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Development of Synthetic Strategies Towards Multiporphyrin Arrays

Submitted by

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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
Declaration

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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


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


Conference Abstracts


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.


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” 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.

Ryan, A., Senge, M. O. “Synthesis of Porphyrin Oligomers for Applications in Photodynamic Therapy” Recent Advances in Synthesis & Chemical Biology VII, CSCB Symposium 2009, Dublin, Ireland. 18th December 2009

Ryan, A., Senge, M. O. “Synthesis of Porphyrin Dimers and Trimers for Applications in Photodynamic Therapy and Non-Linear Optics” Tetrapyrrole Discussion Group, TPDG, Dublin, Ireland. 15th-16th September 2008.
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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       N,N\textsuperscript{-}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
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>microwave</td>
</tr>
<tr>
<td>m/z</td>
<td>mass-to-charge ratio</td>
</tr>
<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>NLO</td>
<td>non-linear optics</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>nuclear overhauer effect spectroscopy</td>
</tr>
<tr>
<td>OAc</td>
<td>acetate</td>
</tr>
<tr>
<td>OELD</td>
<td>organic electroluminescent device</td>
</tr>
<tr>
<td>OEP</td>
<td>2,3,7,8,12,17,18-octaethylporphyrin</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light emitting diode</td>
</tr>
<tr>
<td>OTf</td>
<td>triflate</td>
</tr>
<tr>
<td>PFO</td>
<td>polyfluorene</td>
</tr>
<tr>
<td>PhLi</td>
<td>phenyllithium</td>
</tr>
<tr>
<td>PhOLED</td>
<td>phosphorescent organic light emitting diode</td>
</tr>
<tr>
<td>PIFA</td>
<td>phenyliodine(bis-trifluoroacetate)</td>
</tr>
<tr>
<td>PPh₃</td>
<td>triphenylphosphine</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PVK</td>
<td>poly(N-vinylvarbazole)</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>RC</td>
<td>reaction centre</td>
</tr>
<tr>
<td>Rf</td>
<td>retention factor</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>TEA</td>
<td>triethylamine</td>
</tr>
<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>TOCSY</td>
<td>total correlation spectroscopy</td>
</tr>
<tr>
<td>tol</td>
<td>tolyl</td>
</tr>
<tr>
<td>2PA</td>
<td>two-photon absorption</td>
</tr>
<tr>
<td>TPP</td>
<td>5,10,15,20-tetraphenylporphyrin</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
</tbody>
</table>
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.\[^6,7\]](image)

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 $\beta$-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 $\beta$-positions form chlorins and bacteriochlorins whilst addition reactions at the meso positions generate phlorins or porphodimethenes.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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 Rothemund\[23-25\] 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, dipyrryl and tripyrryl analogues, namely MacDonald [2+2] condensation,\[28\] which utilises dipyrrromethane 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 dipyrryl 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.](image)

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.\textsuperscript{[41-43]} These require prior activation via halogenation and these haloporphyrins provide an essential entry to meso functionalisations.\textsuperscript{[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.\textsuperscript{[46]} The main issue with such functionalisations is regioselectivity. As the meso position is more reactive towards electrophilic substitution reactions over the $\beta$-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 $\beta$ positions over meso, via iridium catalysed reactions.\textsuperscript{[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\textsuperscript{[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.\textsuperscript{[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,\textsuperscript{[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, 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.

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., 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. \(\lambda_{\text{max}}\). 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 \(\pi\)-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 \(\beta-\beta\), meso-meso, \(\beta-\beta\) linked porphyrin are geometrically co-planar and these arrays exhibit a substantial red shift in absorption due to the enhanced \(\pi\)-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 \(\pi\)-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. 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. 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. 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 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.
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. The diseased tissue is then illuminated with light of an appropriate wavelength which activates the accumulated drug to the excited singlet state ($S_1$).
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 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.\[^{69}\] 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' 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 \(\pi\)-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 to 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 (\(\sigma\)) and molecules exhibiting high \(\sigma\) 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 \(\pi\)-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 \(\pi\)-conjugation results in a substantial increase in \(\sigma\) values, as seen with Anderson’s butadiyne linked dimers\(^{[81]}\) which have \(\sigma\) values of \(1 \times 10^4\) 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 a 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\textsuperscript{®}-liposomal formulations,\[^{88}\] such as Foslip\textsuperscript{®}\[^{89}\] and Fospeg\textsuperscript{®}\[^{90}\] 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.
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. 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. 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.

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. These conjugated polymers are attractive as OLED materials as they have good hole transporting abilities and they have high triplet energy.
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.\cite{97, 103-106} Platinum porphyrins 7 and 8 have also been shown to have high external quantum efficiencies when doped into OLED devices.\cite{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 $\pi$-conjugation of the structure. Also, the non-planarity of the structure enhances this shift making the dye a NIR emitter.\cite{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.\cite{96}

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.\cite{111} Additionally, multiporphyrin arrays, if exhibiting enhanced delocalised $\pi$-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 $\beta$ 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.\textsuperscript{[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,\textsuperscript{[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 $\pi$-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.\textsuperscript{[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.\textsuperscript{[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 stoeichiometric amounts for the Eglington reaction.
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. The incorporation of the alkynyl moiety to the porphyrin periphery can also be achieved using a condensation reaction with propargyl aldehyde, along with the organolithium approach 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. 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.
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 coordination 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

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.\cite{124-125}

Scheme 1.2: Synthesis of $\beta$-$\beta$ 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,\cite{116} Sonogashira coupling and subsequent deprotection \cite{126} and also via condensation approaches.\cite{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.\cite{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.\cite{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 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. 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.\textsuperscript{[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.\textsuperscript{[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, $\beta$-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 $\beta$-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.

In attempts to mimic the cylindrical structure of the light harvesting complex in natural systems, cyclic and square \textsuperscript{[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 shown with square-shaped tetramer 18,[135] synthesised via copper-free Sonogashira coupling of 5,10 A2B2 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 AgPF6 with an ultimate oxidative coupling under dilute conditions to give the desired porphyrin wheel-like array containing up to 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 a 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.

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

![Image](image_url)

**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 dipyrrromethane 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 dipyrrromethane with tetrakis(5-formyl-2-pyrrol)ethane,\(^{[143]}\) nickel-mediated Ulmann coupling,\(^{[144]}\) oxidative fusing of free meso porphyrins using various oxidants such as hypervalent iodine reagents (e.g., PIFA),\(^{[145-146]}\) silver salts (AgPF$_6$),\(^{[147-151]}\) 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 metalloporphyrins 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 a₂u 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 a₁u 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.\textsuperscript{162-165} Their use in the synthesis of biaryl compounds via an efficient single-electron transfer mechanism\textsuperscript{166-167}\textsuperscript{168} prompted the application of such reagents for the synthesis of directly linked porphyrin dimers in excellent yields with short reaction times.\textsuperscript{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 \textsuperscript{26}.\textsuperscript{169-170} This was synthesised from a meso trisubstituted precursor, using tris(4-bromophenyl)aminium hexachloroantimonate (BAHA) as oxidant.\textsuperscript{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)\textsubscript{3} \textsuperscript{173} and PIFA \textsuperscript{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 \textsuperscript{26} and \textsuperscript{27}.\textsuperscript{175} This can be attributed to electronic properties as discussed for the singly linked arrays.

Using 5,15-disubstituted porphyrins, porphyrin tapes \textsuperscript{28} and \textsuperscript{29}, of up to 12 porphyrin units, were synthesised\textsuperscript{173} employing DDQ/Sc(OTf)\textsubscript{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.
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) \( \beta-\beta \), meso-meso, \( \beta-\beta \) 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).\textsuperscript{156}

![Figure 1.10: Square-shaped and T-shaped fused arrays 30 and 31 developed by Osuka and co-workers.](image)

Work by Davis \textit{et al.} has produced triply linked systems with anthracene fused at the porphyrin periphery using Osuka’s oxidative method.\textsuperscript{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 $\lambda_{\text{max}}$ of 1495 nm. Other triply fused porphyrin arrays incorporating fused aromatic moieties, e.g., pyrene \textsuperscript{33}\textsuperscript{179-180} and perylene,\textsuperscript{181} have been developed, with similar effects in comparison with anthracene derivative 32 on the overall electronic properties.

![Figure 32](image)

where $R = 2,4,6$-trimethylphenyl

![Figure 33](image)
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 $\beta$-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 \(44, 45, 46, 47, 48, 49, 51, 50, 186, 187, 188\) 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.
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. This method can also be adopted for the synthesis of substituted dipyrromethanes, allowing for the “trans” tetrasubstituted 5,15-A2B2 porphyrins to be synthesised, although scrambling issues from this synthetic route can prove problematic. 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. 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 $A_2$ 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 $\text{para-nitrophenylporphyrin 49}$, where a condensation yield of only 4% was obtained. These 5,15- $A_2$ 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-$A_2$ 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 $\beta$-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 $\beta$-unsubstituted 5,15-$A_2$ porphyrins, the synthesis of $A_2B$ 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 \textit{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 generated 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,\cite{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\cite{116} or, the anionic species can be trapped with electrophilic reagents to generate unsymmetric $A_2BC$ monomeric systems,\cite{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 \cite{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\cite{206} and thus functionalisation of 49 was abandoned.

