 134.4, 134.5, 134.6, 143.0, 143.2, 143.3, 144.5, 149.6, 149.7, 149.8, 150.0, 150.4, 150.7, 152.6, 153.0, 153.5, 157.9 ppm; UV/vis (CH₂Cl₂):

$\lambda_{\max}$ (log ϵ) = 452 (5.06), 481 (5.22), 568 (4.08), 696 (4.64) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{74}\text{H}_{46}\text{N}_8\text{O}_2\text{Zn}_2](\text{M}^+)$: 1206.2327, found 1206.2341.

7.4.3 Symmetric fused dimers

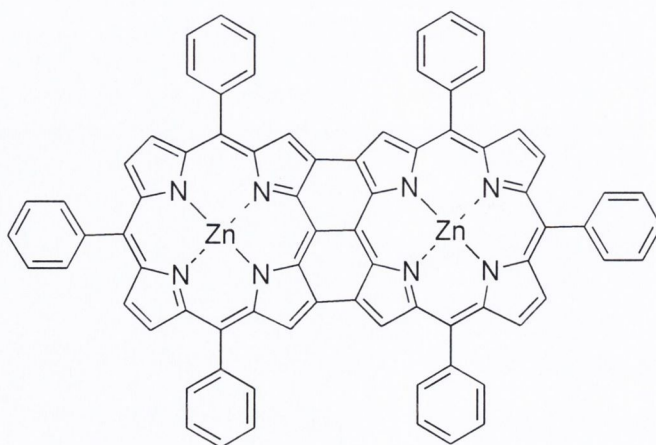
General procedure K: Oxidative coupling of 5,10,15 trisubstituted porphyrins using DDQ/Sc(OTf)₃

Metallatoporphyrin (1 equiv.) was charged to a 100 mL Schlenk tube and dissolved in dry toluene. Solution degassed via three freeze-pump-thaw cycles. DDQ (5 equiv.) and Sc(OTf)₃ (5 equiv.) added and the reaction heated to 50 °C under argon for 3-18 h. THF added and reaction stirred at room temperature for a further 1 h. The reaction mixture was then passed through a short plug of alox or silica gel, using CH₂Cl₂ then THF as eluent and the solvent was removed *in vacuo*. The residue was then purified using column chromatography on silica gel to yield the desired triply-fused dimer.

General procedure L: Oxidative coupling using PIFA.

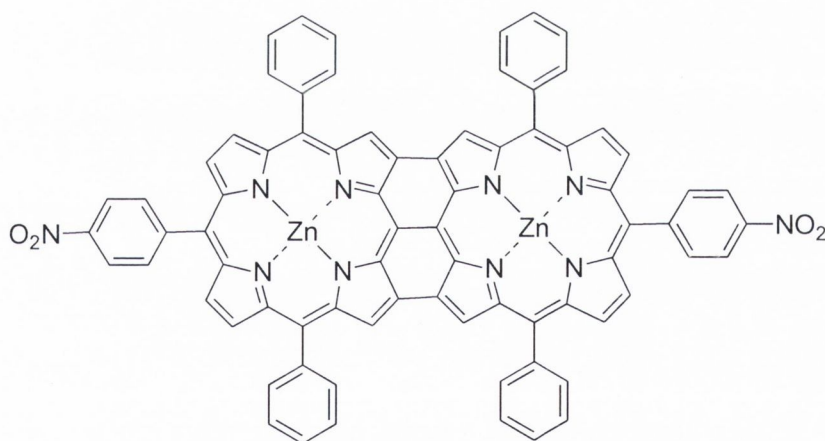
Trisubstituted metalloporphyrin (1 equiv.) was charged to a 100 mL Schlenk tube and dissolved in dry CH₂Cl₂. Solution degassed via vacuum and cooled to -78 °C. PIFA (2.5 equiv.) added and the reaction allowed to warm to rt and stirred at this temperature for 3 h. NaBH₄ (10 equiv.) in MeOH added and reaction stirred at room temperature for a further 1 h. The reaction mixture was then passed through a short plug of alox or silica gel, using DCM then THF as eluent and the solvent was removed *in vacuo*. The residue was then purified using column chromatography on silica gel to yield the desired singly or triply-fused dimer.

Bis{5,10,15-triphenylporphyrin-13,15,17-triylato}zinc(II)} (214):^[174]



Synthesised according to general procedure K from (5,10,15-triphenylporphyrinato)zinc(II) **116** (60 mg, 0.010 mmol), DDQ (113 mg, 0.498 mmol), Sc(OTf)₃ (245 mg, 0.498 mmol) in dry toluene (60 mL), heated at 50 °C for 3.5 h. THF (15 mL) added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of allox using CH₂Cl₂ : THF (1 : 1, v/v) as eluent. Solvents were removed and **214** was isolated as a dark solid (48 mg, 0.040 mmol, 79 %). M.p. > 300 °C; ¹H NMR (600 MHz, CDCl₃/pyridine-D₅, 10:1, TMS): δ = 6.99 (s, 4H, H_β), 7.53 (m, 30H, Ph-H), 7.74 (m, 12H, H_β) ppm; ¹³C NMR (150 MHz, CDCl₃/pyridine-D₅, 10:1): δ = 117.5, 124.3, 124.9, 126.3, 126.4, 126.7, 126.9, 127.1, 130.3, 130.5, 132.6, 132.9, 135.8, 141.4, 141.7, 154.3 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 421 (5.62), 468 (4.40), 560 (4.71), 817 (3.46), 963 (3.82), 1097 (4.06) nm; HRMS (MALDI) *m/z* calcd. for [C₇₆H₄₂N₈Zn₂](M⁺): 1194.2115, found 1194.2141. Spectroscopic data were in agreement with the literature.

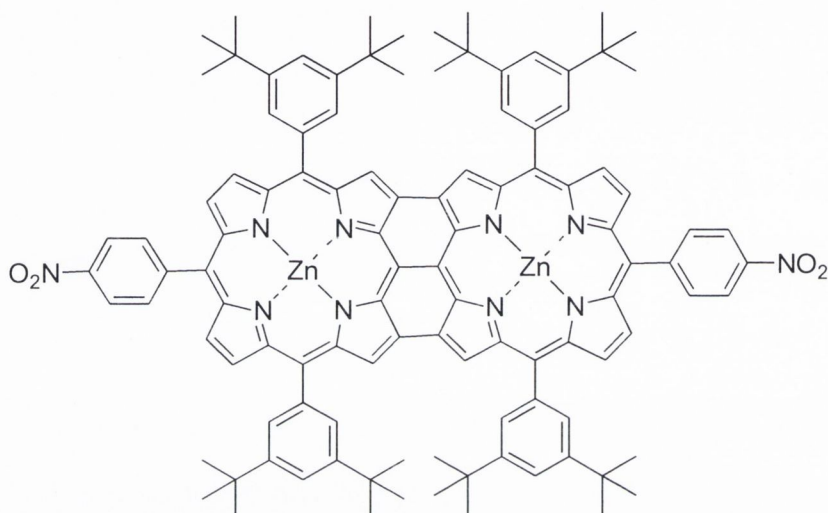
Bis{(5-(4-nitrophenyl)-10,20-diphenylporphyrin-13,15,17-triylato)zinc(II)} (215):



Synthesised according to general procedure K from **137** (40 mg, 0.062 mmol), DDQ (70 mg, 0.309 mmol), Sc(OTf)₃ (152 mg, 0.309 mmol) in dry toluene (40 mL), heated at 50 °C for 4.5 h. THF (8 mL) added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of allox using CH₂Cl₂ : THF (1 : 1, v/v) as eluent. Solvents were removed *in vacuo* and the residue was subjected to column chromatography using CH₂Cl₂ as eluent giving one main fraction. Solvents were removed *in vacuo* to yield **215** as a dark solid (29 mg, 0.040 mmol, 74%). M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃/pyridine-D₅ 10:1): δ = 6.98 (s, 4H, H_β), 7.44-7.45 (d, ³J_{H-H} = 4.6 Hz, H_β), 7.54 (m, 18H, Ph-H/ H_β), 7.71-7.72 (d, ³J_{H-H}

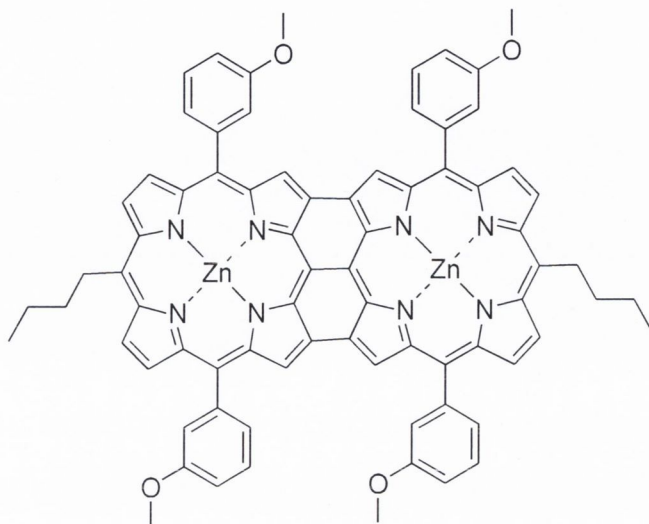
= 6.0 Hz, 8H, Ph-*H*), 7.89-7.92 (d, $^3J_{\text{H-H}} = 8.6$ Hz, 4H, C₆H₄-*H*), 8.39-8.41 (d, $^3J_{\text{H-H}} = 8.6$ Hz, 4H, C₆H₄-*H*) ppm; UV/vis (THF): λ_{max} (log ϵ) = 421 (5.07), 460 (4.76), 563 (5.18), 963 (4.31), 1105 (4.58) nm; HRMS (MALDI) m/z calcd. for [C₇₆H₄₀N₁₀O₄Zn₂](M⁺): 1284.1817, found 1284.1824.

Bis{(5,15-bis(3,5-di-*tert*-butylphenyl)-10-(4-nitrophenyl)porphyrin-13,15,17-triylato)zinc(II)} (216):

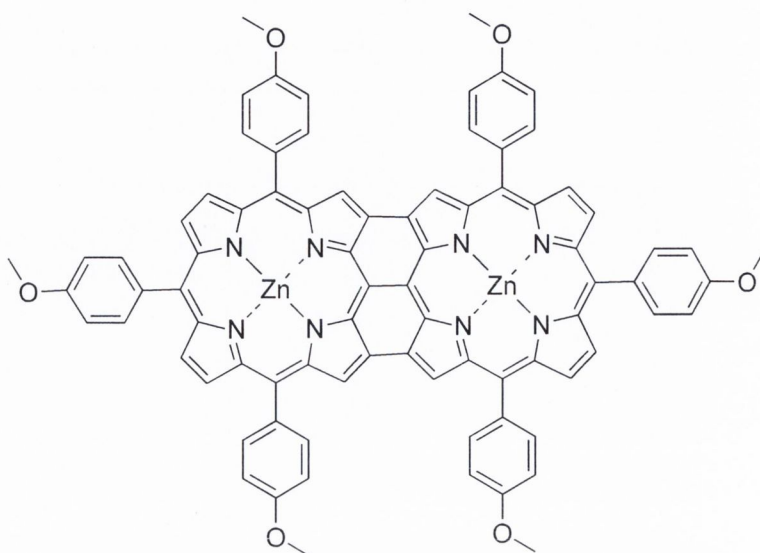


Synthesised according to general procedure K from {5,15-bis(3,5-di-*tert*-butylphenyl)-10-(4-nitrophenyl)porphyrinatozinc(II)} **140** (20 mg, 0.023 mmol), DDQ (26 mg, 0.115 mmol), Sc(OTf)₃ (57 mg, 0.115 mmol) in dry toluene (20 mL), heated at 50 °C for 3 h. THF (5 mL) added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH₂Cl₂ then CH₂Cl₂ : THF (1 : 1, v/v) as eluent to give intense purple fraction. Solvents were removed and the residue was filtered through a second plug of alox using CH₂Cl₂ as eluent. Solvents were removed *in vacuo* and **216** was isolated as a dark solid (13 mg, 0.007 mmol, 64%). M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.48 (s, 72H, *t*-butyl-*H*), 7.37 (s, 4H, *H_β*), 7.60-7.62 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 4H, *H_β*), 7.67 (m, 12H, Ar-*H*), 7.75-7.76 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 4H, *H_β*), 8.00-8.02 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 4H, C₆H₄-*H*), 8.11-8.13 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 4H, C₆H₄-*H*) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 31.5, 106.2, 107.5, 120.9, 122.2, 124.2, 127.7, 128.1, 130.1, 131.9, 133.4, 135.9, 139.5, 147.3, 147.8, 151.6, 153.5, 153.9, 154.1 ppm; UV/vis (THF): λ_{max} (log ϵ) = 423 (5.12), 566 (5.17), 886 (4.00), 967 (4.33), 1110 (4.63) nm; HRMS (MALDI) m/z calcd. for [C₁₀₈H₁₀₄N₁₀O₄Zn₂](M⁺): 1732.6825, found 1732.6816.

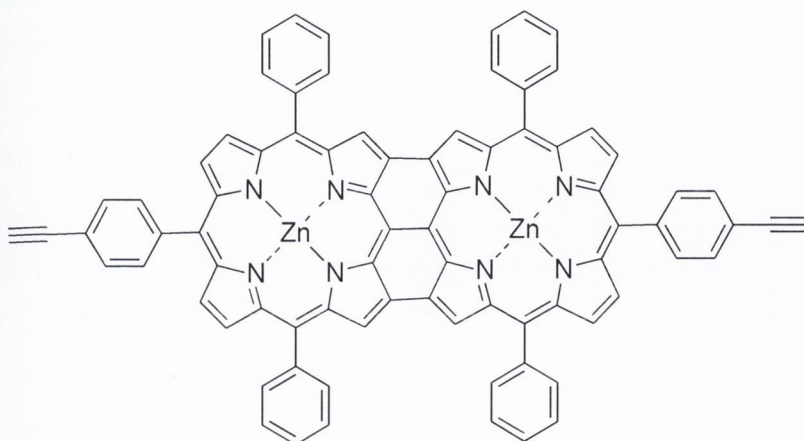
Bis{(5-butyl-10,20-bis(4-methoxyphenyl)porphyrin-13,15,17-triylato)zinc(II)}
(**217**):



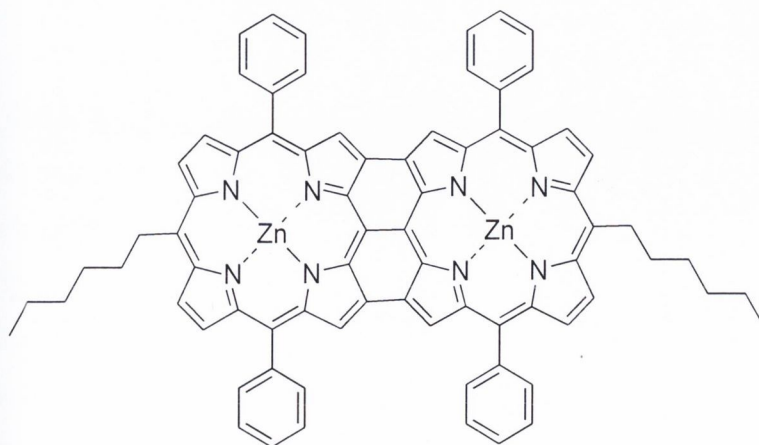
Synthesised from **120** (20 mg, 0.031 mmol), DDQ (35 mg, 0.156 mmol), Sc(OTf)₃ (77 mg, 0.156 mmol) in dry toluene (20 mL), heated at 50 °C for 3 h, according to general procedure K. THF (6 mL) was added and reaction stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH₂Cl₂ as eluent to give side product **226** and using CH₂Cl₂ : THF (1 : 1, v/v) as eluent to give fraction containing dimer **217**. Solvents were removed *in vacuo* and the residue was subjected to column chromatography using CH₂Cl₂ as eluent to give two fractions, the first being side product **226**, the second being desired dimer **217**. Solvents were removed and **217** isolated as a dark solid (14 mg, 0.011 mmol, 70%). M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃/pyridine-D₅, 10:1, TMS): δ = 0.82 (m, 6H, CH₃), 1.46 (m, 4H, CH₂), 1.95 (m, 4H, CH₂), 3.78 (s, 12H, OCH₃), 5.17 (m, 4H, CH₂), 6.99 (m, 6H, H_β/C₆H₄-H), 7.14 (m, 8H, C₆H₄-H), 7.32 (m, 4H, C₆H₄-H), 7.53 (m, 8H, H_β), 8.15 (m, 2H, C₆H₄-H) ppm; UV/vis (THF): λ_{max} (log ε) = 422 (5.20), 459 (4.89), 559 (4.95), 949 (4.14), 1092 (4.41), 1094 (4.41) nm; HRMS (MALDI) *m/z* calcd. for [C₇₆H₅₈N₈O₄Zn₂](M⁺): 1274.3164, found 1274.3123.