\begin{align*}
R^1 \quad R^2 \quad \# \quad \% \\
\begin{array}{cccc}
\text{Ph} & 3-\text{MeO-C}_6\text{H}_4 & 61^{[40]} & 30 \\
\text{Ph} & \equiv & 62^{[116]} & 85 \\
\text{Ph} & 4-\text{O}_2\text{N-C}_6\text{H}_4 & 63^{[209]} & n/d \\
\text{Ph} & 4-\text{H}_2\text{N-C}_6\text{H}_4 & 64^{[116]} & 11 \\
\text{Hexyl} & \text{Hexyl} & 65^{[211]} & 93 \\
\text{Hexyl} & \equiv & 66 & 30 \\
\text{1-ethylpropyl} & \text{Ph} & 67 & 92 \\
\text{1-ethylpropyl} & \equiv & 68 & 35 \\
3-\text{MeO-C}_6\text{H}_4 & 3-\text{MeO-C}_6\text{H}_4 & 69^{[190]} & 65 \\
4-\text{MeO-C}_6\text{H}_4 & 4-\text{MeO-C}_6\text{H}_4 & 70^{[212]} & 71 \\
4-\text{O}_2\text{N-C}_6\text{H}_4 & \text{Ph} & 71 & n/d
\end{array}
\end{align*}

\begin{align*}
R^1 \quad R^2 \quad \# \quad \% \\
\begin{array}{cccc}
\text{Ph} & \text{Ph} & 72^{[207]} & 93 \\
\text{Ph} & \text{Hexyl} & 73^{[208]} & 67 \\
\text{Ar} & \text{Ph} & 74^{[210]} & 92 \\
\text{Ar} & \text{Hexyl} & 75 & 75 \\
4-\text{Me-C}_6\text{H}_4 & 4-\text{Me-C}_6\text{H}_4 & 76^{[120]} & 91 \\
4-\text{Me-C}_6\text{H}_4 & \text{n-Butyl} & 77 & 69 \\
3-\text{MeO-C}_6\text{H}_4 & \text{Ph} & 78^{[40]} & 92 \\
3-\text{MeO-C}_6\text{H}_4 & \text{n-Butyl} & 79^{[208]} & 26 \\
4-\text{MeO-C}_6\text{H}_4 & \text{n-Butyl} & 80 & 33 \\
\end{array}
\end{align*}

\textbf{Scheme 2.2:} Synthesis of A$_3$ and A$_1$B porphyrins 61-80. \textit{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) H$_2$O, 0.4 h. iii) DDQ, 1 h.

For substitutions where the organolithium reagent was not commercially available, these were obtained via the \textit{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\textsuperscript{[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 \textit{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 %, \textsuperscript{[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 and 80 in yields of 26 and 23%, respectively, along with the desired trisubstituted compounds 69 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, and involve an electrophilic aromatic substitution (SeAr). There are two sites where SeAr 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, forming brominated porphyrins 82-102 in yields ranging from 55-95%, the lower yields being those of alkoxy substituted porphyrins 90 and 91, along with monobrominated porphyrins 94, 95, 96, 97, 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 dehyropalladisation, using a palladium catalyst and hydrogen source.\textsuperscript{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 \textit{99}\textsuperscript{217} proved quite insoluble in many organic solvents, such as THF, and thus was not used for further reactions. Hence the 1-ethylpropyl derivative \textit{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.
where $R^1 = H$

$72-76,78,80$

where $R^1 \neq H$

$72-76,78,80$

where $R^1 \neq Br$ or $H$

**Scheme 2.3**: Synthesis of bromoporphyrins 82-102. **Reagents and conditions:** NBS, pyridine, CHCl$_3$, 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. Metal insertions into the porphyrin core are very straightforward and high yielding. 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.

![Scheme 2.4: Metallation of monomeric porphyrins with zinc(II). Reagents and conditions: Zn(OAc)$_2$ in MeOH, CHCl$_3$, 70 °C, 0.5 h.](image)

Where $R^1 = Br$ Where $R^1 = H$

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>#</th>
<th>%</th>
<th>$R^1$</th>
<th>$R^2$</th>
<th>#</th>
<th>%</th>
</tr>
</thead>
<tbody>
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<td>Hexyl</td>
<td>103</td>
<td>89</td>
<td>Ph</td>
<td>Hexyl</td>
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<td>89</td>
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<tr>
<td>Ph</td>
<td>104$^{[129]}$</td>
<td>95</td>
<td></td>
<td>Ph</td>
<td>116$^{[140]}$</td>
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</tr>
<tr>
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<td>105$^{[119]}$</td>
<td>90</td>
<td></td>
<td>Ph</td>
<td>117$^{[202]}$</td>
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<td></td>
</tr>
<tr>
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<td>118</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>107$^{[216]}$</td>
<td>92</td>
<td></td>
<td>4-MeO-C$_6$H$_4$</td>
<td>4-MeO-C$_6$H$_4$</td>
<td>119</td>
<td>87</td>
</tr>
<tr>
<td>4-Me-C$_6$H$_4$</td>
<td>H</td>
<td>108</td>
<td>85</td>
<td>3-MeO-C$_6$H$_4$</td>
<td>n-Butyl</td>
<td>120</td>
<td>85</td>
</tr>
<tr>
<td>4-Me-C$_6$H$_4$</td>
<td>109$^{[129]}$</td>
<td>93</td>
<td></td>
<td>1-Ethylpropyl</td>
<td></td>
<td>121</td>
<td>81</td>
</tr>
<tr>
<td>3-MeO-C$_6$H$_4$</td>
<td>H</td>
<td>110</td>
<td>82</td>
<td>Hexyl</td>
<td>H</td>
<td>122$^{[187]}$</td>
<td>77</td>
</tr>
<tr>
<td>Ph</td>
<td>111</td>
<td>89</td>
<td></td>
<td>Ar</td>
<td>Br</td>
<td>123$^{[228]}$</td>
<td>80</td>
</tr>
<tr>
<td>Ph</td>
<td>112$^{[46]}$</td>
<td>90</td>
<td></td>
<td>4-Me-C$_6$H$_4$</td>
<td>butyl</td>
<td>124</td>
<td>92</td>
</tr>
<tr>
<td>1-Ethylpropyl</td>
<td>Br</td>
<td>114</td>
<td>88</td>
<td>where $Ar = 3,5$-Di-tert-butyl-C$_6$H$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The most predominant metal used was zinc, as not only has this metal been proven to improve efficacy in PDT,\textsuperscript{[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,\textsuperscript{[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 chlorofonn yielding zinc metallated porphyrins \textsuperscript{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 \textsuperscript{108, 110} and \textsuperscript{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.

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

\textbf{Scheme 2.5: Metallation with nickel(II). Reagents and conditions: }Ni(acac)\textsubscript{2}, toluene, 120 °C, 3.5 h.

\begin{center}
\begin{tikzpicture}

\begin{scope}
\node (a) at (0,0) {\includegraphics[width=0.5\textwidth]{porphyrin62}
};\node (b) at (2cm,0) {\includegraphics[width=0.5\textwidth]{porphyrin98}\textsuperscript{125}};\node at (1cm,0) {$\text{Ni(acac)}\textsubscript{2}$};\node at (0,0) {$\text{R}^1, \text{R}^2, \text{R}^3$};\node at (2cm,0) {$\text{M} = \text{Ni}^\text{II}$};\node at (0,0) {$\text{R}^1 = \text{Ph}, \text{R}^2 = 4\text{-ethyne-C}_6\text{H}_4, \text{R}^3 = \text{H}$};\node at (2cm,0) {$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{R}^3 = \text{Br}, \text{M} = \text{Ni}^\text{II}$};\node at (0,0) {$\text{Porphyrin } 62, 98$};\node at (2cm,0) {$\text{Porphyrin } 125$};\node at (0,0) {$\text{Porphyrin } 126$};\end{scope}
\end{tikzpicture}
\end{center}

\textbf{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.\textsuperscript{[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\textsuperscript{[232]} and Suzuki-Miyaura\textsuperscript{[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.\textsuperscript{[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\textsuperscript{[235]} allows for the introduction of alkynyl functionalities via the coupling of a halo porphyrin with a terminal alkyne. Suzuki-Miyaura couplings\textsuperscript{[233, 236]} allow for C-C bond generation via the coupling of an organoborate with a haloporphyrin. 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.

\textit{Borylation}

Organoboranes\textsuperscript{[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.,\textsuperscript{[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.\textsuperscript{[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.
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 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, but it is not applicable for meso functionalisations.
Suzuki-Miyura coupling

For the introduction of 4-nitrophenyl and 4-bromophenyl substituents, Suzuki Pd° 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 but, on optimisation of reaction conditions, it proceeds in excellent yield with only 3.5 equivalents.

![Reaction diagram](image)

### 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 recovered in yields of 28 and 22 %, respectively. The 4-bromophenyl substituted porphyrin 141 was generated in 71 % yield using modified conditions with Pd° 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 phenylacetlene 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.\(^1\)

**Sonogashira coupling**

![Sonogashira coupling diagram]

<table>
<thead>
<tr>
<th>( \text{R}^1 )</th>
<th>( \text{R}^2 )</th>
<th>( \text{M} )</th>
<th>TMS product #</th>
<th>Yield</th>
<th>Deprotected #</th>
<th>Yield</th>
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</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>2H</td>
<td>145(^{[247]})</td>
<td>58</td>
<td>151</td>
<td>91</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>Zn(^{II})</td>
<td>143(^{[247]})</td>
<td>68</td>
<td>152(^{[248]})</td>
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<tr>
<td>Ph</td>
<td>H</td>
<td>2H</td>
<td>144(^{[45]})</td>
<td>55</td>
<td>153(^{[209]})</td>
<td>92</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>Zn(^{II})</td>
<td>145(^{[119]})</td>
<td>84</td>
<td>154(^{[119]})</td>
<td>90</td>
</tr>
<tr>
<td>Ph</td>
<td>TMS-ethyne</td>
<td>2H</td>
<td>145(^{[249]})</td>
<td>52</td>
<td>155(^{[228]})</td>
<td>88</td>
</tr>
<tr>
<td>Ar</td>
<td>H</td>
<td>Zn(^{II})</td>
<td>146(^{[228]})</td>
<td>65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ar</td>
<td>Ph</td>
<td>2H</td>
<td>147</td>
<td>36</td>
<td>156</td>
<td>92</td>
</tr>
<tr>
<td>Ar</td>
<td>Ph</td>
<td>Zn(^{II})</td>
<td>148(^{[250]})</td>
<td>46</td>
<td>157(^{[251]})</td>
<td>94</td>
</tr>
<tr>
<td>Ar</td>
<td>Hexyl</td>
<td>2H</td>
<td>149</td>
<td>83</td>
<td>158</td>
<td>61</td>
</tr>
<tr>
<td>Ph</td>
<td>3-MeO-C(_6)H(_4)</td>
<td>2H</td>
<td>150</td>
<td>48</td>
<td>159</td>
<td>90</td>
</tr>
</tbody>
</table>

where \( \text{Ar} = (3,5\text{-Di-tert-buty})\text{C}_6\text{H}_3 \)

**Scheme 2.8:** Sonogashira coupling to give TMS-acetylene products 142-150 and TBAF deprotection to give alkylnyl porphyrins 151-159. *Reagents and conditions:* i) TMS-ethyne, PdCl\(_2\)(PPh\(_3\))\(_2\), Cul, TEA, THF, 40-60 °C, 16 h. ii) TBAF (1M in THF), CH\(_2\)Cl\(_2\), 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, Cul as a co-catalyst and a base. The reaction mechanism
Chapter 2: Synthesis of monomeric precursors

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.\textsuperscript{[232]}

Porphyrins \textbf{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 \textbf{142-150} in yields of 36-88\%. An alternative method for this synthesis is a one-step condensation reaction\textsuperscript{[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 \textbf{148} this did not increase the yield significantly. Porphyrins \textbf{142-145} and \textbf{147-150} were subsequently deprotected using TBAF forming the free alkynyl porphyrins \textbf{151-159} in yields of 61-94\%, the lowest yield being that for hexyl substituted porphyrin \textbf{158}.

2.3 Spectroscopic studies

2.3.1 $^1$H 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 $\pi$-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 $\beta$-protons are strongly deshielded (~8-10 ppm). The meso protons are attached to more electron deficient carbons and hence are deshielded further downfield than $\beta$-protons.

$^1$H NMR of monomeric porphyrins

The substitution arrangement on the porphyrin periphery can easily be deduced by $^1$H NMR spectra via the pattern of $\beta$-pyrrolic hydrogen signals, which depend on the overall symmetry of the molecule. Taking 1-ethylpropyl A$_2$, A$_2$B and A$_2$BC 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 $\beta$-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: $^1$H NMR spectra of 1-ethylpropyl substituted porphyrins 46, 67 and 88 in CDCl$_3$ with porphyrin numbering system inset.](image)

With phenyl substituted A$_2$B 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$_2$BC substituted porphyrin 88, exerts a different pattern. Again, four $\beta$-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 \(^1\)H 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\(_2\)Cl\(_2\).](image)
The most pronounced bathochromic shift for monomeric porphyrins was observed with trimethylsilylalkynyl and alkynyl substituted porphyrins 142-159 whereby a $\lambda_{\text{max}}$ 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 $\pi-\pi^*$ 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. 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. Currently commercially available photosensitisers show absorption in the 530 to 630 nm range, which limits the penetration of tissue by light. 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. 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. 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. 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. 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.

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, 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.\textsuperscript{[119, 130, 258]} Some directly linked dimers were synthesised via Suzuki coupling \textsuperscript{[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,\textsuperscript{[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 \textit{para} methoxy group over the \textit{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, 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. 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.
**Scheme 3.2:** Synthesis of alkyne linked dimers. *Reagents and conditions:* Sonogashira - PdCl$_2$(PPh$_3$)$_2$, CuI, TEA, THF, 40-60 °C, 16 h; copper-free Sonogashira - Pd$_2$(dba)$_3$, AsPh$_3$, 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

![Diagram showing the synthesis of phenylacetylene and butadiyne linked dimers.](image)

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<th>$R^1$</th>
<th>$R^2$</th>
<th>$R^3$</th>
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<th>$M$</th>
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<td>45</td>
<td>179</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Zn$^{II}$</td>
<td>21</td>
<td>180</td>
<td>(3,5-di-tert-butyl)C₆H₃</td>
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<td>H</td>
<td>Ph</td>
<td>H</td>
<td>Zn$^{II}$</td>
<td>25</td>
<td>181</td>
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</tr>
<tr>
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<td>Ph</td>
<td>Ar</td>
<td>Ph</td>
<td>2H</td>
<td>22</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>H</td>
<td>Zn$^{II}$</td>
<td>35</td>
<td>183</td>
<td></td>
</tr>
</tbody>
</table>

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 - Pd$_2$(dba)$_3$, THF, TEA, 60 °C, 16 h. Pd-Glaser coupling - toluene, Pd(PPh$_3$)$_2$Cl$_2$ (0.01 eq.), Cul (0.05 eq.), I$_2$ (0.5 eq.).
The phenylacetylene linked dimers were prepared in a similar manner to dimers 163-176. In general, the copper-free method\textsuperscript{[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 \textit{et al.}, was used.\textsuperscript{[263]} However, this method proved less successful with yields of 25 and 35\% for dimers 181,\textsuperscript{[202]} and 183,\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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-C\textsubscript{6}H\textsubscript{3})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.

![Chemical structures and equations](image)

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>M¹</th>
<th>M²</th>
<th>Yield %</th>
<th>#</th>
<th>Linker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>2H</td>
<td>2H</td>
<td>40</td>
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</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>2H</td>
<td>2H</td>
<td>38</td>
<td>185</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>Zn²</td>
<td>Zn²</td>
<td>45</td>
<td>186</td>
<td></td>
</tr>
<tr>
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<td>Ar</td>
<td>Zn²</td>
<td>2H</td>
<td>28</td>
<td>188</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>Ar</td>
<td>Zn²</td>
<td>Zn²</td>
<td>46</td>
<td>189</td>
<td></td>
</tr>
</tbody>
</table>

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 dibromo-
dihexylporphyrin 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 - Pd₂(dba)₃, AsPh₃, 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
Chapter 3: Conjugated porphyrin arrays

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. 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.

![Scheme 3.6: Side product formation during the synthesis of trimers.](image)

<table>
<thead>
<tr>
<th>R^1</th>
<th>R^2</th>
<th>R^3</th>
<th>#</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Ethylpropyl</td>
<td>1-Ethylpropyl</td>
<td>Br</td>
<td>192</td>
<td>40</td>
</tr>
<tr>
<td>Ph</td>
<td>1-Ethylpropyl</td>
<td>Br</td>
<td>193</td>
<td>42</td>
</tr>
</tbody>
</table>

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 $^1$H 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: $^1$H-NMR spectra (400 MHz) of oligomers 160, 166 and 188 in CDCl$_3$ showing $\beta$ 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: $^1$H-$^1$H COSY NMR (600 MHz) spectra of trimer 189 in $d_6$-THF showing aryl and porphyrin regions.
The highest field signals are observed for the ‘inner’ $\beta$ protons due to the close proximity of the alkynyl group. Also, these $\beta$ 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 $\beta$ protons, being more pronounced for the inner $\beta$ protons of the central porphyrin unit than the $\beta$ protons of the outer porphyrins. This is evident from the $^1$H NMR spectrum of 188 (Figure 3.2).

Using $^1$H-$^1$H COSY NMR analysis (Figure 3.3), $\beta$-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 $\beta$ 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 $\pi$-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.\cite{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,\cite{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,\cite{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 CH₂Cl₂. 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: $1.7 \times 10^{-7}$ 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 $\pi$-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 $\pi$-conjugation.
Chapter 3: Conjugated porphyrin arrays

![Figure 3.5](image)

**Figure 3.5:** a) Absorbance spectrum of unsymmetric dimers 165 and 166 versus monomer 156 in CH$_2$Cl$_2$. Inset: Emission spectrum of 165 and 166 excited at Soret bands 410 nm and 470 nm versus monomer 156 in THF. Concentration: $1.7 \times 10^{-3}$ 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 $^1$H-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 $\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ 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 couplings,$^{144}$ oxidative fusing of free meso porphyrins with oxidants such as hypervalent iodine (PIFA),$^{145}$ silver salts (AgPF$_6$)$^{147, 150}$ and DDQ/Sc(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

![Diagram of dimerisation process](image)

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Dimer</th>
<th>Yield %</th>
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<tbody>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>194</td>
<td>68</td>
</tr>
<tr>
<td>Ph</td>
<td>n-Butyl</td>
<td>195</td>
<td>59</td>
</tr>
<tr>
<td>Ar</td>
<td>Ph</td>
<td>196</td>
<td>63</td>
</tr>
<tr>
<td>Ph</td>
<td>4-H₂N-C₆H₄</td>
<td>197</td>
<td>n/d</td>
</tr>
<tr>
<td>Ph</td>
<td>4-O₂N-C₆H₄</td>
<td>198</td>
<td>n/d</td>
</tr>
</tbody>
</table>

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. 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, 195, 196 were obtained in good yields of 59-68 %. Minor products which can arise from the reaction are the tri- and tetrar substituted monomers which may have an effect on yield. Syntheses of zinc derivatives of 194 and 196 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

Hypervalent iodine reagents can be applied for the synthesis of directly linked porphyrin arrays. These reagents possess many advantages over powerful oxidants such as AgPF$_6$ and DDQ/Sc(OTf)$_3$ in that they are safer but have a similar reactivity to those of metal oxidisers. Hypervalent iodine reagents such as PIFA can activate the porphyrin by oxidative addition, generating the corresponding aryliodide intermediate. The aryliodonium ion so generated can then undergo a tandem cyclisation to form the fused porphyrin array. In this section, we describe the preparation of a number of fused porphyrin arrays via PIFA oxidation. Reagents and conditions: i) PIFA, CH$_2$Cl$_2$, -78 °C ii) rt, 0.75 h. iii) NaBH$_4$, MeOH.