Bis{(5,10,15-bis(4-methoxyphenyl)porphyrin-13,15,17-triylato)zinc(II)} (218):

Synthesised according to general procedure K, from **119** (40 mg, 0.058 mmol), DDQ (66 mg, 0.289 mmol), Sc(OTf)₃ (142 mg, 0.289 mmol) in dry toluene (40 mL), heated at 50 °C for 4.5 h. THF (8 mL) was added and the reaction was stirred for a further 0.8 h at room temperature. The reaction mixture was filtered through a short plug of silica gel using CH₂Cl₂ as eluent giving one fraction which was discarded as no fusing product was detected via UV/vis/NIR analysis. Using CH₂Cl₂ : THF (1 : 1, v/v) as eluent a second (main) fraction containing **218** was isolated. Solvents were removed *in vacuo* and **218** was isolated as a dark purple solid (33 mg, 0.024 mmol, 83%). M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃/pyridine-D₅, 10 : 1, TMS): δ = 3.88 (s, 12H, OCH₃), 3.94 (s, 6H, OCH₃), 7.01 (s, 4H, H_β), 7.02 (d, ³J_{H-H} = 8.3 Hz, 6H, C₆H₄-H), 7.08-7.10 (dd, ³J_{H-H} = 8.3, 2.4 Hz, 4H, C₆H₄-H), 7.27-7.28 (m, 2H, C₆H₄-H), 7.29 (m, 2H, C₆H₄-H), 7.37-7.42 (t, ³J_{H-H} = 15.6 Hz, 6H, C₆H₄-H), 7.51-7.52 (d, ³J_{H-H} = 4.6 Hz, 4H, H_β), 7.55-7.57 (d, ³J_{H-H} = 4.6 Hz, 4H, H_β), 7.62-7.64 (d, ³J_{H-H} = 8.3 Hz, 4H, C₆H₄-H) ppm; ¹³C NMR (150 MHz, CDCl₃/pyridine-D₅, 10 : 1): δ = 55.4, 112.3, 112.9, 118.8, 124.1, 124.8, 126.1, 126.5, 127.3, 130.3, 130.7, 133.8, 134.2, 135.9, 142.9, 152.8, 153.1, 154.4, 157.8, 158.9 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 420 (4.91), 471 (4.52), 562 (4.86), 584 (4.82), 820 (4.62), 952 (4.00), 1092 (4.23) nm; HRMS (MALDI) *m/z* calcd. for [C₈₂H₅₄N₈O₆Zn₂](M⁺): 1374.2749, found 1374.2723.

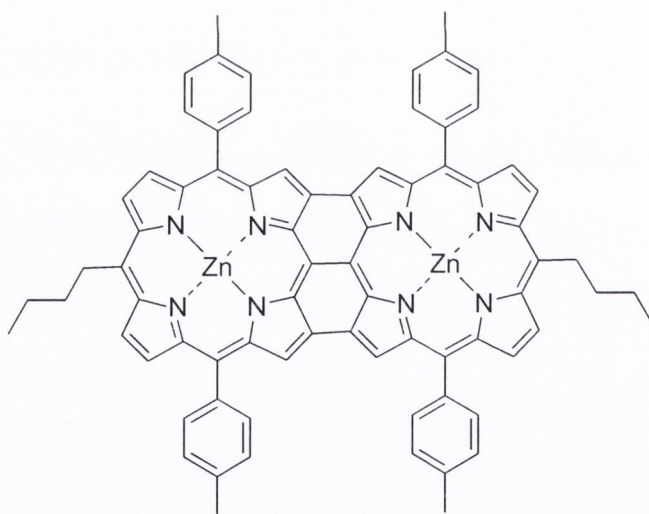
Bis{(5-(4-ethynylphenyl)-10,20-diphenylporphyrin-13,15,17-triylato)zinc(II)} (219)

Synthesised following general procedure K from **117** (60 mg, 0.010 mmol), DDQ (113 mg, 0.498 mmol), Sc(OTf)₃ (245 mg, 0.498 mmol) in dry toluene (60 mL), 50 °C for 3.5 h. THF (15 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH₂Cl₂ : THF (1 : 1, v/v) as eluent. Solvents were removed and **219** was isolated as a dark solid (48 mg, 0.040 mmol, 79%). M.p. >300 °C; ¹H NMR (600 MHz, CDCl₃/pyridine-D₅, 10 : 1, TMS): δ = 3.22 (s, 2H, C≡C-H), 6.98 (s, 4H, H_β), 7.50 (m, 20H, Ph-H), 7.66-7.67 (d, ³J_{H-H} = 8.0 Hz, 8H, H_β), 7.71 (m, 8H, H_β) ppm; ¹³C NMR (150 MHz, CDCl₃/pyridine-D₅, 10:1): δ = 77.7, 83.7, 126.4, 126.5, 127.0, 130.6, 132.9, 135.9, 139.4 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 421 (5.01), 563 (4.85), 586 (4.85), 671 (4.83), 968 (4.01), 1096 (4.27) nm; HRMS (MALDI) *m/z* calcd. for [C₈₀H₄₂N₈Zn₂](M⁺): 1242.2115, found 1242.2145.

Bis{5-hexyl-10,20-diphenylporphyrin-13,15,17-triylato}zinc(II)} (220):

Synthesised from {5-hexyl-10,20-diphenylporphyrinato}zinc(II) **115** (60 mg, 0.098 mmol), DDQ (112 mg, 0.492 mmol), Sc(OTf)₃ (242 mg, 0.492 mmol) in dry toluene (60 mL), following general procedure K. The reaction was heated at 50 °C for 4 h. THF (12 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of allox using CH₂Cl₂ as eluent to give dimer **227** as a side product and using CH₂Cl₂ : THF (1 : 1, v/v) as eluent a section fraction containing **220** was removed. Solvents were removed and **220** was isolated as a dark solid (35 mg, 0.025 mmol, 51%). M.p. >300 °C; *R*_f = 0.42 (CH₂Cl₂ : CH₃OH, 40:1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = 0.90 (t, ³*J*_{H-H} = 13.4 Hz, 6H, CH₃), 1.58 (m, 4H, CH₂), 1.84 (m, 4H, CH₂), 1.98 (m, 4H, CH₂), 2.07 (m, 4H, CH₂), 3.98 (t, ³*J*_{H-H} = 14.3 Hz, 4H, CH₂), 7.00 (s, 4H, *H*_β), 7.56 (m, 20H, Ar-*H*), 7.74 (m, 4H, *H*_β), 8.23 (m, 4H, *H*_β), ppm; UV/vis (THF): λ_{max} (log ε) = 423 (5.13), 468 (4.98), 599 (4.96), 817 (4.25), 1055 (4.35) nm; HRMS (MALDI) *m/z* calcd. for [C₇₆H₅₈N₈Zn₂](M⁺): 1210.3367, found 1210.3319.

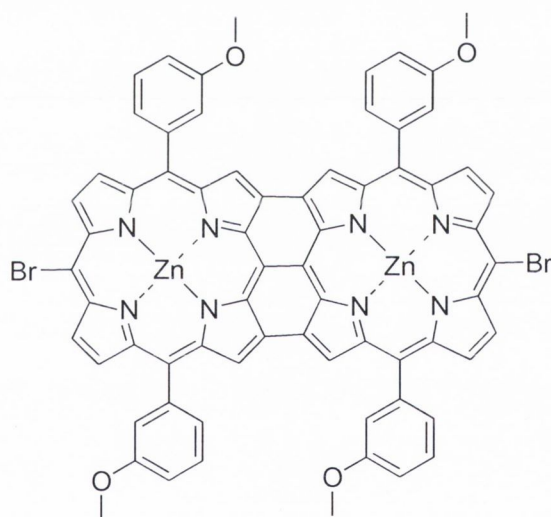
Bis{(5-butyl-10,20-bis(4-methylphenyl)porphyrin-13,15,17-triylato)zinc(II)} (221):



Synthesised according to general procedure K from **124** (30 mg, 0.049 mmol), DDQ (56 mg, 0.246 mmol), Sc(OTf)₃ (121 mg, 0.246 mmol) in dry toluene (30 mL), heated at 50 °C for 3.5 h. THF (7 mL) was added and the reaction was stirred for a further 0.5 h at room temperature. The reaction mixture was filtered through a short plug of allox using CH₂Cl₂ as eluent to give side product **228** and using THF as eluent to give a second fraction containing dimer **221**. Solvents were removed *in vacuo* and the residue was subjected to column chromatography (silica gel, CH₂Cl₂ : *n*-hexane, 9 : 1 + 1%

TEA) to give **221** as the main fraction. Solvents were removed and **221** was isolated as a dark purple solid (16 mg, 0.013 mmol, 54%). M.p. >300 °C; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{pyridine-}D_5$, 10 : 1, TMS): δ = 0.96-0.99 (t, $^3J_{\text{H-H}}$ = 14.6 Hz, 6H, CH_3), 1.47 (m, 4H, CH_2), 2.04 (m, 4H, CH_2), 2.57 (s, 12H, tolyl- CH_3), 3.89 (m, 4H, CH_2), 7.01 (s, 4H, H_β), 7.31-7.33 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 8H, $\text{C}_6\text{H}_4\text{-}H$), 7.59-7.60 (m, 4H, $\text{C}_6\text{H}_4\text{-}H$), 7.59-7.61 (m, 4H, H_β), 8.21-8.22 (d, $^3J_{\text{H-H}}$ = 4.3 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, $\text{CDCl}_3/\text{pyridine-}D_5$, 10 : 1): δ = 14.0, 20.9, 22.7, 35.0, 40.7, 117.5, 122.3, 126.8, 127.5, 135.7, 139.9, 148.4, 154.9 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 406 (4.99), 460 (4.70), 555 (4.89), 976 (4.16), 1044 (4.22) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{76}\text{H}_{58}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1210.3367, found 1210.3375.

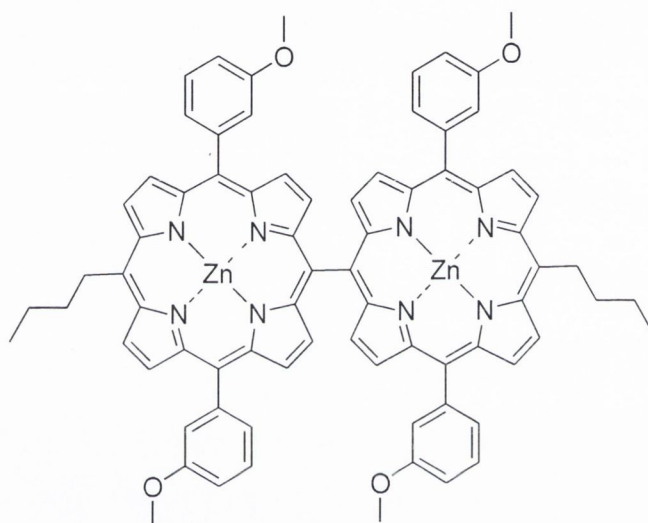
Bis{5-bromo-10,20-bis(3-methoxyphenyl)porphyrin-13,15,17-triylato}zinc(II)
(**225**):



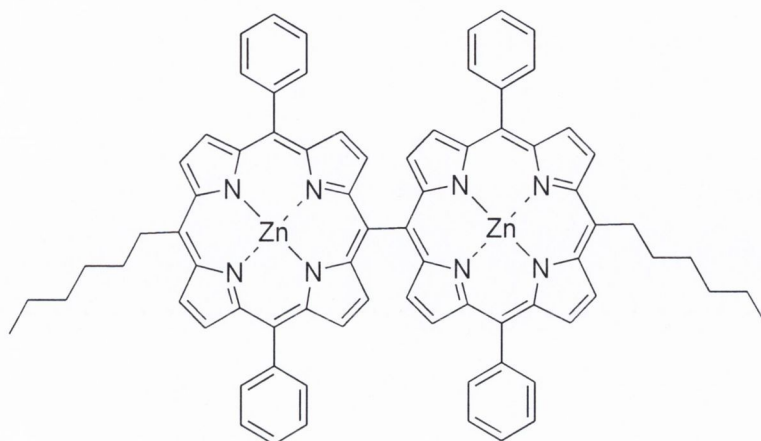
Synthesised according to general procedure L from {5-bromo-10,20-(3-methoxyphenyl)porphyrinato}zinc(II) **110** (20 mg, 0.030 mmol) in CH_2Cl_2 (60 mL). PIFA (32 mg, 0.075 mmol) was added at -78 °C, the reaction mixture was warmed to rt and stirred at this temperature for 2 h. NaBH_4 (12 mg, 0.305 mmol) in MeOH (5 mL) was added and the reaction stirred for a further 45 min. The reaction mixture was added to H_2O (100 mL) and organic layer extracted using CH_2Cl_2 : THF (1 : 1, v/v). The organic layer was then washed with NaHCO_3 (2 $\times$ 50 mL), H_2O (30 mL) and dried over Na_2SO_4 , which was then filtered and solvents were removed *in vacuo*. The dark residue was redissolved and filtered through short plug of silica using CHCl_3 : THF (1 : 1, v/v) as eluent to give a green fraction. Solvents were removed *in vacuo* and the residue was

recrystallised from $\text{CH}_2\text{Cl}_2/n$ -hexane to give a dark purple solid (3 mg, 0.002 mmol, 14%). M.p. $>300^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 3.93 (s, 12H, OCH_3), 7.04 (s, 4H, H_β), 7.16 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.70 (m, 6H, $\text{C}_6\text{H}_4\text{-H}$), 7.73 (m, 10H, $\text{C}_6\text{H}_4\text{-H}/H_\beta$), 8.45 (m, 2H, H_β), 8.61 (m, 2H, H_β) ppm; UV/vis (CH_2Cl_2 : THF, 1 : 1, v/v): λ_{max} (log ϵ) = 425 (5.01), 459 (4.66), 566 (4.68), 871 (3.98), 1110 (4.17) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{68}\text{H}_{40}\text{Br}_2\text{N}_8\text{O}_4\text{Zn}_2](\text{M}^+)$: 1318.0122, found 1318.0150.