Scheme 4.2: Synthesis of directly linked porphyrin dimers via PIFA oxidation. Reagents and conditions: i) PIFA, CH$_2$Cl$_2$, -78 °C ii) rt, 0.75 h. iii) NaBH$_4$, MeOH.
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 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 AgPF\(_6\) and I\(_2\).\[^{160}\] 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-Miyuara coupling, between a bromo-porphyrin and borylated porphyrin to give singly linked bisporphyrins (Section 3.2.1).\textsuperscript{[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 and 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.\textsuperscript{[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).
Chapter 4: Fused porphyrin arrays

Scheme 4.3: Synthesis of directly linked porphyrin dimers via Suzuki coupling. Reagents and conditions: Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$, 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: Pd$_3$(dba)$_3$, AsPh$_3$, THF, TEA, 60 °C, 24 h.](image)

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.
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\cite{173-174, 280} which have been developed for their generation since their first synthesis via electrochemical oxidation by Osuka and co-workers.\cite{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 Sc(OTf)₃/DDQ and hypervalent iodine (PIFA), although other oxidants such as gold derivatives\cite{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 A₃ and A₂B 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.

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{R}^1 & \text{R}^2 & \text{Oxidant} & \# & \text{Yield \%} \\
\hline
\text{Ph} & \text{Ph} & \text{DDQ/Sc(OTf)$_3$} & 214 & 67 \\
\text{Ph} & 4-\text{O}_2\text{N-C$_6$H$_4$} & 215 & 54 \\
\text{Ar} & 4-\text{O}_2\text{N-C$_6$H$_4$} & 216 & 56 \\
3-\text{MeO-C$_6$H$_4$} & \text{n-Butyl} & 217 & 60 \\
4-\text{MeO-C$_6$H$_4$} & 4-\text{MeO-C$_6$H$_4$} & 218 & 73 \\
\text{Ph} & 4-\text{Ethynyl-C$_6$H$_4$} & 219 & 67 \\
\text{Ph} & \text{Hexyl} & 220 & 42 \\
4-\text{Me-C$_6$H$_4$} & \text{n-Butyl} & 221 & 58 \\
\text{Ph} & \text{H} & \text{DDQ/Sc(OTf)$_3$ or PIFA} & 222 & \text{n/d} \\
\text{Hexyl} & \text{H} & 223 & \text{n/d} \\
\text{Ph} & \text{Br} & 224 & 12 \\
3-\text{MeO-C$_6$H$_4$} & \text{Br} & 225 & 15 \\
\hline
\end{array}
\]

where Ar = 3,5-Di-tert-butyl-C$_6$H$_3$

Scheme 4.6: Synthesis of fused symmetric dimers Reagents and conditions: a) DDQ, Sc(OTf)$_3$, toluene, 50 °C, 3 h. b) i) PIFA, CH$_2$Cl$_2$, -78 °C − rt, 3 h. ii) NaBH$_4$, 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.

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>Dimer</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-MeO-C$_6$H$_4$</td>
<td>$n$-Butyl</td>
<td>226</td>
<td>23</td>
</tr>
<tr>
<td>Ph</td>
<td>Hexyl</td>
<td>227</td>
<td>30</td>
</tr>
<tr>
<td>4-Me-C$_6$H$_4$</td>
<td>$n$-Butyl</td>
<td>228</td>
<td>29</td>
</tr>
</tbody>
</table>

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.\textsuperscript{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.
Chapter 4: Fused porphyrin arrays

203, 204, 206, 207, 209

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>Dimer</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexyl</td>
<td>Hexyl</td>
<td>Ph</td>
<td>H</td>
<td>229</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>4-Me-C₆H₄</td>
<td>H</td>
<td>230</td>
<td>n/d</td>
</tr>
<tr>
<td>3-MeO-C₆H₄</td>
<td>Ph</td>
<td>3-MeO-C₆H₄</td>
<td>H</td>
<td>231</td>
<td>n/d</td>
</tr>
<tr>
<td>3-MeO-C₆H₄</td>
<td>Ph</td>
<td>4-Me-C₆H₄</td>
<td>H</td>
<td>232</td>
<td>n/d</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>3-MeO-C₆H₄</td>
<td>Ph</td>
<td>233</td>
<td>56</td>
</tr>
</tbody>
</table>

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, CH$_2$Cl$_2$, -78 °C – rt, 3 h. ii) NaBH$_4$, 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 \( \pi \)-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.\textsuperscript{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 \( \beta \)-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 \( \beta \)-H2/H18 low-field signals on fusing. The other eight \( \beta \)-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-\( CH_3 \) signals, at slightly higher field strength with regard to the monomer.
Figure 4.1: $^1$H NMR spectrum (600 MHz) of monomer 119 (black) and fused dimer 218 (purple) showing the aryl and porphyrin regions in CDCl$_3$. ($R^1 = 4$-MeO-C$_6$H$_4$)

These resonances are further confirmed via 2-dimensional $^1$H-$^1$H NMR total correlation analysis (TOCSY) of 218, showing the $\beta$ 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 $\beta$-protons, with the doublets at 7.5 ppm signifying the resonances for the other eight $\beta$-protons. Although specific to dimer 218, the general pattern of signals can be applied for the deduction of structures of symmetrically fused arrays.
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 CDCl₃. In
some cases, using pyridine-D₅ in CDCl₃ 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-D₅ had a negative effect on the ¹³C-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: $^1$H NMR spectrum (400 MHz) of aryl regions of tetramer 212 (green), dimer 213 (red) and fused tetramer 234 (blue) in CDCl$_3$. (R = 3-OMe-C$_6$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 $\beta$-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 $\beta$-protons of the central porphyrin units. These are substantial shifts from starting materials 212 and 213, whereby the $\beta$-protons are observed between 9 and 10.5 ppm.
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$_2$Cl$_2$-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 $\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ 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.](image)

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 alkylnyl-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.

![Absorbance vs Wavelength](image)

**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, 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.\cite{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.

![UV/vis/NIR spectrum of dimers 214 (blue) and 218 (green) in a) CH$_2$Cl$_2$ (solid line) and b) CH$_2$Cl$_2$ with 1% TEA (dashed line).](image)

**Figure 4.7:** UV/vis/NIR spectrum of dimers 214 (blue) and 218 (green) in a) CH$_2$Cl$_2$ (solid line) and b) CH$_2$Cl$_2$ 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-functionalisations 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.
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.\textsuperscript{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,\textsuperscript{284} whereby the mono-bromination can be controlled and is very high yielding,\textsuperscript{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

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
$R^1$ & $R^2$ & $R^3$ & # & Yield % \\
\hline
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 \\
\hline
\end{tabular}
\end{table}
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. 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.

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, dimmer 194 was nitrated via electrophilic aromatic substitution, using sodium nitrite in TFA. This generates the \( \text{NO}_2^+ \) 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 NaNO\(_3\) did not enhance the reaction, only when more than 200 equivalents of NaNO\(_2\) 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
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. Resulting from the perturbation of the macrocycle, these species have interesting photophysical properties and exhibit a bathochromic shift in their absorption profile. 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 dehydorpurpurin-porphyrin dyad formed. 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) Pd$_2$(dba)$_3$, (o-Tol)$_3$P, toluene, N,N-dicyclohexylamine, 120 °C, 24 h. b) DDQ, Sc(OTf)$_3$, toluene, rt, 3 h. c) CHCl$_3$, 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 CHCl₃ and stirring open to the air overnight. Initial attempts using smaller volumes of CHCl₃ exhibited minimal decomposition of the dehydropurpurin, reflecting a somewhat more stable adduct than that described in the literature. Attempts to triply-fuse 244 employing standard oxidative conditions using DDQ/Sc(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 Pd⁰ 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 palladacycle (C) and following this, reductive elimination to give the cyclised porphyrin (dehydropurpurin) 251 and regenerated Pd⁰ (Scheme 5.4).
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 dizazepine 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, 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: Pd$_2$(dba)$_3$, (o-Tol)$_3$P, toluene, N,N-dicyclohexylamine, 120 °C, 24 h.](image)

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 $[C_{84}H_{62}N_6O_2Zn_2]$ 1342.3579.

$$\text{Zn} \quad \text{Ph} \quad \text{R}^1 \quad \text{R}^2 \quad \text{R}^3$$

237, 238

$[3+2]$ Annulation

$$\text{Ph} \quad \text{Zn} \quad \text{Ph}$$


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 $^1$H 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: $^1$H 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 CDCl$_3$. (where R = 3-OMe-C$_6$H$_4$)

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 $\beta$-signals from between 8.8 and 9.8 ppm to 7.2 to 8.2 ppm. Also, with 111 there are four $\beta$-proton signals, with six signals for the $\beta$-protons in 245, due to the distortion of the macrocycle. This most evident for the $\beta$-protons closest to the cyclopentadiene ring which occur as two singlets. The methoxy CH$_3$ 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 $\beta$-signals resonating in the region of 8.6-9.1 ppm. The ketone functional groups were also confirmed via $^{13}$C NMR analysis with low field resonances of 194.5 and 199.3 ppm for the carbonyl carbons attached to the $\beta$ and
meso carbons respectively. Diazepine-fused porphyrin 252 exhibits a slight difference in chemical shifts for the \( \beta \)-protons, typical of fused moieties, with the two closest to the fused ring occurring as singlets of highest field strength in the \( \beta \)-region. The structure was confirmed by HRMS, with a parent ion of \( m/z \) 864.2222, calculated for \([\text{C}_{54}\text{H}_{36}\text{N}_{6}\text{O}_{2}\text{Zn}]\) 864.2191, and also the loss of signals at 194 and 198 ppm in \( ^{13}\text{C} \) NMR analysis for the carbonyl carbons.

![Figure 5.4](image)

**Figure 5.4:** Low frequency region of \( ^{1}\text{H} \) 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 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 \( \beta \)-protons furthest from the fusing, with the other \( \beta \)-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 \( ^{13}\text{C} \) 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\(_2\)Cl\(_2\). (where Ar = (3,5-di-t-butyl)C\(_6\)H\(_3\))](image)

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 \( \lambda_{\text{max}} \) 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.
For fused dimer 256, identifying whether the cycloaddition took place was more difficult due to 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 5.6: UV-vis absorption spectrum of 202 (purple) and 254 (blue) in CH$_2$Cl$_2$. (where R = 3-OMe-C$_6$H$_4$)

Figure 5.7: UV-vis and NIR spectra of 238 (blue) and 256 (red) in CH$_2$Cl$_2$. (R = 1-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.\textsuperscript{[198,302]}

Scheme 5.9. Synthesis of β-butylated dimer 258 via RLi. Reagents and conditions: i) n-BuLi, -78 °C, THF, 1 h ii) H\textsubscript{2}O, 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.\textsuperscript{[182-183]} Adopting a method developed by Senge et al., whereby TPP was monobutylated at the β-postion in 17 % yield, the fused dimer 214 was butylated under standard organolithium conditions.\textsuperscript{[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 dibutyalted dimer were detected.

\textit{NMR analysis}

The \textsuperscript{1}H NMR spectrum of 258 shows the typical chlorin CH\textsubscript{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 \(^1\)H NMR spectra of fused dimer 214 (blue) and chlorin dimer 258 (green) in CDC\(_3\).](image)

### 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 \textit{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 \(^1\)H NMR analysis
proved inconclusive and thus further investigations into the reduction of fused dimers are necessary.

![Diagram of diimide reduction of fused dimer 214 and 259.]

**Scheme 5.10:** Diimide reduction of fused dimer 214. *Reagents and conditions:* Tosyl hydrazine, β-picoline, K$_2$CO$_3$, 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.\textsuperscript{93-94, 99} For example, the polymeric carbazole, poly(\textit{N-vinylcarbazole}) (PVK)\textsuperscript{102} and polyfluorene (PFO)\textsuperscript{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.\textsuperscript{306} As porphyrins are highly chromophoric and strongly emissive materials, there is much research into the development of such for use in OLEDs.\textsuperscript{97, 104} Most previous studies on porphyrin-based OLED materials focused on substituted monomeric porphyrin dopants\textsuperscript{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.](image)

Published studies have incorporated chromophores such as fluorenes and carbazoles into the porphyrin periphery.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{[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.

![Carbazole structure](image)

**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\textsuperscript{[236, 239]} in porphyrin chemistry and our current developments thereof\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[318-320]} The strategies employed all involved the generation of biaryl compounds via known coupling methods such as Suzuki-Miyaura\textsuperscript{[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.\textsuperscript{[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\textsuperscript{[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.

The mechanism for the ring-closing carbazole generation step involves the overall deoxygenation of the nitro biphenyl via nucleophilic attack by the tervalent 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.\textsuperscript{[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%. 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. 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. 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) HNO₃, AcOH, 120 °C, 20 h. ii) (EtO)₃P, 160 °C, overnight. ii) a) i-BuOK, DMF, rt, 2 h. b) bromohexane, 130 °C, 16 h. iii) a) n-BuLi, -78 °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%.

![Scheme 6.4](image)

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**Scheme 6.4.** Synthesis of carbazole porphyrins via Suzuki coupling and metallations. *Reagents and conditions:* i) Borylated carbazole, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF, K<sub>3</sub>PO<sub>4</sub>, 67 °C, 16 h. ii) a) Zn(OAc)<sub>2</sub>, MeOH, 70 °C, 0.5 h. b) Pd(OAc)<sub>2</sub>, toluene, 120 °C, 20 h., c) InCl<sub>3</sub>, 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.](image)

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 $^1$H 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 $\beta$-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 $\beta$-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.
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 6.2:** $^1$H NMR comparison of 274 (blue) and borylated carbazole 266 (green) in CDCl$_3$

**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]

![Absorbance vs Wavelength](image)

Figure 6.4: UV-vis absorption spectrum of 274 (pink) and 285 (cyan) in CH₂Cl₂. 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.

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

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

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 P₂O₅ were used. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 400 (400 MHz for ¹H NMR; 100.6 MHz for ¹³C NMR) and/or Bruker AV 600 (600 MHz for ¹H NMR; 150.9 MHz for ¹³C 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. 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 % H₂O, Brockmann Grade III). Photophysical measurements were performed in ethylacetate, THF, CH₂Cl₂ 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$_2$Cl$_2$ (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$_2$Cl$_2$ as eluent. The porphyrin containing fractions were collected and solvent was removed *in vacuo*. The dark purple residue was recrystallised from CH$_2$Cl$_2$/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 pink solid. M.p. >300 °C; Rf = 0.2 (DCM : ethyl acetate = 10 : 1, v/v); 1H NMR (600 MHz, CDCl3/d-TFA, 10:1): δ = 8.73 (d, 3J_H-H = 8.4 Hz, 4H, C6H4-H), 8.92 (d, 3J_H-H = 8.4 Hz, 4H, C6H4-H), 9.05 (d, 3J_H-H = 4.8 Hz, 4H, Hβ), 9.63 (d, 3J_H-H = 4.8 Hz, 4H, Hβ), 11.05 (s, 2H, Hmeso) ppm; 13C NMR (150 MHz, CDCl3): 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 (CH2Cl2/MeOH): λmax (log ε) = 428 (4.87), 555 (3.11), 594 (3.24), 656 (3.06) nm; HRMS (MS ES+) m/z calcd. for [C32H21N604] (M+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):

\[
\text{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 : CH2Cl2, 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; Rf = 0.53 (CH2Cl2 : n-hexane = 1 : 1, v/v); 1H NMR (400 MHz, CDCl3, TMS): δ = -2.97 (s, 2H, NH), 4.01 (s, 3H, OCH3), 7.35-7.38 (m, 1H, C6H4-H), 7.65-7.69 (t, 3JH-H = 15.6 Hz, 1H, C6H4-H), 7.83 (m, 8H, Ph-H), 8.28 (m, 4H, Ph-H), 8.93-8.96 (m, 4H, Hβ), 9.04-9.05 (d, 3JH-H = 4.6 Hz, 2H, Hβ), 9.36-9.38 (d, 3JH-H = 4.6 Hz, 2H, Hβ) 10.26 (s, 1H, Hmeso) ppm; 13C NMR (150 MHz, CDCl3): δ = 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): λmax (log ε) = 411 (5.65), 508 (4.20), 541 (3.44), 581 (3.77), 640 (3.50) nm; HRMS (ESI) m/z calcd. for [C39H29N4O](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 (CH2Cl2 : 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 CH2Cl2/MeOH gave purple crystals (72 mg, 0.125 mmol, 30%). M.p. >300 °C; Rf = 0.57 (CH2Cl2 : n-hexane = 1 : 1, v/v); 1H NMR (600 MHz, CDCl3, TMS): δ = -2.84 (s, 2H, NH), 0.96-0.98 (t, 3JH-H = 14.9 Hz, 6H, CH3), 1.43 (m, 4H, CH2), 1.54 (m, 4H, CH2), 1.85 (m, 4H, CH2), 2.55 (m, 4H, CH2), 3.36 (s, 1H, C=CH), 5.01 (t, 3JH-H = 15.8 Hz 4H, CH2), 7.91-7.93 (d, 3JH-H = 6.3 Hz, 2H, C6H4-H), 8.18-8.19 (d, 3JH-H = 6.3 Hz, 2H, C6H4-H), 8.88-8.89 (d, 3JH-H = 4.5 Hz, 2H, Hβ), 9.36-9.37 (d, 3JH-H = 4.5 Hz, 2H, Hβ), 9.46-9.47 (d, 3JH-H = 4.5 Hz, 2H, Hβ), 9.55-9.56 (d, 3JH-H = 4.5 Hz, 2H, Hβ), 10.07 (s, 1H, Hmeso) ppm; 13C NMR (150 MHz,
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 NH₄Cl (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 CH₂Cl₂ as eluent. Solvents were removed in vacuo and the dark residue was recrystallised from CH₂Cl₂/MeOH to give purple crystals. Yield: 422 mg (0.801 mmol, 80%). M.p. >300 °C; Rᵣ = 0.67 (CH₂Cl₂: n-hexane = 1 : 1, v/v); ^1H NMR (400 MHz, CDCl₃): δ = -2.45 (s, 2H, NH), 0.95-0.99 (t, 3J_H-H = 14.8 Hz, 12H, CH₃), 2.82 (m, 4H, CH₂), 2.98 (m, 4H, CH₂), 5.05 (m, 2H, CH), 7.77 (m, 3H, Ph-CH), 8.22-8.24 (d, 3J_H-H = 6.8 Hz, 4H, Ph-H), 8.88 (m, 2H, H₉), 9.40-9.41 (d, 3J_H-H = 4.4 Hz, 2H, H₉), 9.58 (m, 2H, H₉), 9.70-9.73 (m, 2H, H₉), 10.16 (s, 1H, H_meso) ppm; ^13C NMR (100 MHz, CDCl₃): δ = 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 ε) = 409 (5.34), 509 (4.07), 541 (3.50), 585 (3.43), 641 (3.21) nm; HRMS (ESI) m/z calcd. for [C₃₆H₃₉N₄](M+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; Rᵣ = 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, J₁₂-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, J₁₂-H = 7.7 Hz, 2H, C₆H₄-H), 8.19-8.20 (d, J₁₂-H = 7.7 Hz, 2H, C₆H₄-H), 8.84 (m, 2H, H₉), 9.39-9.40 (m, 2H, H₉), 9.59-9.60 (m, 2H, H₉), 9.69-9.71 (m, 2H, H₉), 10.16 (s, 1H, H₉) 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 [C₃₈H₅₉N₄](M+H)^+: 551.3175, found 551.3170.
5,10,15-Tris(4-methoxyphenyl)porphyrin (70): [212]

\[ \text{HN} / \text{O} \]