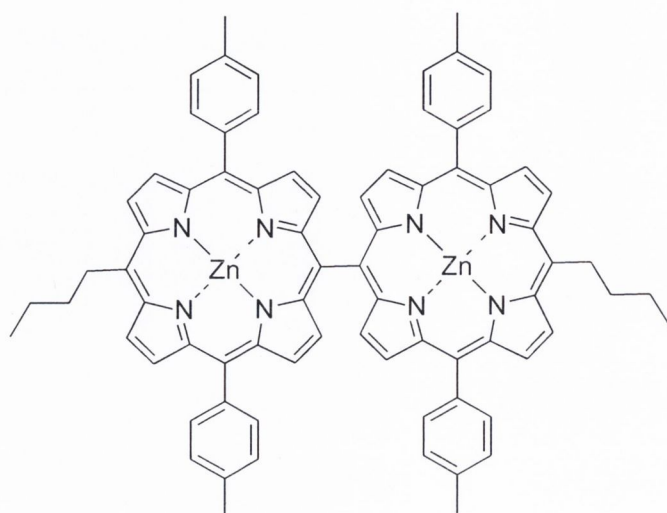
Bis{(5-*n*-butyl-10,20-bis(3-methoxyphenyl)porphyrin-15-ylato)zinc(II)} (226):



Isolated as side product from the synthesis of **217**. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 as eluent to give a fraction containing **226**. Solvents were removed *in vacuo* yielding a red-purple solid (4 mg, 0.003 mmol, 19%). M.p. $>300^\circ\text{C}$; R_f = 0.53 (CH_2Cl_2 : n -hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.89-0.93 (m, 6H, CH_3), 1.19 (m, 4H, CH_2), 1.93 (m, 4H, CH_2), 3.93 (s, 12H, OCH_3), 5.18-5.22 (t, $^3J_{\text{H-H}}$ = 15.9 Hz, 4H, CH_2), 7.24-7.27 (d, $^3J_{\text{H-H}}$ = 8.6 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.56-7.60 (t, $^3J_{\text{H-H}}$ = 15.8 Hz, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.82 (m, 8H, $\text{C}_6\text{H}_4\text{-H}$), 8.08 (m, 4H, H_β), 8.67 (m, 4H, H_β), 9.12-9.13 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 4H, H_β), 9.71-9.72 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 14.0, 22.5, 29.6, 41.0, 55.8, 109.9, 112.6, 119.6, 120.9, 127.9, 128.9, 131.7, 133.5, 142.5, 149.2, 154.9, 157.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 424 (5.35), 457 (5.27), 568 (4.59) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{76}\text{H}_{62}\text{N}_8\text{O}_4\text{Zn}_2](\text{M}^+)$: 1278.3477, found 1278.3438.

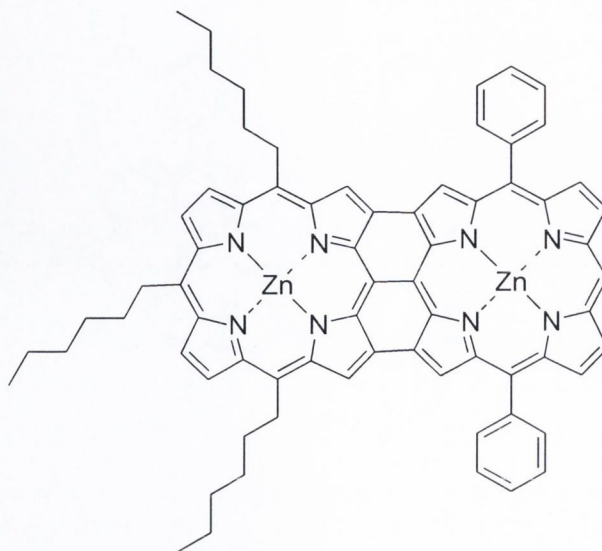
Bis{(5-hexyl-10,20-diphenylporphyrin-15-ylato)zinc(II)} (227):

Isolated from as a side product from the synthesis of **220**. The reaction mixture was filtered through a short plug of alox using CH_2Cl_2 as eluent to give the first fraction containing **227**. Solvents were removed *in vacuo* and **227** was isolated as a red-purple solid (18 mg, 0.015 mmol, 29%). M.p. $>300^\circ\text{C}$. $R_f = 0.55$ (*n*-hexane : $\text{CH}_2\text{Cl}_2 = 1 : 2$, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta = 0.98\text{--}1.01$ (t, $^3J_{\text{H-H}} = 14.4$ Hz, 6H, CH_3), 1.44 (m, 4H, CH_2), 1.64 (m, 4H, CH_2), 1.92 (m, 4H, CH_2), 2.66 (m, 4H, CH_2), 5.15–5.18 (t, $^3J_{\text{H-H}} = 15.3$ Hz, 4H, CH_2), 7.70 (s, 12H, Ph-*H*), 8.08–8.09 (d, $J = ^3J_{\text{H-H}} = 4.5$ Hz, 4H, H_β), 8.25 (m, 8H, Ph-*H*), 8.62–8.63 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 4H, H_β), 9.07–9.08 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 4H, H_β), 9.69–9.70 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 13.7, 22.3, 29.2, 29.9, 31.5, 38.6, 120.8, 125.9, 126.9, 128.6, 131.4, 131.6, 133.2, 133.8, 142.3, 148.9, 149.6, 154.5$ ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 421 (5.48), 454 (5.41), 561 (4.88) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{76}\text{H}_{62}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1214.3680, found 1214.3661.

Bis{(5-*n*-butyl-10,20-bis(4-methylphenyl)porphyrin-15-ylato)zinc(II)} (228)

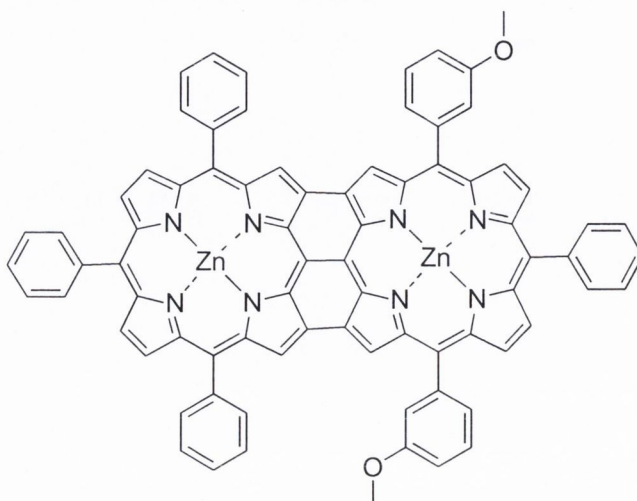
Synthesised as a side product of **221**, **228** was isolated as the first fraction from filtration through a plug of alox using CH_2Cl_2 as eluent. Solvents were removed to give a red-purple solid **228** (8 mg, 0.007 mmol, 27%) M.p. $>300^\circ\text{C}$; $R_f = 0.45$ (CH_2Cl_2 : *n*-hexane = 3 : 2, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 0.89\text{--}0.93$ (t, $^3J_{\text{H-H}} = 16.2$ Hz, 6H, CH_3), 1.19 (m, 4H, CH_2), 1.97 (m, 4H, CH_2), 2.64 (s, 12H, tolyl- CH_3), 5.15–5.19 (t, $^3J_{\text{H-H}} = 15.6$ Hz, 4H, CH_2), 7.49–7.51 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 8H, $\text{C}_6\text{H}_4\text{-H}$), 8.07–8.08 (d, $^3J_{\text{H-H}} = 4.9$ Hz, 4H, H_β), 8.11–8.13 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 8H, $\text{C}_6\text{H}_4\text{-H}$), 8.65–8.66 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 4H, H_β), 9.09–9.11 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_β), 9.68–9.69 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.2, 21.3, 23.7, 35.6, 41.1, 118.7, 121.2, 122.1, 127.0, 128.8, 131.7, 131.9, 133.4, 134.1, 136.8, 139.7, 149.4, 149.9, 150.1, 154.9$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 423 (5.54), 456 (5.45), 566 (4.80) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{76}\text{H}_{62}\text{N}_8\text{Zn}_2](\text{M}^+)$: 1214.3680, found 1214.3663.

{(5,10,15-Trihexyl-20-(10',20'-diphenylporphyrin-5'-yl)-13,15,17-triylato}zinc(II)
(229):



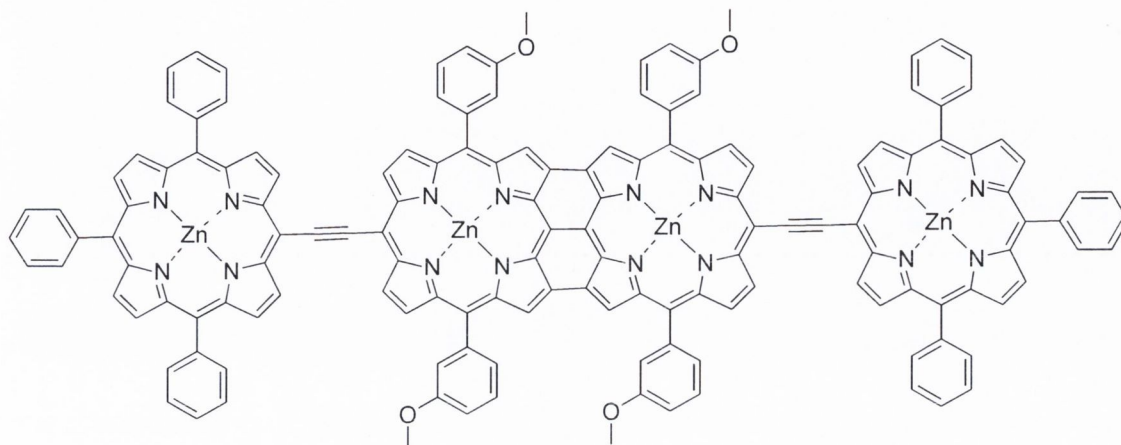
Synthesised from directly linked dimer **203** (20 mg, 0.019 mmol), DDQ (22 mg, 0.096 mmol), Sc(OTf)₃ (47 mg, 0.096 mmol) in dry toluene (20 mL), heated at 50 °C for 3 h. THF (6 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH₂Cl₂ : THF (1 : 1, v/v) as eluent. Solvents were removed and the residue was subjected to column chromatography (CH₂Cl₂ : *n*-hexane, 5 : 1, v/v) to give three fractions, the first being unreacted starting material **203**, the second of which contained **229** and the third was oligomerised product. Solvents were removed and **229** was isolated as a dark solid (3 mg, 0.002 mmol, 15 %). UV/vis (THF): λ_{max} (log ϵ) = 416 (4.97), 578 (4.70), 672 (4.56), 987 (3.87), 1106 (4.09) nm; HRMS (MALDI) m/z calcd. for [C₇₀H₆₂N₈Zn₂](M⁺): 1142.3680, found 1142.3625.

{5-(5'-Phenyl-10',20'-bis(4-methoxyphenyl)porphyrin-13',15',17'-triylato)-10,15,20-triphenylporphyrinato}zinc(II) (233):



Synthesised from dimer **209** (40 mg, 0.032 mmol), DDQ (36 mg, 0.158 mmol), Sc(OTf)₃ (78 mg, 0.158 mmol) in toluene (50 mL). The reaction was heated to 80 °C and stirred at this temperature for 3 h. THF (8 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through plug of allox using CH₂Cl₂, then CH₂Cl₂ : THF (1 : 1, v/v) as eluent. Solvents were removed *in vacuo* to give a dark residue which was redissolved in CH₂Cl₂ and subjected to column chromatography (*n*-hexane : ethyl acetate, 6 : 1, v/v) to give two fractions, the first yielding unreacted starting material **209** and the second containing desired fused dimer **233**. Solvents were removed *in vacuo* to yield a dark coloured solid (21 mg, 0.017 mmol, 52%). M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃/pyridine-D₅, 20 : 1, TMS): δ = 3.93 (s, 6H, OCH₃), 7.03 (m, 4H, H_β), 7.13 (m, 4H, C₆H₄-H), 7.23 (m, 2H, C₆H₄-H), 7.43 (m, 2H, C₆H₄-H), 7.49-7.62 (m, 20H, Ph-H/ H_β), 7.70-7.83 (m, 8H, Ph-H/H_β) ppm; ¹³C NMR (100 MHz, CDCl₃/pyridine-D₅, 20 : 1): δ = 55.4, 112.9, 126.5, 126.9, 127.3, 128.8, 130.6, 130.9, 157.8 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 422 (5.15), 455 (4.11), 556 (4.53), 579 (4.50), 917 (3.66), 1039 (3.90) nm; HRMS (MALDI) *m/z* calcd. for [C₇₈H₄₆N₈O₂Zn₂](M⁺): 1254.2327, found 1254.2286.

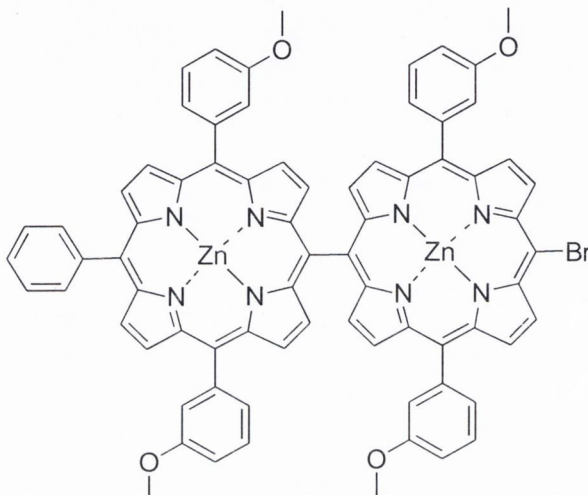
Bis{5-[(10',20'-bis(3-methoxyphenyl)porphyrinato-15'-yl)zinc(II)]ethynyl-10,15,20-triphenyl}porphyrin-13',15',17'-triylato}zinc(II) (234**):**



Synthesised from dimer **213** (20 mg, 0.017 mmol), DDQ (19 mg, 0.083 mmol), Sc(OTf)₃ (41 mg, 0.083 mmol) in toluene (30 mL). The reaction was heated to 50 °C and stirred at this temperature for 3 h. THF (10 mL) was added and the reaction was stirred for a further 45 min at room temperature. The reaction mixture was filtered through plug of silica using CH₂Cl₂, then CH₂Cl₂ : THF (2 : 1, v/v) as eluent. Solvents were removed to give a dark green residue which was subjected to column chromatography (silica, CH₂Cl₂ : THF, 4 : 1, v/v) to give fused tetramer **234** as the main fraction. Solvents were removed *in vacuo* to yield a dark brown solid **234** (12 mg, 0.005 mmol, 59%). M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.97 (m, 12H, OCH₃), 6.82-6.84 (d, ³J_{H-H} = 8.6 Hz, 8H, C₆H₄-H), 6.92 (s, 4H, H_β), 7.12-7.14 (d, ³J_{H-H} = 8.6 Hz, 8H, Ph-H), 7.43 (m, 10H, Ph-H/H_β), 7.54-7.56 (t, ³J_{H-H} = 14.6 Hz, 12H, C₆H₄-H), 7.65 (t, ³J_{H-H} = 14.6 Hz, 8H, C₆H₄-H), 7.73-7.90 (m, 24H, Ph-H/H_β), 7.95-7.96 (d, ³J_{H-H} = 7.5 Hz, 8H, Ph-H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 54.4, 106.1, 107.5, 113.2, 114.4, 118.3, 127.1, 127.9, 128.4, 128.6, 128.9, 130.7, 132.5, 133.9, 143.5 ppm; UV/vis (EtOAc): λ_{max} (log ε) = 427 (4.89), 573 (4.43), 714 (4.13) nm; HRMS (MALDI) *m/z* calcd. for [C₁₄₈H₈₈N₁₆O₄Zn₄](M+2H)⁺: 2408.4340, found 2408.4282.