\( n \)-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 CH\(_2\)Cl\(_2\). The solvents were removed under reduced pressure and the residue was purified using silica gel column chromatography (CH\(_2\)Cl\(_2\) : 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; \( R_f = 0.44 \) (CH\(_2\)Cl\(_2\) : n-hexane = 2 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \( \delta = -2.99 \) (s, 2H, NH), 4.04 (m, 6H, OCH\(_3\)), 4.13 (s, 3H, OCH\(_3\)), 7.37-7.39 (d, \( J_{H-H} = 8.5 \) Hz, 2H, C\(_6\)H\(_4\)-H), 7.70 (m, 2H, C\(_6\)H\(_4\)-H), 7.83 (m, 4H, C\(_6\)H\(_4\)-H), 8.14 (m, 4H, C\(_6\)H\(_4\)-H), 8.92-8.93 (d, \( J_{H-H} = 4.7 \) Hz, 2H, \( H_\beta \)), 8.96-8.97 (d, \( J_{H-H} = 4.7 \) Hz, 2H, \( H_\beta \)), 9.08-9.09 (d, \( J_{H-H} = 4.7 \) Hz, 2H, \( H_\beta \)), 9.36-9.37 (d, \( J_{H-H} = 4.7 \) Hz, 2H, \( H_\beta \)), 10.24 ppm (s, 1H, \( H_{meso} \)); UV/vis (THF): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 413 (5.58), 509 (4.14), 544 (3.50), 585 (3.69), 639 nm (3.54); HRMS (MALDI) \( m/z \) calcd. for [C\(_{41}\)H\(_{32}\)O\(_3\)N\(_4\)](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. H₂O : 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 CH₂Cl₂ (20 mL) and filtered through a plug of silica. The purple solution was purified by column chromatography (silica, CH₂Cl₂ : n-hexane : 1 : 2, v/v) to yield a purple solid. Yield: 84.1 mg (0.109 mmol, 75%). M.p. >300 °C; Rf = 0.35 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H-NMR (400 MHz, CDCl₃, TMS): δ = -2.91 (s, 2H, NH), 0.94-1.00 (t, ³J_H-H = 14.9 Hz, 3H, CH₃), 1.49 (m, 4H, CH₂), 1.60 (s, 36H, t-butyl-H), 1.88 (m, 2H, CH₂), 2.63 (m, 2H, CH₂), 5.13 (t, ³J_H-H = 15.9 Hz, 2H, CH₂), 7.82 (m, 2H, Ar-H), 8.14 (m, 4H, Ar-H), 9.04-9.08 (dd, ³J_H-H = 7.2 Hz, 4.6 Hz, 4H, H₂), 9.30-9.31 (d, ³J_H-H = 4.7 Hz, 2H, H₂), 9.59-9.60 (d, ³J_H-H = 4.7 Hz, 2H, H₂), 10.13 (s, 1H, H_meso) ppm; ¹³C-NMR (150 MHz, CDCl₃): δ = 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 [C₅₄H₆₇N₄(M+H)]⁺: 771.5366, found 771.5360.
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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), \(H_2O\) 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); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.18\) (t, \(^3\)J\(_{H-H} = 14.9\) Hz, 3H, \(CH_3\)), 1.90 (m, 2H, \(CH_2\)), 2.60 (m, 2H, \(CH_2\)), 2.80 (s, 6H, tolyl-\(CH_3\)), 5.13 (t, \(^3\)J\(_{H-H} = 15.3\) Hz, 2H, \(CH_2\)), 7.65 (d, \(^3\)J\(_{H-H} = 7.9\) Hz, 4H, C\(_6\)H\(_4\)-\(H\)), 8.14 (d, \(^3\)J\(_{H-H} = 7.9\) Hz, 4H, C\(_6\)H\(_4\)-\(H\)), 9.08 (d, \(^3\)J\(_{H-H} = 4.7\) Hz, 2H, \(H_\beta\)), 9.10 (d, \(^3\)J\(_{H-H} = 4.7\) Hz, 2H, \(H_\beta\)), 9.39 (d, \(^3\)J\(_{H-H} = 4.7\) Hz, 2H, \(H_\beta\)), 9.69 (d, \(^3\)J\(_{H-H} = 4.7\) Hz, 2H, \(H_\beta\)), 10.18 (s, 1H, \(H_{meso}\)) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 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 (CH\(_2\)Cl\(_2\)): \(\lambda_{max} (\log e) = 415\) (5.07), 452 (3.89), 544 (3.53), 580 (3.50), 639 (3.51) nm; HRMS (MALDI) \(m/z\) calcd. for [C\(_{38}\)H\(_{34}\)N\(_4\)]\(\text{M}^+\): 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 : CH\(_2\)Cl\(_2\) = 1 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta = -2.99\) (s, br., 1H, NH), 1.14 (d, \(^3\)J\(_{H-H} = 14.9\) Hz,
3H, CH₃), 1.87-1.79 (m, 2H, CH₂), 2.59-2.51 (m, 2H, CH₂), 4.13 (s, 6H, OCH₃), 5.14-5.05 (m, 2H, CH₂), 7.32 (d, ³J_H-H = 8.5 Hz, 4H, C₆H₄-H), 8.15 (d, ³J_H-H = 8.5 Hz, 4H, C₆H₄-H), 8.99 (t, ³J_H-H = 5.1 Hz, 4H, Hβ), 9.29-9.23 (m, 2H, Hβ), 9.57-9.52 (m, 2H, Hβ), 10.09 (s, 1H, Hmeso) ppm; ¹³C-NMR (150 MHz, CDCl₃): δ = 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 (CH₂Cl₂): λₘₐₓ (log ε) = 414 (5.48), 511 (4.10), 544 (3.49), 583 (3.66), 640 (3.50) nm; HRMS (ESI) m/z calcd. for [C₃8H₃₅N₄O₂]⁺: 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; Rf = 0.41 (CH₂Cl₂ : n-hexane, 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.77 (s, 2H, NH), 4.01 (s, 6H, OCH₃), 7.34-7.37 (dd, ³J_H-H = 5.3, 2.3 Hz, 2H, C₆H₄-H), 7.65-7.69 (t, ³J_H-H = 15.2 Hz, 2H, C₆H₄-H), 7.79 (m, 10H, Ph-H), 8.24-8.25 (d, ³J_H-H = 5.8 Hz, 4H, Ph-H), 8.86-8.87 (d, ³J_H-H = 4.6 Hz, 4H, Hβ), 8.91-8.92 (d, ³J_H-H = 4.7 Hz, 4H, Hβ) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 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): λₘₐₓ (log ε) = 417 (5.41), 513 (4.05), 547 (3.73), 588 (3.71), 647 (3.66) nm; HRMS (ESI) m/z calcd. for [C₄₆H₃₄N₄O₂]⁺: 675.2760, found 675.2748.
7.2.3 Brominated precursors

Bromorporphyrins 83-85, 87, 93, 96-102 were synthesised via methods developed by Boyle and co-workers and NMR data were in accordance to those reported in the literature.

General Procedure B: Bromination

The porphyrin (1 equiv.) was dissolved into CHCl₃ and NBS (0.8 - 2.1 equiv.) and pyridine (0.1 mL) were added. The reaction progression was monitored by TLC using CHCl₃ : 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 CH₂Cl₂/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 CHCl₃, following general procedure B to give the purple product 82 (110 mg, 97%). M.p. >300 °C; Rf = 0.41 (CH₂Cl₂ : n-hexane, 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.74 (s, 2H, N/7) 4.00 (s, 3H, OCH₃), 7.34-7.36 (m, 1H, C₆H₄-H), 7.66 (m, 1H, C₆H₄-H), 7.76 (m, 8H, C₆H₄/Ph-H), 8.21-8.23 (d, 3J_H-H = 7.5 Hz, 4H, Ph-H), 8.81-8.83 (d, 3J_H-H = 4.4 Hz, 2H, Hβ), 8.87-8.88 (d, 3J_H-H = 4.4 Hz, 2H, Hβ), 8.92-8.93 (d, 3J_H-H = 4.4 Hz, 2H, Hβ), 9.69-9.71 (d, 3J_H-H = 4.7 Hz, 2H, Hβ) ppm; ¹³C NMR (150 MHz, CDCl₃): 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): λₘₐₓ (log e) = 419 (5.46), 517 (4.09), 550 (3.81), 595 (3.64), 655 (3.77) nm; HRMS (MALDI) m/z calcd. for [C₃₉H₂₂BrO₄]⁺(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 CHCl₃, following the general procedure B. After 50 min the solvent was removed in vacuo and the residue purified by column chromatography (silica, CH₂Cl₂ : n-hexane, 1:2, v/v) to yield a purple solid. Yield: 75 mg (0.088 mmol, 91%). M.p. >300 °C; Rᵣ = 0.53 (CH₂Cl₂ : n-hexane, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.64 (s, 2H, NH₂), 0.94-0.98 (t, ³Jₜ-H = 14.5 Hz, 3H, CH₃), 1.41 (m, 2H, CH₂), 1.57 (s, 36H, t-butyl-H), 1.66 (m, 2H, CH₂), 1.86 (m, 2H, CH₂), 2.57 (m, 2H, CH₂), 4.99 (m, 2H, CH₂), 7.85 (m, 2H, C₆H₃-H), 8.05-8.07 (m, 4H, C₆H₃-H), 8.92 (m, 4H, H₂), 9.46-9.47 (d, ³Jₜ-H = 4.8 Hz, 2H, H₂), 9.62-9.63 (d, ³Jₜ-H = 4.8 Hz, 2H, H₂) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 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 (CH₂Cl₂): λₘₐₓ (log ε) = 421 (5.86), 486 (4.39), 557 (4.52), 659 (4.42) nm; HRMS (ESI) m/z calcd. for [C₅₄H₆₆BrN₄](M+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 CH\(_2\)Cl\(_2\)/MeOH. M.p. >300 °C; \(R_f = 0.78\) (CH\(_2\)Cl\(_2\) : n-hexane = 1 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = -2.40\) (s, 2H, NH), 0.95-0.98 (t, \(^3\)J\(_{H-H} = 14.8\) Hz, 12H, CH\(_2\)), 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, \(^3\)J\(_{H-H} = 8.3\) Hz, 2H, Ph-H), 8.79-8.80 (d, \(^3\)J\(_{H-H} = 4.9\) Hz, 2H, H\(_p\)) ppm; \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 14.2, 34.6, 50.1, 123.7, 126.5, 127.7, 128.4, 129.6, 132.0, 132.9, 143.0, 148.0\) ppm; UV/vis (EtOAc): \(\lambda_{\text{max}}\) (log \(\varepsilon\)) = 417 (5.32), 520 (3.97), 553 (3.68), 602 (3.33), 657 (3.47) nm; HRMS (ESI) \(m/z\) calcd. for [C\(_{36}\)H\(_{38}\)N\(_4\)Br](M+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-methoxy)phenyl-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 CH\(_2\)Cl\(_2\)/MeOH. M.p. = 260-263 °C; \(R_f = 0.33\) (CH\(_2\)Cl\(_2\) : n-hexane = 1 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = -2.73\) (s, 2H, NH), 4.03 (s, 6H, OCH\(_3\)), 7.36-7.39 (dd, \(^3\)J\(_{H-H} = 8.3\) Hz, 2H, C\(_6\)H\(_4\)-H), 7.66-7.71 (t, \(^3\)J\(_{H-H} = 15.7\) Hz, 2H, C\(_6\)H\(_4\)-H), 7.78 (m, 7H, Ph/C\(_6\)H\(_4\)-H), 8.20-8.21 (d, \(^3\)J\(_{H-H} = 6.2\) Hz, 2H, Ph-H), 8.82-8.83 (d, \(^3\)J\(_{H-H} = 4.7\) Hz, 2H, H\(_p\)), 8.97-8.98 (d, \(^3\)J\(_{H-H} = 4.7\) Hz, 2H, H\(_p\)), 9.86-9.87 (d, \(^3\)J\(_{H-H} = 4.8\) Hz, 2H, H\(_p\)) ppm; \(^1^3\)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): \(\lambda_{\text{max}}\) (log \(\varepsilon\)) = 418 (5.41), 516 (4.05), 550 (3.69), 596 (3.45), 651 (3.40) nm; HRMS (MALDI) \(m/z\) calcd. for [C\(_{40}\)H\(_{29}\)N\(_4\)O\(_2\)Br](M+H\(^+\)): 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$_2$Cl$_2$ : n-hexane = 2 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = -2.75$ (s, 2H, NH), 4.00 (s, 3H, OCH$_3$), 4.02 (s, 6H, OCH$_3$), 7.36 (m, 4H, C$_6$H$_4$-H), 7.67 (m, 4H, C$_6$H$_4$-H), 7.79 (m, 4H, C$_6$H$_4$-H), 8.86 (s, 4H, H$_b$), 8.97 (d, $^3$$J_{H-H} = 4.6$ Hz, 2H, $H_b$) ppm; $^1^3$C NMR (150 MHz, CDCl$_3$): $\delta = 55.4$, 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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 421 (5.46), 517 (4.11), 553 (3.76), 595 (3.47) nm; HRMS (ESI) m/z calcd. for [C$_{41}$H$_{32}$BrN$_4$O$_3$](M+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$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = -2.74$ (s, 2H, NH), 4.09 (s, 3H, OCH$_3$), 4.11 (s, 6H, OCH$_3$), 7.30 (d, $^3$$J_{H-H} = 4.6$ Hz, 2H, $H_b$) ppm; $^1^3$C NMR (150 MHz, CDCl$_3$): $\delta = 55.4$, 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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 421 (5.46), 517 (4.11), 553 (3.76), 595 (3.47) nm; HRMS (ESI) m/z calcd. for [C$_{41}$H$_{32}$BrN$_4$O$_3$](M+H)$^+$: 707.1658, found 707.1655.
8.6 Hz, 6H, C₆H₄-H), 8.09 (m, 6H, C₆H₄-H), 8.82 (s, 4H, H₈), 8.92 (d, 3J_H-H = 4.7 Hz, 2H, H₈), 9.66 (d, 3J_H-H = 4.7 Hz, 2H, H₈) 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 calcld. for [C₄₁H₃₂BrN₄O₃](M⁺): 707.1658, found 707.1671.

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

![Diagram]

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; Rf = 0.36 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.70 (s, 2H, NH), 1.12 (t, 3J_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, 3J_H-H = 8.3 Hz, 4H, Ph-H), 8.09 (d, 3J_H-H = 8.3 Hz, 4H, Ph-H), 8.88 (m, 4H, H₈), 9.44 (d, 3J_H-H = 4.8 Hz, 2H, H₈), 9.59 (d, 3J_H-H = 4.8 Hz, 2H, H₈) 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 calcld. for [C₃₈H₃₄BrN₄O₂](M+H)⁺: 657.1865, found 657.1854.

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

![Diagram]

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\(_2\)Cl\(_2\) : \( n \)-hexane = 2 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \( \delta = -2.48 \) (s, 2H, NH), 0.96 (t, \( J_{H-H} = 14.6 \) 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, \( J_{H-H} = 3.1 \) Hz, 2H, \( H_\beta \)), 9.66 (m, 4H, \( H_\beta \)), 9.87 (d, \( J_{H-H} = 3.4 \) Hz, 4H, \( H_\beta \)), 10.11 (s, 1H, \( H_{meso} \)) ppm; \(^13\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 13.9, 14.0, 34.7, 50.4, 77.2, 124.8, 132.7 \) ppm; UV/vis: \( \lambda_{max} \) (log \( \varepsilon \)) = 414 (5.44), 514 (4.14), 546 (3.64), 592 (3.54), 648 (3.42) nm; HRMS (MALDI) \( m/z \) calcd. for [C\(_{30}H_{34}N_4Br\)](M+H\(^+\))\(^+\): 529.1967, found 529.1967.

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

![Diagram of porphyrin structure]

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\(_2\)Cl\(_2\) : \( n \)-hexane = 2 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \( \delta = -2.34 \) (s, 2H, NH), 0.97 (t, \( J_{H-H} = 15.0 \) 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, \( H_\beta \)), 9.75 (d, \( J_{H-H} = 4.8 \) Hz, 4H, \( H_\beta \)) ppm; \(^13\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 13.8, 24.4, 34.4, 50.0, 67.0, 124.4, 129.8, 133.1 \) ppm; UV/vis (THF): \( \lambda_{max} \) (log \( \varepsilon \)) = 422 (5.55), 524 (4.16), 558 (4.05), 606 (3.60), 664 (3.84) nm; HRMS (MALDI) \( m/z \) calcd. for [C\(_{30}H_{33}N_4Br_2\)](M+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 \textit{in vacuo} and the residue was redissolved in CH$_2$Cl$_2$. This solution was passed through a plug of silica using CH$_2$Cl$_2$ as eluent. Solvents were removed \textit{in vacuo} to give a pink/purple solid followed by recrystallisation CH$_2$Cl$_2$/MeOH.