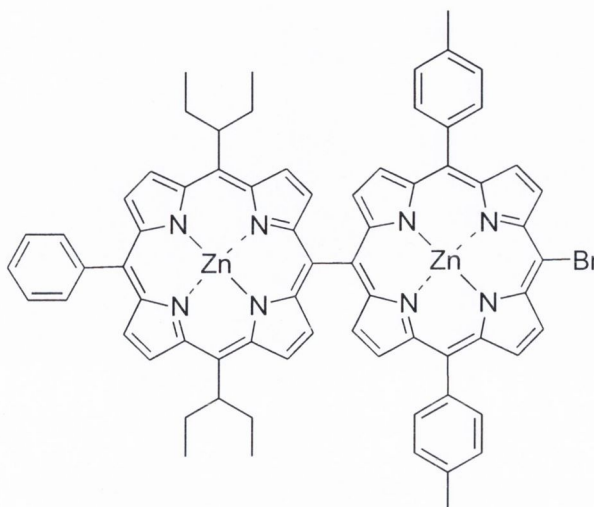
7.5 Reactivity of porphyrin arrays

{5-(5'-Bromo-10',20'-bis(3-methoxyphenyl)porphyrin-15'-ylato)-10,20-bis(4-methoxy)-15-phenyl}porphyrinato}zinc(II) (235):



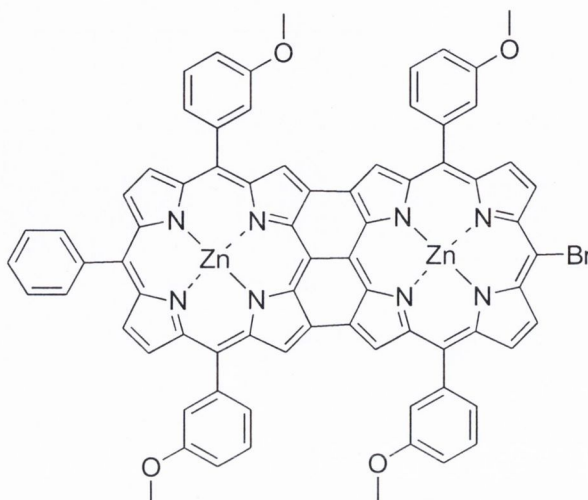
Produced from dimer **206** (150 mg, 0.120 mmol), NBS (32 mg, 0.180 mmol), CHCl_3 (50 mL) and pyridine (0.1 mL) following general procedure B. After 2.5 h at room temperature, solvents removed and the residue was filtered through plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* to give a purple solid **235** (120 mg, 0.091 mmol, 76%). M.p. $>300^\circ\text{C}$; $R_f = 0.54$ (CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 3.91$ (s, 12H, OCH_3), 7.23 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.56 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.80 (m, 11H, $\text{Ph/C}_6\text{H}_4\text{-H}$), 8.03 (m, 4H, H_β), 8.11–8.13 (d, $^3J_{\text{H-H}} = 5.3$ Hz, 2H, Ph-H), 8.64 (m, 2H, H_β), 8.68 (m, 2H, H_β), 9.02–9.06 (q, $^3J_{\text{H-H}} = 12.1$ Hz, 4H, H_β), 9.08–9.09 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β), 9.84–9.86 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.4, 113.3, 120.2, 120.3, 121.6, 122.6, 126.6, 127.2, 127.5, 131.8, 132.8, 133.7, 134.1, 134.5, 143.0, 143.4, 143.9, 144.1, 149.9, 150.2, 150.5, 150.9, 155.3, 157.7$ ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$) = 418 (5.21), 450 (5.17), 558 (4.55) nm.^[333]

{5-(5'-Bromo-10',20'-bis(4-methylphenyl)porphyrin-15'-ylato)-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (236):



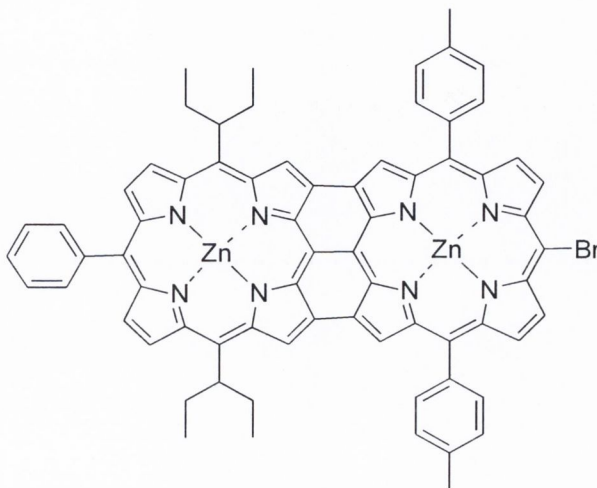
Produced from dimer **207** (30 mg, 0.026 mmol), NBS (5 mg, 0.026 mmol), CHCl_3 (40 mL) and pyridine (0.1 mL) following general procedure B. After 1.5 h at room temperature, solvents removed and the residue was filtered through plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* to give a purple solid **236** (29 mg, 0.024 mmol, 91%). M.p. $>300^\circ\text{C}$; $R_f = 0.48$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 0.97\text{--}1.00$ (t, $^3J_{\text{H-H}} = 13.9$ Hz, 12H, CH_3), 2.66 (s, 6H, tolyl-*H*), 2.80 (m, 8H, CH_2), 5.05 (m, 1H, *CH*), 5.16 (m, 1H, *CH*), 7.50–7.52 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, C_6H_4 -*H*), 7.83 (m, 3H, Ph-*H*), 8.08 (m, 4H, Ph-*H/H}_\beta*), 8.12–8.14 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, C_6H_4 -*H*), 8.32–8.33 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 2H, H_β), 8.66–8.67 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_β), 9.04 (m, 2H, H_β), 9.10–9.11 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β), 9.39–9.43 (d, $^3J_{\text{H-H}} = 17.3$ Hz, 2H, H_β), 9.76–9.79 (d, $^3J_{\text{H-H}} = 12.8$ Hz, 2H, H_β), 9.87–9.88 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 2H, H_β) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.4, 21.5, 22.7, 29.7, 34.8, 50.5, 105.0, 113.5, 121.1, 122.5, 124.9, 126.4, 127.2, 127.4, 130.1, 132.1, 132.8, 133.1, 134.2, 134.3, 137.2, 139.6, 143.5, 143.6, 149.6, 150.3, 151.2, 155.3$ ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 414 (5.32), 450 (5.27), 554 (4.54) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{70}\text{H}_{57}\text{N}_8\text{Zn}_2\text{Br}](\text{M}^+)$: 1216.2472, found 1216.2509.

{10,20-bis(3-methoxyphenyl)-5-phenyl-20-(10',20'-bis(4-methoxyphenyl)porphyrin-5'-yl)-13,15,17-triylato}zinc(II) (237**):**

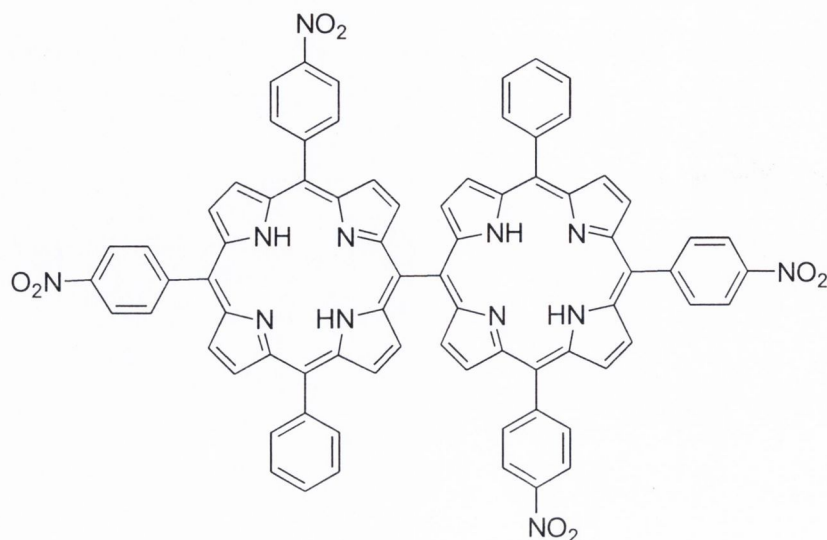


Synthesised from bromo-dimer **235** (20 mg, 0.038 mmol), PIFA (35 mg, 0.094 mmol) in CH_2Cl_2 (60 mL). The reaction was stirred at room temperature for 3 h. NaBH_4 (7 mg, 0.190 mmol) in MeOH (5 mL) was added and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was poured on H_2O (50 mL) and extracted with CH_2Cl_2 . The organic layer was washed with NaHCO_3 (2×50 mL) and H_2O (50 mL), dried over Na_2SO_4 and filtered. Solvents were removed to give a dark green residue which was redissolved in CH_2Cl_2 and filtered through a short plug of alox. Solvents were removed *in vacuo* to yield a dark green solid **237** (22 mg, 0.011 mmol, 44%). M.p. >300 °C; ^1H NMR (600 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$, 10 : 1, TMS): δ = 3.86–3.93 (m, 12H, OCH_3), 6.55 (d, $^3J_{\text{H-H}} = 4.3$ Hz, 2H, H_β), 6.95 (m, 2H, aryl- H), 7.04 (m, 4H, C_6H_4 - H), 7.12 (d, $^3J_{\text{H-H}} = 4.3$ Hz, 2H, H_β), 7.16 (m, 4H, C_6H_4 - H), 7.35 (m, 2H, aryl- H), 7.45 (m, 4H, aryl- H), 7.64 (d, $^3J_{\text{H-H}} = 4.3$ Hz, 2H, H_β), 7.75 (m, 4H, C_6H_4 - H), 8.44 (d, $^3J_{\text{H-H}} = 4.3$ Hz, 2H, H_β), 9.09–9.11 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_β), 9.68–9.69 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_β) ppm; ^{13}C NMR (C-H COSY 150 MHz, CDCl_3): δ = 54.4, 112.7, 113.1, 114.7, 119.4, 120.2, 122.2, 123.0, 123.8, 127.3, 128.9, 131.2, 132.0, 133.2, 136.0 ppm; UV/vis (THF): λ_{max} ($\log \epsilon$) = 423 (5.10), 562 (4.64), 1037 (3.94) nm.^[334]

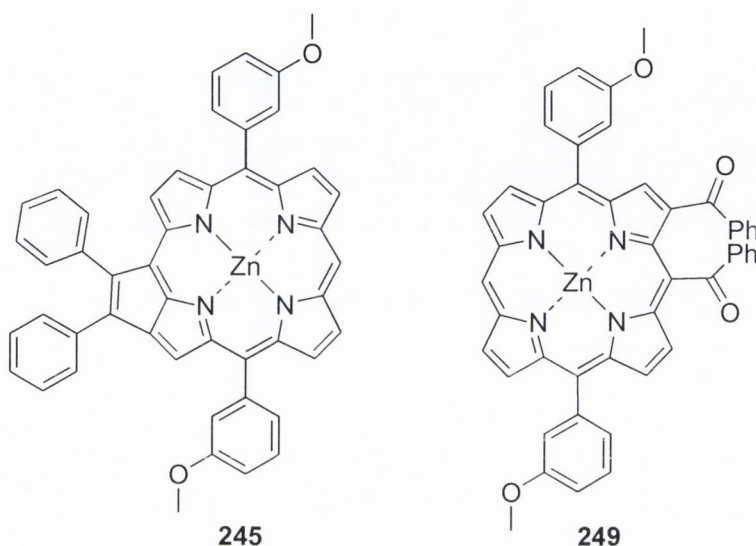
{5-(5'-Bromo-10',20'-bis(4-methylphenyl)porphyrin-13',15',17'-ylato)-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (238):



Synthesised from bromodimer **236** (20 mg, 0.016 mmol), DDQ (19 mg, 0.082 mmol), Sc(OTf)₃ (40 mg, 0.082 mmol) and toluene (25 mL). The reaction was heated to 60 °C and stirred at this temperature for 3 h. THF (8 mL) was added and the reaction was stirred for a further 0.5 h at room temperature. The reaction mixture was filtered through a short plug of alox using CH₂Cl₂ as eluent to give fraction one, which contained starting material **236** and CH₂Cl₂ : THF (1 : 1, v/v) as eluent to give fused dimer **238**. Solvents were removed *in vacuo* to give a dark green solid **238** (12 mg, 0.010 mmol, 65%). M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.92 m, 12H, CH₃), 2.31 (m, 8H, CH₂), 2.53 (s, 6H, tolyl-CH₃), 5.44 (m, 2H, CH₂), 6.84 (m, 2H, H_β), 7.16 (m, 2H, H_β), 7.39-7.87 (m, 21H, Ph-H/H_β) ppm; UV/vis (THF): λ_{max} (log ε) = 422 (5.18), 565 (5.04), 965 (4.32) nm; HRMS (MALDI) *m/z* calcd. for [C₇₀H₅₃N₈Zn₂Br](M⁺): 1212.2159, found 1212.2200.

Bis{(5,10-(4-nitrophenyl)-20-phenyl-porphyrin-15-yl)} (240):

Dimer **194** (50 mg, 0.047 mmol) was dissolved in TFA (10 mL). NaNO_2 (300 mg, 4.347 mmol) was added and the reaction was stirred for 1 h at room temperature. H_2O (70 mL) was added and extracted with CH_2Cl_2 . The organic layer was washed with sat. NaHCO_3 and H_2O , dried over Na_2SO_4 and filtered. The solvents were removed and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica. Solvents removed to give a purple solid **240** (22 mg, 0.018 mmol, 38%). M.p. $>300^\circ\text{C}$; $R_f = 0.29$ (CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3 , TMS): $\delta = -2.13$ (s, 4H, NH), 7.72 (m, 6H, Ph-H), 8.12 (m, 4H, H_β), 8.23-8.24 (d, 4H, $^3J_{\text{H-H}} = 6.8$ Hz, Ph-H), 8.42-8.44 (d, 4H, $^3J_{\text{H-H}} = 7.7$ Hz, C_6H_4 -H), 8.50-8.52 (m, 4H, H_β), 8.59-8.61 (d, 4H, $^3J_{\text{H-H}} = 7.7$ Hz, C_6H_4 -H), 8.72-8.73 (d, 4H, $^3J_{\text{H-H}} = 7.7$ Hz, C_6H_4 -H), 8.95-8.88 (m, 8H, H_β) ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 424 (5.34), 458 (5.19), 532 (4.54), 590 (4.12), 656 (3.97) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{76}\text{H}_{46}\text{N}_{12}\text{O}_8](\text{M}^+)$: 1254.3562, found 1254.3580.

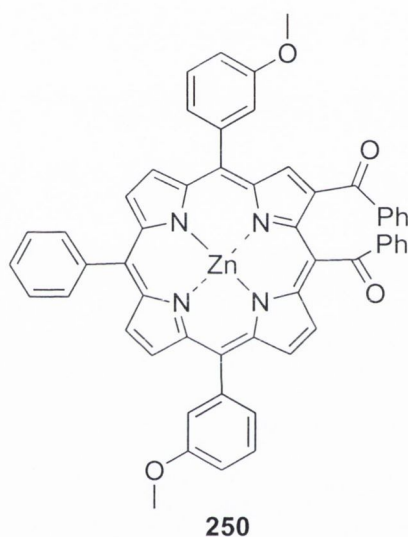
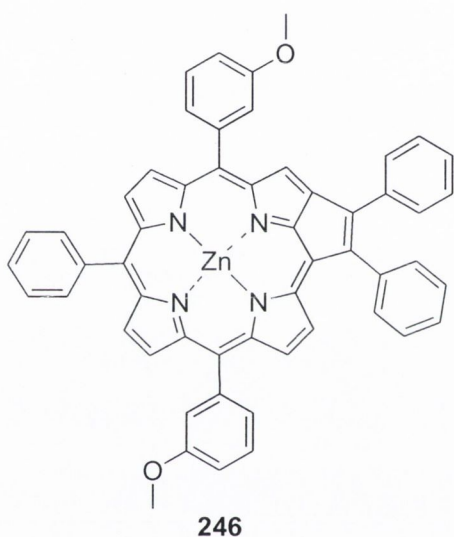
7,8-dehydropurpurin (**245**) and{3,5-Diphenylmethanone-10,20-bis(3-methoxy)phenylporphyrinato}zinc(II) (**249**):

Bromoporphyrin **110** (25 mg, 0.038 mmol), diphenylacetylene **243** (10 mg, 0.056 mmol) and (o-Tol)P₃ (2.5 mg, 0.008 mmol) were charged to a 25 mL Schlenk tube and dried under high vacuum for 20 min. Toluene (2.5 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. Pd₂(dba)₃ (2 mg, 0.002 mmol) and *N,N*-dicyclohexylmethylamine (37 mg, 0.165 mmol) were added and the reaction was heated to 110 °C and stirred at this temperature for 19 h, shielded from ambient light. Reaction mixture filtered through short plug of silica using CH₂Cl₂ as eluent. Solvents were removed to yield a crude dark orange solid containing **245** confirmed by UV-vis and HRMS analysis. UV/vis (CH₂Cl₂): λ_{max} (log ε) = 414, 537, 571 nm; HRMS (MALDI) *m/z* calcd. for [C₄₈H₃₂N₄O₂Zn](M⁺): 760.1817; found 760.1853. Compound **245** (25 mg) was dissolved in CHCl₃ (3000 mL) and was stirred, open to the air at room temperature, for 20 h. The transformation was monitored via UV-vis analysis, and the purpurin changed to porphyrin **249**. Upon completion, solvents were removed *in vacuo* and the residue was purified via a short column of silica (CH₂Cl₂ : *n*-hexane, 4 : 1, v/v). Solvents were removed to yield porphyrin **249** (24 mg, 0.030 mmol, 80%). M.p. >300 °C; *R*_f = 0.37 (*n*-hexane : EtOAc, 3 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.91 (s, 3H, OCH₃), 3.96 (s, 3H, OCH₃), 7.04-7.08 (t, ³*J*_{H-H} = 15.2 Hz, 2H, C₆H₄-*H*), 7.24-7.27 (t, ³*J*_{H-H} = 13.5 Hz, 2H, C₆H₄-*H*), 7.33 (m, 4H, Ph-*H*), 7.49 (m, 1H, C₆H₄-*H*), 7.59 (m, 1H, C₆H₄-*H*), 7.63 (m, 2H, C₆H₄-*H*), 7.74 (m, 4H, Ph-*H*), 7.79 (m, 2H, Ph-*H*), 8.91 (m, 3H, *H*_β), 9.09 (m, 2H, *H*_β), 9.38 (m, 2H, *H*_β), 10.28 (s, 1H, *H*_{meso}) ppm; ¹³C

NMR (100 MHz, CDCl_3): δ = 55.4, 55.5, 108.0, 113.5, 120.5, 122.3, 127.4, 127.6, 127.7, 128.0, 130.4, 131.6, 132.2, 132.4, 132.7, 132.8, 135.5, 138.0, 141.1, 142.8, 143.3, 143.6, 144.2, 144.9, 148.8, 150.3, 150.4, 151.0, 151.8, 157.8, 157.9, 194.4, 198.9 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 415 (5.47), 479 (4.15) 543 (4.15) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{48}\text{H}_{32}\text{N}_4\text{O}_4\text{Zn}](\text{M}^+)$: 792.1715, found 792.1732.

7,8-dehydropurpurin (**246**) and

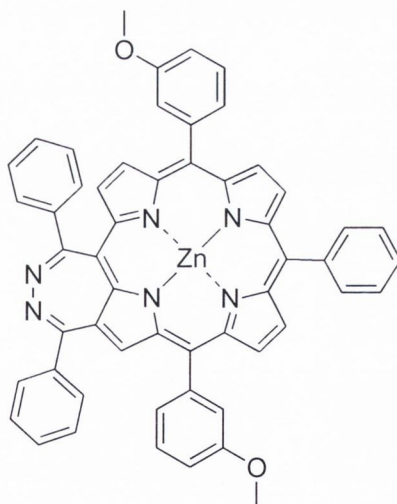
3,5-Diphenylmethanone-10,20-bis(3-methoxy)phenyl-15-phenylporphyrinato}zinc(II) (**250**):



Bromoporphyrin **111** (70 mg, 0.094 mmol), diphenylacetylene **243** (25 mg, 0.142 mmol) and (*o*-Tol) P_3 (6 mg, 0.021 mmol) were charged to a 10 mL Schlenk tube and dried under high vacuum for 20 min. Toluene (3 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $\text{Pd}_2(\text{dba})_3$ (4 mg, 0.005 mmol) and *N,N*-dicyclohexylmethylamine (85 mg, 0.470 mmol) were added and the reaction was heated to 120 °C and stirred at this temperature for 24 h, shielded from ambient light. The reaction mixture was filtered through a short plug of silica using CH_2Cl_2 as eluent. Solvents were removed to yield a dark orange solid **246**, confirmed by UV/vis and HRMS analysis. UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 416 (5.33), 489 (5.18), 619 (4.02) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{54}\text{H}_{36}\text{N}_4\text{O}_2\text{Zn}](\text{M}^+)$: 836.2130, found 836.2136. A solution of crude **246** (65 mg) in CHCl_3 (3000 mL) was stirred, open to the air at room temperature, for 20 h. The transformation was monitored via UV-vis analysis, with the formation porphyrin **250**. Upon completion, solvents were removed *in vacuo* and the

residue was purified via a short column of silica (CH_2Cl_2 : *n*-hexane, 4 : 1, v/v) to give two fractions, the first of which was debrominated starting material and the second contained **250**. Solvents were removed to yield porphyrin **250** (62 mg, 0.066 mmol, 76%). M.p. $>300^\circ\text{C}$; $R_f = 0.32$ (*n*-hexane : EtOAc = 3 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 3.97$ (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 7.10 (m, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.25 (m, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.37 (m, 2H, Ph-H), 7.56 (m, 4H, $\text{C}_6\text{H}_4\text{-H}$), 7.63 (m, 2H, Ph-H), 7.75 (m, 7H, Ph-H), 7.97 (d, $^3J_{\text{H-H}} = 7.9$ Hz, 2H, Ph-H), 8.20 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, Ph-H), 8.87 (m, 5H, H_β), 8.96 (d, $^3J_{\text{H-H}} = 2.1$ Hz, 1H, H_β), 9.09-9.07 (dd, $^3J_{\text{H-H}} = 4.7$ Hz, 1H, H_β) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 55.4, 55.5, 113.1, 113.2, 120.6, 120.9, 122.5, 122.9, 123.1, 123.4, 126.4, 127.1, 127.2, 127.5, 127.6, 127.8, 128.0, 130.5, 131.5, 131.7, 132.0, 132.1, 132.6, 132.7, 132.8, 134.4, 135.2, 135.5, 135.7, 135.9, 141.8, 142.9, 143.3, 143.9, 144.2, 145.7, 145.8, 148.9, 149.1, 149.3, 150.2, 150.4, 150.6, 151.0, 151.5, 157.7, 157.8, 194.8, 199.3$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 428 (5.22), 553 (4.07), 596 (3.64) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{54}\text{H}_{36}\text{N}_4\text{O}_4\text{Zn}](\text{M}^+)$: 868.2028, found 868.1988.

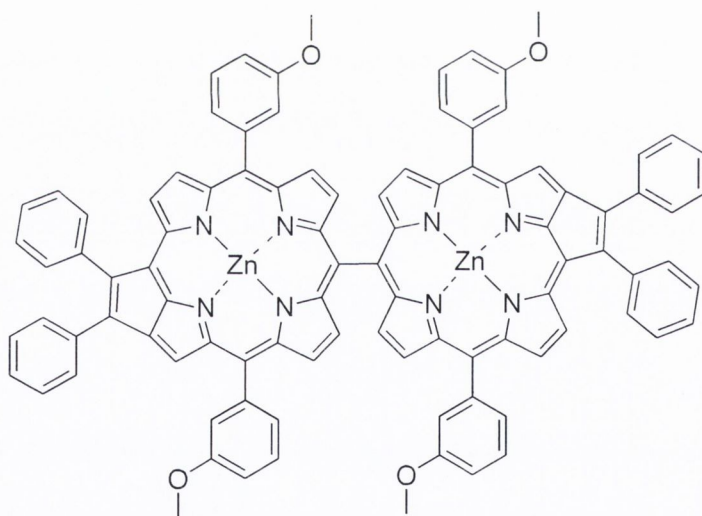
5,15-Bis(3-methoxyphenyl)-10-phenyl-18,20-diphenyldiazepine (**252**):



Porphyrin **250** (20 mg, 0.023 mmol), hydrazine hydrate (0.1 mL) mmol, acetic acid (1 mL) and toluene (1 mL) were charged to an 5 mL open flask and the mixture was irradiated under microwave conditions at 375 W for 7 mins. After completion, the reaction mixture was allowed to cool and was diluted with CH_2Cl_2 . The solution was washed with H_2O (2×10 mL), extracted with CH_2Cl_2 , dried over Na_2SO_4 and filtered. The solvents were removed to yield a green solid which was redissolved in CH_2Cl_2 and

filtered through a short plug of silica. Solvents were removed to give green solid **252** (17 mg, 0.020 mmol, 86%). M.p. >300 °C; R_f = 0.27 (CH₂Cl₂ : EtOAc 10 : 1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 3.93 (s, 3H, OCH₃), 3.95 (s, 3H, OCH₃), 7.16-7.18 (d, ³ $J_{\text{H-H}}$ = 15.7 Hz, 2H, C₆H₄-H), 7.24-7.27 (dd, ³ $J_{\text{H-H}}$ = 8.7, 2.5 Hz, 2H, C₆H₄-H), 7.35 (m, 2H, C₆H₄-H), 7.38-7.42 (t, ³ $J_{\text{H-H}}$ = 15.5 Hz, 2H, C₆H₄-H), 7.55-7.58 (t, ³ $J_{\text{H-H}}$ = 13.7 Hz, 2H, C₆H₄-H), 7.63 (m, 2H, Ph-H), 7.75 (m, 2H, Ph-H), 7.82 (m, 5H, Ph-H), 7.93-7.94 (d, ³ $J_{\text{H-H}}$ = 8.0 Hz, 2H, Ph-H), 8.23 (m, 2H, Ph-H), 8.90-8.91 (d, ³ $J_{\text{H-H}}$ = 4.8 Hz, 2H, H _{β}), 8.96 (m, 5H, H _{β}) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 55.4, 55.5, 113.5, 113.7, 120.4, 122.8, 123.2, 126.7, 127.4, 127.5, 127.8, 128.1, 129.3, 130.5, 130.9, 132.4, 132.5, 132.9, 134.3, 135.6, 138.2, 141.7, 142.3, 142.9, 143.4, 143.5, 145.6, 146.0, 149.0, 150.4, 150.6, 150.8, 150.9, 151.6, 157.8, 157.9 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ϵ) = 428 (5.01), 555 (3.95), 703 (3.80) nm; HRMS (MALDI) m/z calcd. for [C₅₄H₃₆N₆O₂Zn](M⁺): 864.2191, found 864.2222.

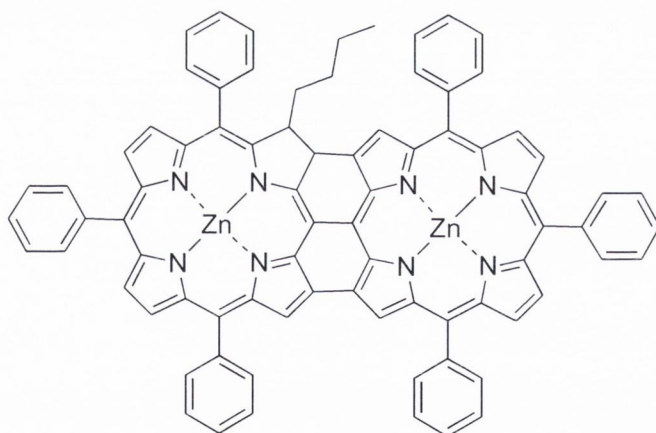
Bis-dehydropurpurin (254):



Bromoporphyrin dimer **202** (30 mg, 0.023 mmol), diphenylacetylene **243** (12 mg, 0.068 mmol) and (o-Tol)P₃ (3 mg, 0.009 mmol) were charged to a 25 mL Schlenk tube and dried under high vacuum for 20 min. Toluene (3 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. Pd₂(dba)₃ (2 mg, 0.002 mmol) and *N,N*-dicyclohexylmethylamine (45 mg, 0.230 mmol) were added and the reaction was heated to 110 °C and stirred at this temperature for 24 h, shielded from ambient light. The reaction mixture was filtered through short plug of silica using CH₂Cl₂ as eluent. Solvents were removed and the residue was subjected to column chromatography

(silica, CH_2Cl_2 : *n*-hexane, 2 : 1, 4 : 1, v/v) to yield one main fraction, orange in colour. Solvents were removed to give dark solid **254** (28 mg, 0.018 mmol, 78%). M.p. > 300 °C; R_f = 0.21 (CH_2Cl_2 : *n*-hexane = 3 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = 3.81 (s, 6H, OCH_3), 3.85 (s, 6H, OCH_3), 6.93 (s, 1H, H_β), 6.97 (s, 1H, H_β), 7.07-7.08 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.12-7.13 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 2H, $\text{C}_6\text{H}_4\text{-H}$), 7.23-7.27 (m, 4H, aryl-*H*), 7.38-7.41 (m, 24H, aryl-*H/H* $_\beta$), 7.59-7.60 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 6H, aryl-*H*), 7.69-7.71 (m, 2H, H_β), 7.79-7.81 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 4H, aryl-*H*), 7.86-7.88 (m, 2H, aryl-*H*), 8.06-8.07 (d, $^3J_{\text{H-H}}$ = 4.8 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 55.2, 55.3, 113.1, 113.3, 119.1, 119.2, 119.5, 120.0, 123.9, 124.9, 125.5, 126.4, 126.6, 126.9, 127.3, 127.4, 127.5, 127.6, 127.9, 128.1, 128.3, 128.5, 128.7, 128.8, 130.1, 130.4, 134.2, 134.3, 134.5, 135.7, 137.1, 141.2, 142.7, 143.4, 149.7, 150.3, 150.7, 151.5, 152.7, 153.1, 153.8, 154.4, 157.7, 157.9, 163.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 410 (5.46), 513 (5.54) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{96}\text{H}_{62}\text{N}_8\text{O}_4\text{Zn}_2](\text{M}^+)$: 1518.3477; found 1518.3505.

{2-Butyl-5-(5',10',20'-triphenylporphyrin-13',15',17'-ylato)-10,15,20-triphenyl}chlorinzinc(II) (258):



Porphyrin **214** (40 mg, 0.033 mmol) and THF (30 mL) were charged to a 100 mL Schlenk tube. Solution degassed via three freeze-pump-thaw cycles and vessel cooled to -78 °C using a cool bath. *n*-BuLi (0.1 mL, 0.200 mmol, 2.5 M solution in hexane) was added dropwise over 10 mins. Cool bath was removed and the reaction was allowed to warm to room temperature and stirred for a further 3 h. THF : H_2O (5 mL, 2 : 3, v/v) added and the reaction was stirred for 0.5 h. DDQ (75 mg, 0.330 mmol) in THF (10 mL) was added and the reaction was stirred for 1 h. The reaction mixture was filtered through plug of silica and solvents were removed *in vacuo*. The residue was redissolved

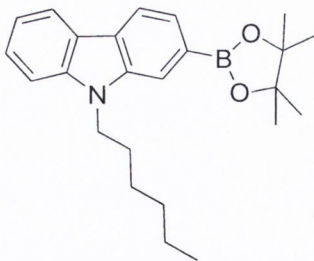
in CH_2Cl_2 and filtered through a second plug of silica to give two fractions, the first of which contained desired dimer **257** (6 mg, 0.005 mmol, 15%). M.p. $>300^\circ\text{C}$; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{pyridine-}D_5$, 10 : 1, TMS): δ = 0.68–0.73 (t, $^3J_{\text{H-H}}$ = 15.2 Hz, 3H, CH_3), 1.60 (m, 2H, CH_2), 2.02 (m, 2H, CH_2), 3.95 (m, 2H, CH_2), 4.06 (m, 1H, pyrrole-CH), 4.15–4.18 (dd, $^3J_{\text{H-H}}$ = 11.0 Hz, 2H, pyrrole- CH_2), 6.82 (m, 2H, H_β), 7.13 (m, 2H, H_β), 7.20 (m, 2H, H_β), 7.40–7.81 (m, 32H, Ph/ H_β), 8.25 (d, $^3J_{\text{H-H}}$ = 6.9 Hz, 2H, Ph- H) ppm; ^{13}C NMR (150 MHz, $\text{CDCl}_3/\text{pyridine-}D_5$, 10 : 1): δ = 13.9, 22.5, 29.5, 44.6, 61.8, 68.6, 113.8, 113.9, 120.9, 126.4, 127.0, 127.1, 127.6, 128.2, 130.6, 130.8, 131.8, 132.6, 132.7, 134.3, 140.9, 142.6, 150.1, 153.4, 156.2 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 418 (5.21), 564 (5.05), 808 (3.89), 910 (4.22), 1027 (4.41) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{80}\text{H}_{50}\text{N}_8\text{Zn}_2][\text{M-2H}]^+$: 1250.2741; found 1252.2770.

7.5 Porphyrin-carbazole conjugates

7.5.1 Carbazole synthesis

Carbazoles **264–266** were synthesised according to standard procedures via methods developed by Tavasli *et al.*^[322] Carbazoles **269–273** were synthesised via methods developed by Tang *et al.*^[326] and spectroscopic data agreed with those in the literature.

9-Hexylcarbazol-2-[4',4',5',5'-tetramethyl(1',3',2')dioxaborolan-2-yl] (**266**):

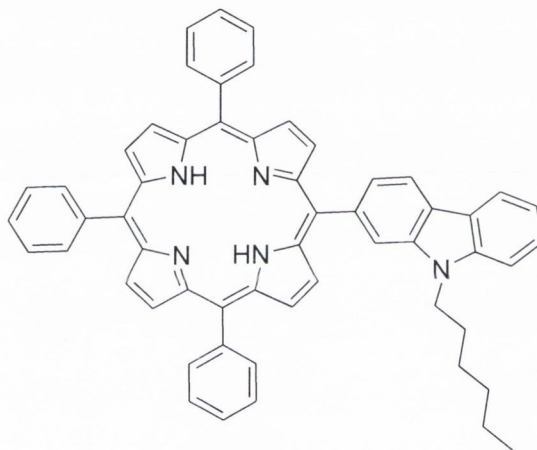


n-BuLi (2.5 M in hexanes, 1.9 mL, 4.6 mmol) was added dropwise to a solution of 2-bromo-9-hexylcarbazole (1.3g, 3.8 mmol) in dry THF (25 mL) at -78°C over 0.5 h. The reaction mixture was stirred at -78°C for 2 h, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.5 mmol, 1.5 mL) was added and the reaction was allowed stir at RT for 18 h. The milky solution was then poured onto ice water and extracted using diethylether. The organic layer was then washed with sat. NaCl and dried over Na_2SO_4 . Solvents were removed *in vacuo* and the yellow oily residue was recrystallised from ethanol to give white crystals (1.01 g, 2.7 mmol, 71%). M.p. = 86°C ; R_f = 0.37 (*n*-hexane : EtOAc = 20 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ =

0.90-0.94 (t, $^3J_{\text{H-H}} = 13.8$ Hz, 3H, CH_3), 1.31 (m, 6H, CH_2), 1.45 (s, 12H, CH_3), 1.92 (m, 2H, CH_2), 4.36-4.40 (t, $^3J_{\text{H-H}} = 14.6$ Hz, 2H, CH_2), 7.25-7.29 (t, $^3J_{\text{H-H}} = 14.5$ Hz, 1H, carbazole-*H*), 7.44-7.46 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 1H, carbazole-*H*), 7.51-7.55 (t, $^3J_{\text{H-H}} = 15.1$ Hz, 1H, carbazole-*H*), 7.73-7.75 (d, 1H, $^3J_{\text{H-H}} = 7.8$ Hz, 1H, carbazole-*H*), 7.93 (s, 1H, carbazole-*H*), 8.15-8.16 (d, $^3J_{\text{H-H}} = 3.0$ Hz, 1H, carbazole-*H*), 8.17-8.18 (d, $^3J_{\text{H-H}} = 3.0$ Hz, 1H, carbazole-*H*) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 13.6, 22.1, 24.5, 26.5, 28.6, 31.2, 42.5, 83.3, 108.4, 114.6, 118.2, 119.2, 120.1, 124.5, 125.7, 139.5, 140.5$ ppm; HRMS (ESI) m/z calcd. for $[\text{C}_{24}\text{H}_{33}\text{BNO}_2](\text{M}+\text{H})^+$ 378.2604, found 378.2606.

7.5.2 Porphyrin-carbazole conjugates

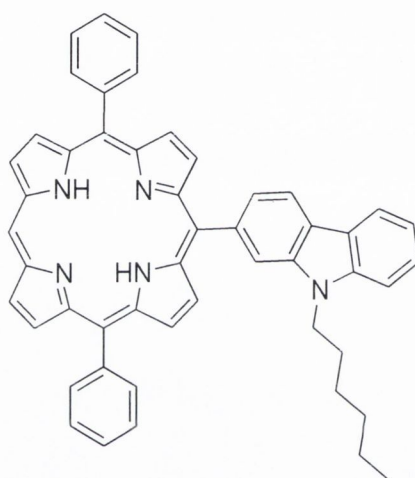
2-(5',10',15'-Triphenylporphyrin-20'-yl)-9-hexyl-carbazole (**274**):



Porphyrin **83** (50 mg, 0.08 mmol), borylated carbazole **266** (61 mg, 0.16 mmol) and K_3PO_4 (210 mg, 0.97 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 mins. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $\text{Pd}(\text{PPh}_3)_4$ (9 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 hrs. Solvents were removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with saturated NaHCO_3 , brine and H_2O . The organic layers were dried over MgSO_4 and solvents were removed *in vacuo*. The residue was subjected to column chromatography (CH_2Cl_2 : *n*-hexane 1 : 1) to yield purple product **274** (49 mg, 0.06 mmol, 75%,). M.p. = 201 °C; $R_f = 0.68$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.68$ (s, 2H, NH), 0.76-0.80 (t, $^3J_{\text{H-H}} = 14.0$ Hz, 3H, CH_3), 0.91 (m, 2H, CH_2), 1.26 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 1.97 (m, 2H, CH_2), 4.43-4.46 (t, $^3J_{\text{H-H}} = 14.0$ Hz, 2H, CH_2),

7.40-7.43 (t, $^3J_{\text{H-H}} = 15.0$ Hz, 1H, carbazole-*H*), 7.60 (m, 2H, carbazole-*H*), 7.79 (m, 9H, Ph-*H*), 8.14-8.17 (d, $^3J_{\text{H-H}} = 9.4$ Hz, 1H, carbazole-*H*), 8.24-8.28 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6H, Ph-*H*), 8.28 (s, 1H, carbazole-*H*), 8.37-8.39 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.44-8.45 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.87 (m, 6H, H_β), 8.92-8.93 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 13.9, 22.5, 26.9, 29.1, 31.5, 43.3, 109.1, 115.7, 117.9, 119.2, 120.1, 127.7, 131.2, 134.5, 139.3, 139.7, 141.2, 142.2$ ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 422 (5.40), 517 (4.43), 522 (4.31) 591 (4.28), 646 (4.23) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{56}\text{H}_{45}\text{N}_5](\text{M}^+)$ 787.3675, found 787.3652.

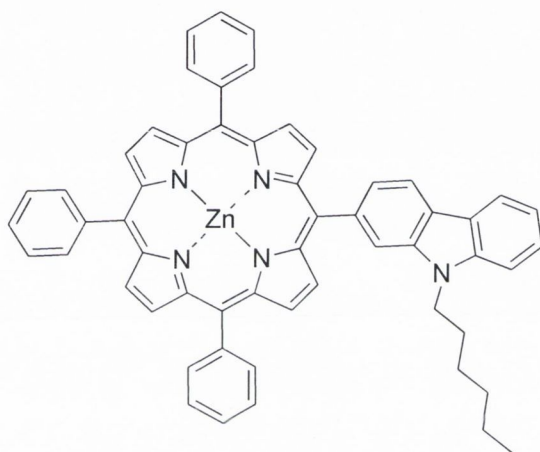
2-(5',15'-Diphenylporphyrin-10'-yl)-9-hexyl-carbazole (275):



Porphyrin **94** (50 mg, 0.09 mmol), borylated carbazole **266** (35 mg, 0.09 mmol) and K_3PO_4 (197 mg, 0.92 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 mins. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $\text{Pd}(\text{PPh}_3)_4$ (10.7 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 hrs. The solvents were removed *in vacuo*, the residue dissolved in CH_2Cl_2 and washed with saturated NaHCO_3 , brine and H_2O . The organic layers were dried over MgSO_4 and solvents were removed *in vacuo*. The residue was subjected to column chromatography (CH_2Cl_2 : *n*-hexane 1 : 1) and the product recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give purple crystals **275** (38 mg, 0.05 mmol, 61%). M.p. = 182 °C; $R_f = 0.54$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = -2.91$ (s, 2H, NH), 0.75-0.79 (t, $^3J_{\text{H-H}} = 13.4$ Hz, 3H, CH_3), 1.24 (m, 4H, CH_2), 1.41 (m, 2H, CH_2), 1.96 (m, 2H, CH_2), 4.41-4.45 (t, $^3J_{\text{H-H}} = 14.0$ Hz, 2H, CH_2), 7.39-7.43 (t, $^3J_{\text{H-H}} = 12.8$ Hz, 1H, carbazole-*H*), 7.61 (m, 2H, carbazole-*H*), 7.80 (m, 6H, Ph-*H*), 8.15-8.17 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.27 (m, 4H, Ph-*H*), 8.30 (m, 1H, carbazole-*H*), 8.38-8.39 (d, $^3J_{\text{H-H}}$

$_{\text{H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.43-8.45 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.91-8.92 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_{β}), 8.95-8.96 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_{β}), 9.06-9.07 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, H_{β}), 9.06-9.07 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H, H_{β}) 10.27 (s, 1H, H_{meso}) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 13.9, 22.5, 27.1, 29.1, 31.5, 43.3, 109.1, 115.8, 117.9, 119.2, 119.7, 120.7, 121.6, 122.2, 122.8, 125.9, 126.7, 126.8, 126.9, 127.7, 130.7, 131.3, 131.4, 131.8, 134.6, 134.7, 136.6, 139.2, 140.1, 141.2, 141.8, 147.5$ ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 424 (5.43), 518 (4.48), 524 (4.33) 590 (4.30), 647 (4.26) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{50}\text{H}_{41}\text{N}_5](\text{M}^+)$ 711.3362, found 711.3362.

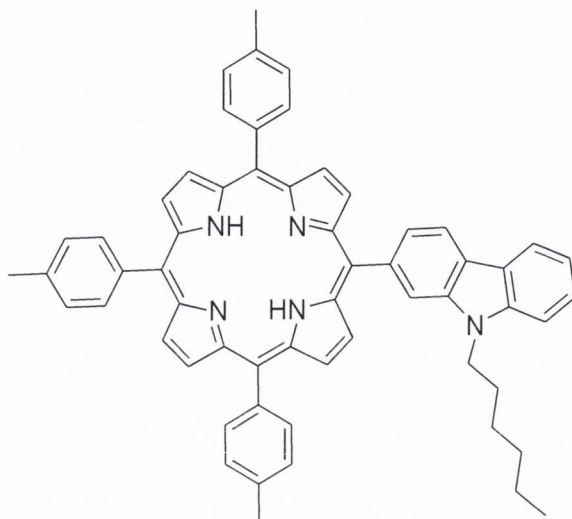
2-(5',10',15'-Triphenylporphyrinato(zinc)(II)-20'-yl)-9-hexyl-carbazole (276):



Porphyrin **274** (27 mg, 0.03 mmol) was dissolved in CHCl_3 (10 mL) and heated to 70 °C. $\text{Zn}(\text{OAc})_2$ (26 mg, 0.34 mmol) in MeOH (0.5 mL) was added and the reaction was stirred for 30 mins. Solvents were removed and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica. Solvents were removed *in vacuo* to yield a bright purple solid **276** (24 mg, 0.03 mmol, 74%). M.p. = 182 °C; $R_f = 0.53$ (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 0.78$ -0.82 (t, $^3J_{\text{H-H}} = 14.0$ Hz, 3H, CH_3), 1.27 (m, 4H, CH_2), 1.42 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 4.42-4.46 (t, $^3J_{\text{H-H}} = 14.6$ Hz, 2H, CH_2), 7.38-7.42 (t, $^3J_{\text{H-H}} = 14.6$ Hz, 1H, carbazole-*H*), 7.61 (m, 2H, carbazole-*H*), 7.80 (m, 9H, Ph-*H*), 8.17-8.19 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.27 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 6H, Ph-*H*), 8.30 (m, 1H, carbazole-*H*), 8.36-8.38 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.44-8.46 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 1H, carbazole-*H*), 8.95 (m, 8H, H_{β}), 9.00 (m, 6H, H_{β}), 9.06-9.07 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_{β}) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 13.9, 22.6, 27.1, 29.2, 31.6, 43.3, 109.1, 115.6, 117.9, 119.2, 120.7, 121.1, 121.2, 122.1, 122.9, 125.9, 126.5, 126.6, 127.5, 131.9, 132.3, 134.4, 139.2, 140.3, 141.2, 142.8, 150.2, 150.6$ ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 423 (5.42), 549 (4.45),

587 (4.28) nm; HRMS (MALDI) m/z calcd. for $[C_{56}H_{43}N_5Zn](M^+)$ 849.2810, found 849.2801.

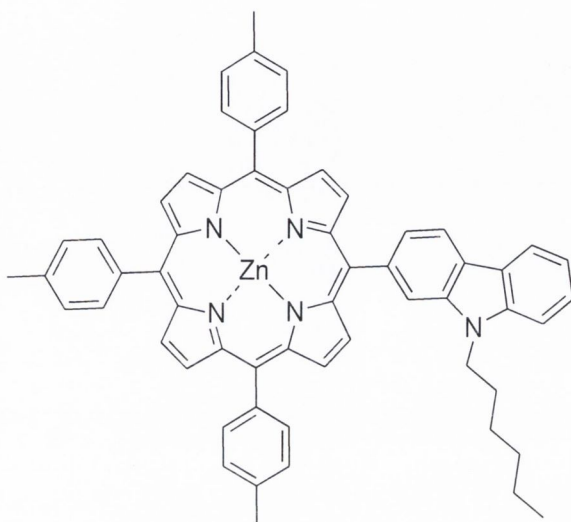
2-(5',10',15'-Tris(4-methylphenyl)porphyrin-20'-yl)-9-hexyl-carbazole (277):



Porphyrin **93** (50 mg, 0.08 mmol), borylated carbazole **266** (60 mg, 0.16 mmol) and K_3PO_4 (194 mg, 0.91 mmol,) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 mins. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9 mg, 0.01 mmol) was added, the reaction was heated to 80 °C under argon and left to stir at this temperature for 18 hrs. Solvents were removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O . The organic layers were dried over $MgSO_4$ and solvents were removed *in vacuo*. The residue was subjected to column chromatography (CH_2Cl_2 : *n*-hexane, 1 : 1, v/v) to yield purple product **277** (54 mg, 0.07 mmol, 86%). M.p. = 184 °C; R_f = 0.58 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); 1H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.66 (s, 2H, NH), 0.76-0.81 (t, $^3J_{H-H}$ = 13.9 Hz, 3H, CH_3), 0.91 (m, 2H, CH_2), 1.26 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 1.96 (m, 2H, CH_2), 2.73 (s, 6H, tolyl- CH_3), 2.75 (s, 3H, tolyl- CH_3), 4.42-4.46 (t, $^3J_{H-H}$ = 13.9 Hz, 2H, CH_2), 7.40-7.43 (t, $^3J_{H-H}$ = 14.0 Hz, 1H, carbazole-*H*), 7.57 (m, 6H, C_6H_4 -*H*), 7.60 (m, 2H, carbazole-*H*), 8.13-8.15 (d, $^3J_{H-H}$ = 7.0 Hz, 6H, C_6H_4 -*H*), 8.17 (m, 1H, carbazole-*H*), 8.29 (s, 1H, carbazole-*H*), 8.37-8.39 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, carbazole-*H*), 8.44-8.45 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, carbazole-*H*), 8.91 (m, 8H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 11.0, 13.9, 14.1, 21.6, 22.6, 29.1, 30.4, 38.7, 43.3, 68.2, 109.1, 115.8, 117.9, 119.2, 125.9, 127.4, 128.8, 130.9, 134.5, 137.3, 139.3, 139.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 423 (5.50), 518 (4.61),

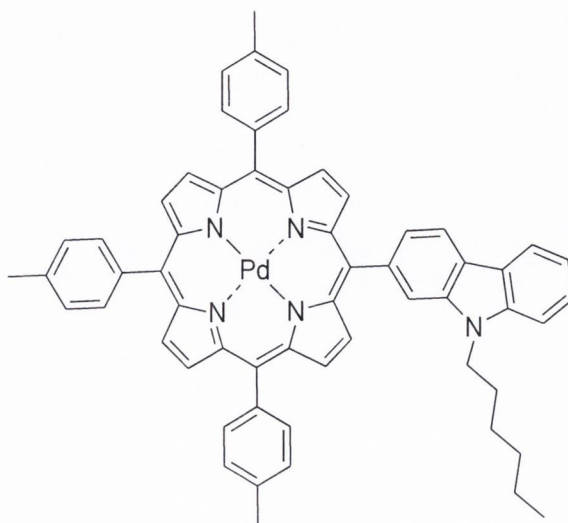
554 (4.50), 591 (4.41), 650 (4.39) nm; HRMS (MALDI) m/z calcd. for $[C_{59}H_{51}N_5](M^+)$ 828.4144, found 828.4121.

2-(5',10',15'-Tris(4-methylphenyl)porphyrinato(zinc)(II)-20'-yl)-9-hexyl-carbazole (278):



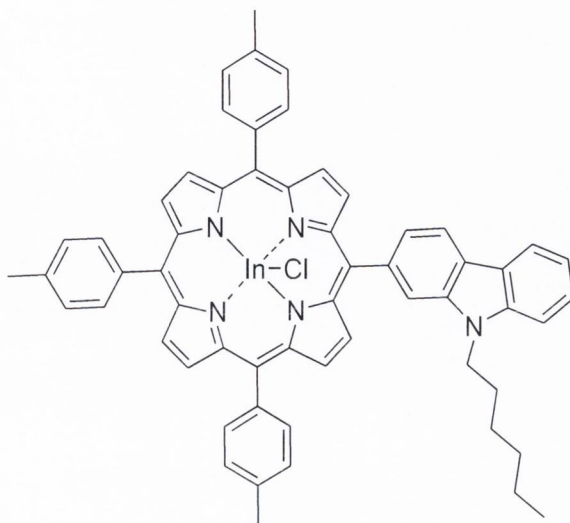
Porphyrin **277** (50 mg, 0.06 mmol) was dissolved in $CHCl_3$ (10 mL) and heated to 70 °C. $Zn(OAc)_2$ (54 mg, 0.30 mmol) in MeOH (0.5 mL) was added and the reaction stirred for 30 min. Solvents were removed and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica. Solvents were removed *in vacuo* to yield a bright purple solid **278** (43 mg, 0.05 mmol, 81%). M.p. = 144 °C; R_f = 0.53 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.77-0.80 (t, $^3J_{H-H}$ = 14.4 Hz, 3H, CH_3), 0.89 (m, 4H, CH_2), 1.19 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 2.74 (s, 6H, tolyl- CH_3), 2.75 (s, 3H, tolyl- CH_3), 4.43-4.45 (t, $^3J_{H-H}$ = 14.4 Hz, 2H, CH_2), 7.40-7.42 (t, $^3J_{H-H}$ = 13.8 Hz, 1H, carbazole-*H*), 7.58 (m, 6H, Ph-*H*), 7.60 (m, 2H, carbazole-*H*), 8.14 (m, 6H, Ph-*H*), 8.17 (m, 1H, carbazole-*H*), 8.29 (s, 1H, carbazole-*H*), 8.37-8.39 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, carbazole-*H*), 8.44-8.45 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, carbazole-*H*), 9.00 (m, 8H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 21.5, 21.9, 22.7, 27.1, 31.6, 53.4, 77.2, 109.0, 115.6, 117.8, 119.2, 120.6, 125.9, 127.3, 127.4, 131.9, 132.1, 134.3, 134.4, 134.5, 147.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 422 (5.52), 547 (4.63), 588 (4.40) nm; HRMS (MALDI) m/z calcd. for $[C_{59}H_{49}N_5Zn](M^+)$ calcd. 891.3279, found 891.3237.

2-[5',10',15'-Tris(4-methylphenyl)porphyrinato(palladium)(II)-20'-yl]-9-hexyl-carbazole (279):

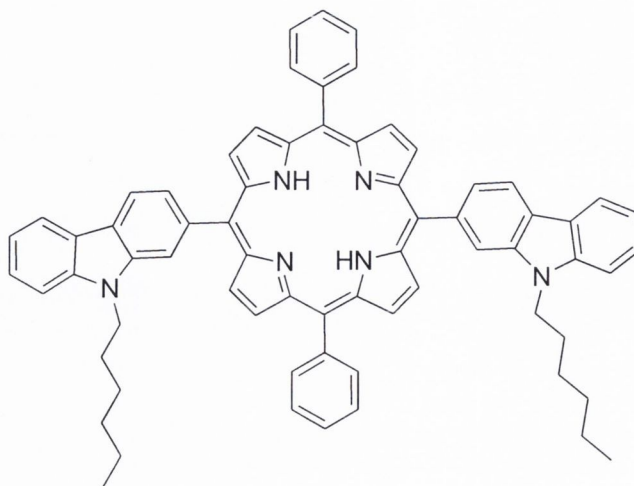


Porphyrin **277** (30 mg, 0.04 mmol), Pd(OAc)₂ (24 mg, 0.11 mmol) and toluene (20 mL) were placed in a two-necked round bottomed flask and heated to 110 °C. Upon reaction completion, the solvent was removed *in vacuo* and the residue was redissolved in CH₂Cl₂. The crude product was filtered through a plug of silica, solvents were removed *in vacuo* to yield a red coloured solid **279** (30 mg, 0.03 mmol, 89%). M.p. = 130 °C; *R*_f = 0.78 (CH₂Cl₂ : *n*-hexane, 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.77-0.81 (t, ³*J*_{H-H} = 14.4 Hz, 3H, CH₃), 1.29 (m, 4H, CH₂), 1.65 (m, 2H, CH₂), 1.96 (m, 2H, CH₂), 2.71(s, 6H, tolyl-CH₃), 2.73 (s, 3H, tolyl-CH₃), 4.40-4.44 (t, ³*J*_{H-H} = 14.4 Hz, 2H, CH₂), 7.41 (m, 1H, carbazole-*H*), 7.47-7.49 (m, 1H, carbazole-*H*), 7.57 (m, 6H, C₆H₄-*H*), 8.08-8.09 (d, ³*J*_{H-H} = 7.8 Hz, 6H, C₆H₄-*H*), 8.12 (m, 1H, carbazole-*H*), 8.24 (s, 1H, carbazole-*H*), 8.36-8.38 (d, ³*J*_{H-H} = 7.8 Hz, 1H, carbazole-*H*), 8.42-8.44 (d, ³*J*_{H-H} = 7.8 Hz, 1H, carbazole-*H*), 8.87 (m, 8H, *H*_β) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 21.6, 22.6, 24.9, 27.1, 29.1, 29.6, 31.6, 34.2, 43.3, 66.7, 109.1, 115.3, 118.1, 119.2, 120.6, 121.8, 122.2, 122.5, 125.9, 126.1, 127.4, 128.2, 128.6, 129.7, 130.9, 131.1, 134.1, 137.4, 138.9, 139.3, 139.4, 141.2, 141.7, 141.9 ppm; UV/vis (CH₂Cl₂): λ_{max} (log ε) = 421 (4.42), 526 (3.53) nm; HRMS (MALDI) *m/z* calcd. for [C₅₉H₄₉N₅Pd](M⁺) 933.3023, found 933.3058.

2-[5',10',15'-Tris(4methylphenyl)porphyrinato(indiumchloride)-20'-yl]-9-hexyl-carbazole (280):

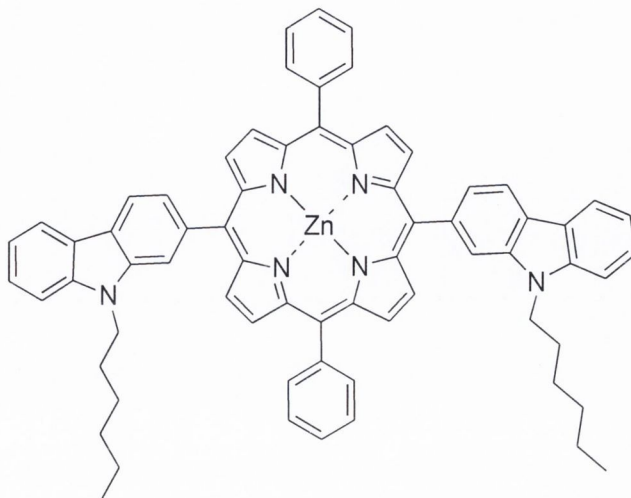


Porphyrin **277** (33 mg, 0.04 mmol), InCl_3 (88 mg, 0.40 mmol), CH_3COONa (298 mg, 4.25 mmol) and glacial acetic acid (15 mL) were placed in a round bottomed flask and heated to 110 °C and left stir for 18 h. Upon reaction completion, the solvent was removed *in vacuo* and the residue was redissolved in CH_2Cl_2 . The crude product was extracted from saturated NaHCO_3 , organic phases washed with brine and dried over MgSO_4 . Solvents were removed *in vacuo* to yield a purple-green coloured solid **280** (23 mg, 0.02 mmol, 59%). M.p. = 141 °C; R_f = 0.27 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.81-0.85 (t, $^3J_{\text{H-H}}$ = 12.9 Hz, 3H, CH_3), 0.91 (m, 2H, CH_2), 1.28 (m, 4H, CH_2), 1.48 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 2.74 (s, 6H, tolyl- CH_3), 2.75 (s, 3H, tolyl- CH_3), 4.45-4.49 (t, $^3J_{\text{H-H}}$ = 13.8 Hz, 2H, CH_2), 7.40-7.44 (t, $^3J_{\text{H-H}}$ = 14.0 Hz, 1H, carbazole-*H*), 7.58 (m, 4H, C_6H_4 -*H*), 7.64 (m, 2H, carbazole-*H*), 8.03-8.05 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 4H, C_6H_4 -*H*), 8.27-8.29 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 4H, C_6H_4 -*H*), 8.37-8.39 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 1H, carbazole-*H*), 8.44 (s, 2H, carbazole-*H*), 8.49-8.50 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 1H, carbazole-*H*), 9.12 (m, 8H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 13.8, 21.4, 22.4, 24.8, 26.9, 28.9, 31.4, 43.4, 109.0, 115.3, 116.4, 117.9, 118.0, 119.2, 120.5, 121.7, 122.3, 126.2, 127.4, 127.5, 132.5, 134.1, 134.8, 137.6, 138.8, 139.1, 141.2, 149.5, 149.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 431 (5.45), 562 (4.47), 603 (4.32) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{59}\text{H}_{49}\text{N}_5\text{InCl}](\text{M}^+)$ 977.2715, found 977.2671.

Bis-(2,2'-{5',15'-diphenyl}porphyrin-10',20'-yl}-9-hexyl-carbazole) (281):

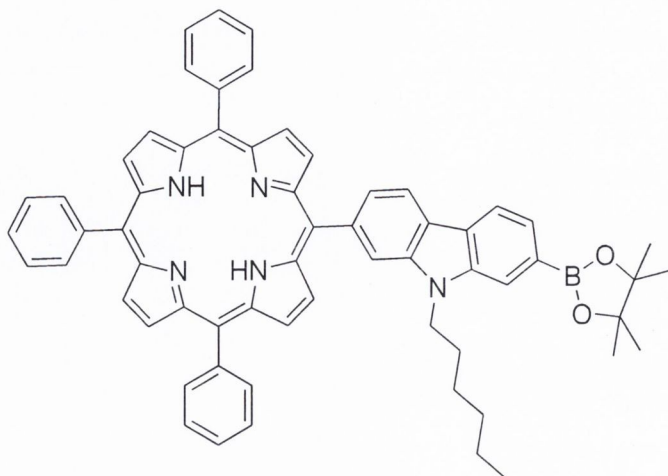
Porphyrin **98** (50 mg, 0.08 mmol), borylated carbazole **266** (303 mg, 0.81 mmol) and K_3PO_4 (345 mg, 1.62 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 hrs. Solvents were removed *in vacuo*, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O . The organic layers were dried over $MgSO_4$ and solvents were removed *in vacuo*. The crude product was redissolved and filtered through a plug of silica gel using CH_2Cl_2 as eluent. Solvents were removed and the purple solid was recrystallised from CH_2Cl_2 /MeOH to yield purple crystals **281** (58 mg, 0.06 mmol, 76%). M.p. = 283–285 °C; R_f = 0.57 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); 1H NMR (600 MHz, $CDCl_3$, TMS): δ = -2.61 (s, 2H, NH), 0.77–0.80 (t, $^3J_{H-H}$ = 14.0 Hz, 6H, CH_3), 0.89 (m, 4H, CH_2), 1.26 (m, 4H, CH_2), 1.98 (m, 4H, CH_2), 4.43–4.47 (t, $^3J_{H-H}$ = 14.0 Hz, 4H, CH_2), 7.42 (m, 2H, carbazole-*H*), 7.62 (m, 4H, carbazole-*H*), 7.77 (m, 6H, Ph-*H*), 8.16–8.18 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, carbazole-*H*), 8.25–8.26 (d, $^3J_{H-H}$ = 7.6 Hz, 4H, Ph-*H*), 8.29–8.30 (d, $^3J_{H-H}$ = 1.8 Hz, 2H, carbazole-*H*), 8.37–8.40 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, carbazole-*H*), 8.44–8.46 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, carbazole-*H*), 8.86–8.88 (d, $^3J_{H-H}$ = 4.7 Hz, 4H, H_β), 8.93–8.94 (d, $^3J_{H-H}$ = 4.7 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.8, 22.4, 24.8, 26.9, 28.9, 31.4, 4.2, 108.9, 115.6, 117.8, 119.1, 120.0, 120.5, 120.9, 122.1, 122.7, 125.8, 126.5, 127.5, 134.4, 139.2, 139.6, 141.1, 142.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 426 (5.49), 518 (4.47), 554 (4.36), 592 (4.30), 648 (4.29) nm; HRMS (MALDI) m/z calcd. for $[C_{68}H_{60}N_6](M^+)$ 960.4879, found 960.4841.

**Bis-(2,2'-{5',15'-diphenyl}porphyrinato(zinc)II-10',20'-yl}-9-hexyl-carbazole)
(282):**



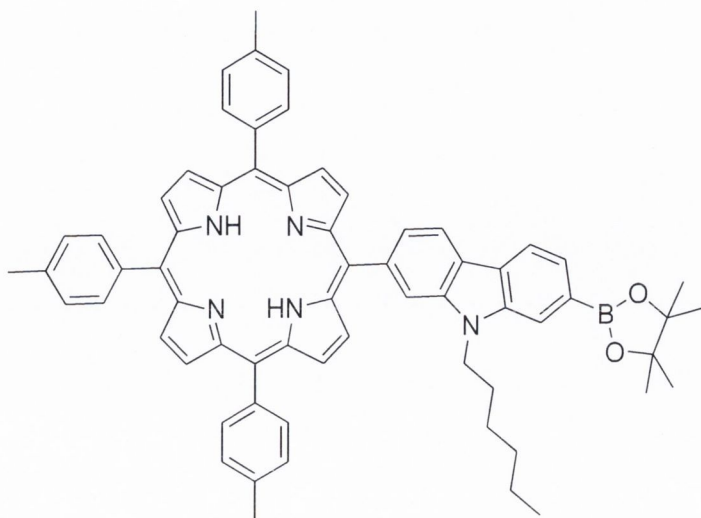
Porphyrin **281** (50 mg, 0.05 mmol) was dissolved in CHCl_3 (10 mL) and heated to 70 °C. $\text{Zn}(\text{OAc})_2$ (56 mg, 0.26 mmol) in MeOH (0.5 mL) was added and the reaction stirred for 30 mins. Solvents were removed and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica. Solvents were removed *in vacuo* to yield a bright purple solid **282** (42 mg, 0.04 mmol, 81%). M.p. = 251-253 °C; R_f = 0.45 (CH_2Cl_2 : *n*-hexane, 1 : 1, v/v); ^1H NMR (600 MHz, CDCl_3 , TMS): δ = 0.78-0.80 (t, $^3J_{\text{H-H}}$ = 13.2 Hz, 6H, CH_3), 1.26 (m, 8H, CH_2), 1.43 (m, 4H, CH_2), 1.99 (m, 4H, CH_2), 4.44-4.46 (t, $^3J_{\text{H-H}}$ = 13.9 Hz, 4H, CH_2), 7.40-7.42 (t, $^3J_{\text{H-H}}$ = 13.9 Hz, 2H, carbazole-*H*), 7.60 (m, 4H, carbazole-*H*), 7.78 (m, 6H, Ph-*H*), 8.18-8.19 (d, $^3J_{\text{H-H}}$ = 7.3 Hz, 2H, carbazole-*H*), 8.27-8.28 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 4H, Ph-*H*), 8.31 (s, 2H, carbazole-*H*), 8.38-8.39 (d, $^3J_{\text{H-H}}$ = 7.4 Hz, 2H, carbazole-*H*), 8.45-8.46 (d, $^3J_{\text{H-H}}$ = 7.4 Hz, 2H, carbazole-*H*), 8.97-8.98 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 4H, H_β), 9.04-9.05 (d, $^3J_{\text{H-H}}$ = 4.4 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 13.8, 22.4, 26.9, 28.9, 31.4, 43.2, 108.9, 115.5, 117.7, 119.0, 120.5, 121.9, 122.8, 125.7, 126.4, 126.5, 127.4, 131.8, 132.1, 134.2, 139.1, 140.2, 141.1, 142.7, 150.1, 150.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 424 (5.52), 548 (4.51), 590 (4.38) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{68}\text{H}_{58}\text{N}_6\text{Zn}](\text{M}^+)$ 1022.4014, found 1022.4061.

**2-(5',10',15'-triphenylporphyrin-20'-yl)-7-[4',4',5',5'-tetramethyl(1',3',2')
dioxaborolan-2'-yl]-9-hexyl-carbazole (283):**



Porphyrin **83** (50 mg, 0.08 mmol), borylated carbazole **273** (90 mg, 0.18 mmol) and K_3PO_4 (343 mg, 1.62 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 mins. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9 mg, 0.01 mmol) was added, the reaction was heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents were removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O . The organic layers were dried over $MgSO_4$ and the solvents were removed *in vacuo*. The residue was subjected to column chromatography (CH_2Cl_2 : *n*-hexane, 1 : 1, v/v) to yield purple product which was recrystallised from CH_2Cl_2 /MeOH to give purple crystals **283** (46 mg, 0.05 mmol, 62%). M.p. = 231-234 °C; R_f = 0.26 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); 1H NMR (600 MHz, $CDCl_3$, TMS): δ = -2.65 (s, 2H, NH), 0.77-0.79 (t, $^3J_{H-H}$ = 13.6 Hz, 3H, CH_3), 0.89 (m, 2H, CH_2), 1.26 (m, 2H, CH_2), 1.56 (s, 12H, CH_3), 2.01 (m, 4H, CH_2), 4.49 (m, 2H, CH_2), 7.62-7.63 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, carbazole-*H*), 7.78 (m, 9H, Ph-*H*), 7.87-7.88 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, carbazole-*H*), 8.16-8.18 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, carbazole-*H*), 8.26 (d, $^3J_{H-H}$ = 7.6 Hz, 6H, Ph-*H*), 8.38-8.39 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, carbazole-*H*), 8.45-8.47 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, carbazole-*H*), 8.87 (m, 6H, H_β), 8.93-8.94 (d, $^3J_{H-H}$ = 4.0 Hz, 2H, H_β) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 22.4, 24.8, 26.8, 29.0, 31.4, 43.1, 83.7, 107.7, 114.9, 115.3, 115.8, 118.3, 118.9, 119.5, 120.0, 120.9, 121.7, 121.8, 125.0, 125.3, 126.5, 127.5, 131.1, 134.4, 139.7, 140.1, 140.6, 140.7, 142.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 422 (5.13), 515 (4.22), 552 (4.17), 592 (4.15), 655 (4.09) nm; HRMS (MALDI) $[C_{62}H_{57}N_5O_2B](M+H)^+$ 914.4605, found 914.4604.

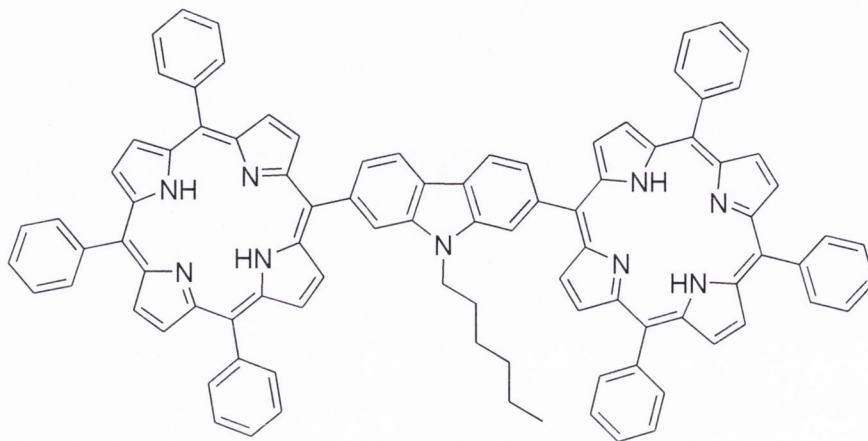
**2-(5',10',15'-tri(4-methylphenyl)-20'-yl)-7-[4',4',5',5'-tetramethyl(1',3',2')
dioxaborolan-2'-yl)-9-hexyl-carbazole (284):**



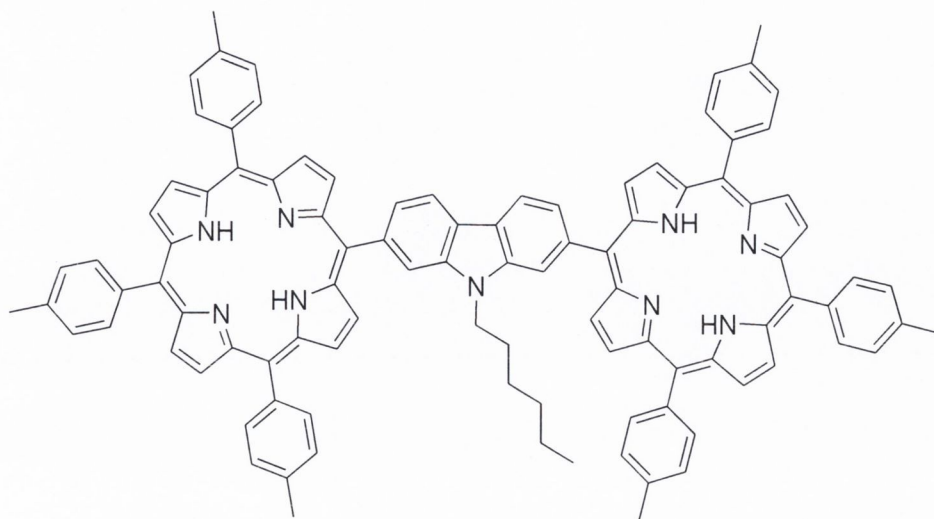
Porphyrin **93** (50 mg, 0.08 mmol), borylated carbazole **273** (190 mg, 0.38 mmol) and K_3PO_4 (322 mg, 1.52 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9 mg, 0.01 mmol) was added, the reaction was heated to 80°C under argon and left to stir at this temperature for 18 h. Solvents were removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O . The organic layers were dried over $MgSO_4$ and solvents were removed *in vacuo*. The residue was filtered through a plug of silica using CH_2Cl_2 : *n*-hexane (1 : 1, v/v) and CH_2Cl_2 as eluent to give three fractions. Solvents were removed to yield purple product **284** (40 mg, 0.04 mmol, 55%). M.p. = 220-223 °C; R_f = 0.61 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); 1H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.67 (s, 2H, NH), 0.77-0.80 (t, $^3J_{H-H}$ = 14.2 Hz, 3H, CH_3), 0.91 (m, 2H, CH_2), 1.29 (m, 4H, CH_2), 1.49 (s, 12H, CH_3), 2.00 (m, 2H, CH_2), 2.73 (s, 6H, tolyl- CH_3), 2.75 (s, 3H, tolyl- CH_3), 4.48-4.51 (t, $^3J_{H-H}$ = 14.2 Hz, 2H, CH_2), 7.58 (m, 6H, C_6H_4 -H), 7.87-7.89 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, carbazole-H), 8.07 (s, 1H, carbazole-H), 8.13-8.15 (d, $^3J_{H-H}$ = 8.3 Hz, 6H, C_6H_4 -H), 8.29 (s, 1H, carbazole-H), 8.36-8.40 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, carbazole-H), 8.45-8.47 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, carbazole-H), 8.90 (s, 8H, H_β) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 21.6, 22.6, 25.0, 27.1, 29.7, 31.6, 43.2, 83.9, 115.6, 115.9, 118.4, 119.9, 120.2, 120.8, 121.9, 125.4, 126.7, 127.4, 130.9, 134.5, 137.3, 139.3, 139.9, 130.4, 140.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 424 (5.60), 518 (4.49), 553

(4.36), 592 (4.27), 649 (4.26) nm; HRMS (ESI) m/z calcd. for $[\text{C}_{65}\text{H}_{63}\text{N}_5\text{O}_2\text{B}](\text{M}+\text{H})^+$ calcd. 956.5075, found 956.5072.

2,7-Bis[5',10',15'-triphenylporphyrin-20'-yl]-9-hexyl-carbazole (285):



Porphyrin **283** (20 mg, 0.02 mmol), bromoporphyrin **83** (14 mg, 0.02 mmol) and K_3PO_4 (37 mg, 0.18 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $\text{Pd}(\text{PPh}_3)_4$ (5 mg, 0.04 mmol) was added, the reaction was heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents were removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with saturated NaHCO_3 , brine and H_2O . The organic layers were dried over MgSO_4 and solvents were removed *in vacuo*. The residue was subjected to column chromatography (CH_2Cl_2 : *n*-hexane, 2 : 1, v/v), giving three fractions, the first of which was debrominated porphyrin **4** and the second of which was the desired product **285** as a purple solid (22 mg, 0.02 mmol, 75%). M.p. >300 °C; R_f = 0.53 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); ^1H NMR (600 MHz, CDCl_3): δ = -2.55 (s, 2H, NH), 0.69-0.71 (t, $^3J_{\text{H-H}}$ = 13.9 Hz, 3H, CH_3), 0.95 (m, 2H, CH_2), 1.22 (m, 4H, CH_2), 2.08 (m, 2H, CH_2), 4.56 (m, 2H, CH_2), 7.81 (m, 18H, Ph-*H*), 8.24-8.25 (d, $^3J_{\text{H-H}}$ = 7.9 Hz, 2H, carbazole-*H*), 8.32 (m, 12H, Ph-*H*), 8.47 (s, 2H, carbazole-*H*), 8.66-8.68 (d, $^3J_{\text{H-H}}$ = 7.9 Hz, 2H, carbazole-*H*), 8.95 (m, 8H, H_β), 8.97-8.98 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 4H, H_β), 9.08-9.09 (d, $^3J_{\text{H-H}}$ = 4.5 Hz, 4H, H_β) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 13.7, 22.4, 27.1, 29.6, 31.4, 43.5, 108.0, 116.0, 118.2, 120.1, 120.9, 122.1, 126.6, 127.0, 127.6, 131.1, 134.5, 139.9, 140.0, 142.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 423 (5.60), 517 (4.61), 554 (4.43), 592 (4.38), 647 (4.37) nm; HRMS (MALDI) m/z calcd. for $[\text{C}_{94}\text{H}_{69}\text{N}_9](\text{M}^+)$ 1323.5676, found 1323.5653.

2,7-Bis[5',10',15'-tri(4-methylphenyl)porphyrin-20'-yl]-9-hexyl-carbazole (286):

Porphyrin **284** (30 mg, 0.03 mmol), bromoporphyrin **93** (21 mg, 0.03 mmol) and K_3PO_4 (53 mg, 0.25 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (11 mg, 0.01 mmol) was added, the reaction was heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents were removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O . The organic layers were dried over $MgSO_4$ and solvents were removed *in vacuo*. The residue was subjected to column chromatography (CH_2Cl_2 : *n*-hexane, 1 : 1, v/v) to yield purple product **286** (17 mg, 0.01 mmol, 40%). M.p. >300 °C; R_f = 0.76 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v); 1H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.63 (s, 2H, NH), 0.67-0.70 (t, $^3J_{H-H}$ = 14.1 Hz, 3H, CH_3), 0.89 (m, 2H, CH_2), 1.19 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 2.04 (m, 2H, CH_2), 2.75 (s, 18H, tolyl- CH_3), 4.51-4.54 (t, $^3J_{H-H}$ = 14.1 Hz, 2H, CH_2), 7.60-7.61 (d, $^3J_{H-H}$ = 6.2 Hz, 12H, C_6H_4 -H), 8.16-8.17 (d, $^3J_{H-H}$ = 6.2 Hz, 12H, C_6H_4 -H), 8.30-8.32 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, carbazole-H), 8.44 (s, 2H, carbazole-H), 8.68-8.70 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, carbazole-H), 8.92 (m, 12H, H_β), 9.02-9.03 (d, $^3J_{H-H}$ = 4.4 Hz, 4H, H_β) ppm; ^{13}C -NMR (100 MHz, $CDCl_3$): δ = 13.9, 21.5, 22.9, 29.7, 31.6, 43.2, 115.6, 120.6, 123.8, 124.7, 127.7, 129.1, 135.0, 139.8, 142.4, 143.6, 149.3, 150.3, 155.8, 156.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 428 (5.47), 518 (4.32), 556 (4.25), 594 (4.07), 649 (4.07) nm; HRMS (MALDI) m/z calcd. for $[C_{100}H_{81}N_9](M^+)$ 1407.6615, found 1407.6569.

References and notes

References and notes

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