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

Produced from 84 (100 mg, 0.159 mmol) dissolved in CHCl$_3$ (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; $R_f = 0.61$ (CH$_2$Cl$_2$ : n-hexane = 2 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = 0.94$-0.97 (t, $^3$J$_{H_1-H_1}$ = 12.8 Hz, 3H, CH$_3$), 1.40 (m, 2H, CH$_2$), 1.51 (m, 2H, CH$_2$), 1.82 (m, 2H, CH$_2$), 2.54 (m, 2H, CH$_2$), 4.98 (m, 2H, CH$_2$), 7.81 (m, 6H, Ph-$\beta$), 8.19-8.21 (d, $^3$J$_{H_1-H_1}$ = 7.9 Hz, 4H, Ph-$H$), 8.88 (m, 4H, $H_\beta$), 9.46-9.47 (d, $^3$J$_{H_1-H_1}$ = 4.3 Hz, 2H, $H_\beta$), 9.61-9.62 ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 14.2$, 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 (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 423 (5.33), 557 (3.79), 646 (3.57) nm; HRMS (MALDI) m/z calcd. for [C$_{38}$H$_{31}$BrN$_4$Zn](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 CHCl₃ (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 °C; \( R_f = 0.31 \) (CH₂Cl₂ : n-hexane = 3 : 2, v/v); \(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 2.75 \) (s, 6H, tolyl-CH₃), 7.57-7.59 (d, \( ^3J_{H-H} = 7.8 \) Hz, 4H, C₆H₄-H), 8.10-8.12 (d, \( ^3J_{H-H} = 7.8 \) Hz, 4H, C₆H₄-H), 9.00-9.02 (t, \( ^3J_{H-H} = 8.7 \) Hz, 4H, \( H_β \)), 9.29-9.31 (d, \( ^3J_{H-H} = 4.6 \) Hz, 2H, \( H_β \)), 9.74-9.76 (d, \( ^3J_{H-H} = 4.8 \) Hz, 2H, \( H_β \)), 10.10 (s, 1H, \( H_{meso} \)) ppm; \(^1^3\)C NMR (100 MHz, CDCl₃): \( \delta = 21.5, 106.1, 120.7, 127.2, 131.7, 134.6, 136.9, 140.1, 149.2, 150.1, 155.0, 150.6 \) ppm; UV/vis (EtOAc): \( \lambda_{max} \) (log \( \varepsilon \)) = 418 (5.47), 552 (4.03), 591 (3.16) nm; HRMS (MALDI) \( m/z \) calcd. for [C₃₄H₂₃N₄ZnBr](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 CHCl₃ (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 °C; \( R_f = 0.40 \) (CH₂Cl₂ : n-hexane = 3 : 2, v/v); \(^1\)H NMR (400 MHz, CDCl₃/pyridine-d₅, 20 : 1): \( \delta = 3.99 \) (s, 6H, OCH₃), 7.32-7.35 (dd, \( ^3J_{H-H} = 8.3 \) Hz, 2.7 Hz, 2H, C₆H₄-H), 7.62-7.66 (t, \( ^3J_{H-H} = 15.1 \) Hz, 2H, C₆H₄-H), 7.79 (m, 4H, C₆H₄-H), 9.02 (m, 4H, \( H_β \)), 9.26-9.28 (d, \( ^3J_{H-H} = 4.8 \) Hz, 2H, \( H_β \)), 9.74-9.75 (d, \( ^3J_{H-H} = 4.8 \) Hz, 2H, \( H_β \)), 10.09 (s, 1H, \( H_{meso} \)) ppm; \(^1^3\)C NMR (100 MHz, CDCl₃/pyridine-d₅ 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): \( \lambda_{max} \) (log \( \varepsilon \)) = 417 (5.37), 550 (3.98), 592 (3.14) nm; HRMS (MALDI) \( m/z \) calcd. for [C₃₄H₂₃N₄O₂ZnBr](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 CHCl₃ (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; Rf = 0.42 (CH₂Cl₂ : n-hexane = 3 : 1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 4.01 (s, 6H, OC₁₃), 7.33-7.35 (dd, J₁-H₁ = 8.7 Hz, 2H, C₆H₄-π), 7.62-7.66 (t, J₁-H₁ = 15.3 Hz, 2H, C₆H₄-π), 7.74 (m, 7H, Ph/C₆H₄-π), 8.17-8.18 (d, J₁-H₁ = 6.5 Hz, 2H, Ph-π), 8.83-8.84 (d, J₁-H₁ = 4.6 Hz, 2H, H₁β), 8.88-8.89 (d, J₁-H₁ = 4.6 Hz, 2H, H₁β), 8.98-8.99 (d, J₁-H₁ = 4.6 Hz, 2H, H₁β) ppm; ¹³C NMR (100 MHz, CDCl₃/pyridine-d₅, 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, 143.2, 143.2, 144.5, 148.3, 149.6, 157.7 ppm; UV/vis (EtOAc): λmax (log ε) = 423 (5.71), 558 (4.24), 598 (3.72) nm; HRMS (MALDI) m/z calcd. for [C₄₀H₂₇N₄O₂ZnBr](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 CHCl₃ (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;
$R_f = 0.57 \ (CH_2Cl_2 : n$-hexane $= 1 : 1, \ v/v)$; $^1 \text{H NMR} \ (400 \text{ MHz}, \text{CDCl}_3): \delta = 0.90-0.93$ (t, $^3J_{\text{HH}} = 14.7 \text{ Hz, } 12\text{H}, \text{CH}_3), 2.81 \ (m, \ 4\text{H, } \text{CH}_2), 2.98 \ (m, \ 4\text{H, } \text{CH}_2), 5.12 \ (m, \ 2\text{H, } \text{CH}), 7.75 \ (m, \ 3\text{H, Ph-H}), 8.16-8.18 \ (d, \ ^3J_{\text{HH}} = 6.9 \text{ Hz, } 2\text{H, Ph-H}), 8.84 \ (s, \ 2\text{H, } H_\beta), 9.62 \ (s, \ 2\text{H, } H_\beta), 9.75 \ (m, \ 4\text{H, } H_\beta) \text{ ppm}; ^{13} \text{C NMR} \ (150 \text{ 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 \text{ ppm}; \text{UV/vis (EtOAc): } \lambda_{\text{max}} \ (\log \varepsilon) = 423 \ (5.65), 561 \ (4.15), 605 \ (3.85) \text{ nm}; \text{HRMS (MALDI) } m/z \text{ calcd. for } [\text{C}_{36}\text{H}_{35}\text{N}_4\text{ZnBr}]^+(M^+) : 666.1337; \text{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 Zn(OAc)$_2$ (301 mg, 1.645 mmol), following general procedure C to yield pink crystals (194 mg, 0.289 mmol, 88%). M.p. $> 300 \text{°C}; R_f = 0.39 \ (\text{CHCl}_3 : n$-hexane $= 1 : 1, \ v/v)$; $^1 \text{H NMR} \ (400 \text{ MHz, CDCl}_3, \text{TMS}): \delta = 0.93 \ (t, \ ^3J_{\text{HH}} = 14.8 \text{ Hz, } 12\text{H, } \text{CH}_3), 2.81 \ (m, \ 4\text{H, } \text{CH}_2), 2.96 \ (m, \ 4\text{H, } \text{CH}_2), 5.06 \ (m, \ 2\text{H, } \text{CH}), 9.57 \ (m, \ 4\text{H, } H_\beta), 9.69 \ (m, \ 4\text{H, } H_\beta) \text{ ppm}; ^{13} \text{C NMR} \ (150 \text{ MHz, CDCl}_3): \delta = 13.9, 34.4, 50.4, 77.2, 124.8, 131.2 132.7 \text{ ppm}; \text{UV/vis (THF): } \lambda_{\text{max}} \ (\log \varepsilon) = 428 \ (5.58), 566 \ (4.02), 614 \ (3.94) \text{ nm}; \text{HRMS (MALDI) } m/z \text{ calcd. for } [\text{C}_{39}\text{H}_{30}\text{N}_4\text{ZnBr}_2]^+(M^+) : 668.0129; \text{found 668.0136}.$
{5,10,15-Tris(4-methoxyphenyl)porphyrinato}zinc(II) (119):

Produced from 70 (80 mg, 0.127 mmol) dissolved in CHCl₃ (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; Rf = 0.17 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.99 (s, 6H, OCH₃), 4.09 (s, 3H, OCH₃), 7.27 (s, 2H, C₆H₄-H), 7.33-7.36 (dd, 3J_H-H = 2.2 Hz, 2H, C₆H₄-H), 7.66-7.70 (t, 3J_H-H = 15.7 Hz, 2H, C₆H₄-H), 7.81 (s, 2H, C₆H₄-H), 7.85-7.87 (d, 3J_H-H = 7.4 Hz, 2H, C₆H₄-H), 8.13-8.15 (d, 3J_H-H = 8.1 Hz, 2H, C₆H₄-H), 9.02-9.03 (d, 3J_H-H = 4.6 Hz, 2H, H₂), 9.05-9.06 (d, 3J_H-H = 4.6 Hz, 2H, H₂), 9.14-9.15 (d, 3J_H-H = 4.6 Hz, 2H, H₂), 9.39-9.40 (d, 3J_H-H = 4.6 Hz, 2H, H₂), 10.23 (s, 1H, Hmeso) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λ_{max} (log ε) = 415 (5.27), 543 (4.09), 579 (3.50) nm; HRMS (MALDI) m/z calcd. for [C₄H₃O₃N₄O₂Zn]⁺: 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 CHCl₃ (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; Rᵣ = 0.37 (CH₂Cl₂ : n-hexane = 2 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.16-1.20 (t, 3J_H-H = 14.8 Hz, 3H, CH₃), 1.90 (m, 2H, CH₂), 2.61 (m, 2H, CH₂), 4.02 (s, 6H, OCH₃), 2.64 (s, 12H, toyl-CH₃), 5.09-5.14 (t, 3J_H-H = 16.1 Hz, 2H, CH₂), 7.36-7.37 (dd, 3J_H-H = 3.2, 1.8 Hz, 1H, C₆H₄-H), 7.38-7.39 (dd, 3J_H-H = 3.2, 1.8 Hz, 1H, C₆H₄-H), 7.66-7.71 (t, 3J_H-H = 15.7 Hz, 2H, C₆H₄-H), 7.81 (m, 2H, C₆H₄-H), 7.87 (m, 2H, C₆H₄-H), 9.09-9.13 (q, 3J_H-H = 11.6, 4.7 Hz, 4H, Hβ), 9.34-9.35 (d, 3J_H-H = 4.7 Hz, 2H, Hβ), 9.64-9.65 (d, 3J_H-H = 4.7 Hz, 2H, Hβ), 10.14 (s, 1H, Hmeso) ppm; ¹³C NMR (100 MHz, CDCl₃): 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): λₘₐₓ (log ε) = 416 (5.56), 550 (4.14), 589 (3.30) nm; HRMS (MALDI) m/z calcd. for [C₃₈H₃₂N₄O₂Zn]^+: 640.1817; found 640.1849.

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

![Diagram](attachment:image.png)

Produced from porphyrin 68 (100 mg, 0.181 mmol) dissolved in CHCl₃ and Zn(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; Rᵣ = 0.43 (CH₂Cl₂ : n-hexane = 2 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.98-1.02 (t, 3J_H-H = 14.6 Hz, 12H, CH₃), 2.88 (m, 4H, CH₂), 3.05 (m, 4H, CH₂), 3.37 (s, 1H, C≡CH), 5.21 (m, 2H, CH), 7.94-7.96 (d, 3J_H-H = 7.8 Hz, 2H, C₆H₄-H), 8.24-8.26 (d, 3J_H-H = 7.8 Hz, 2H, C₆H₄-H), 9.01-9.03 (m, 2H, Hβ), 9.37 (m, 2H, Hβ), 9.85 (m, 4H, Hβ), 10.19 (s, 1H, Hmeso) ppm; ¹³C NMR (150 MHz, CDCl₃): 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): λₘₐₓ (log ε) = 420 (5.73), 554 (4.31), 594 (3.64) nm; HRMS (MALDI) m/z calcd. for [C₃₈H₃₂N₄O₂Zn]^+: 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 CHCl₃ (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; Rᵣ = 0.33 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.14-1.18 (t, Jₜ-H = 14.7 Hz, 3H, C₁), 1.88 (m, 2H, C₂), 2.77 (s, 6H, C₆H₄-CH₃), 5.07-5.10 (t, Jₜ-H = 15.9 Hz, 2H, C₂), 5.07-5.10 (t, Jₜ-H = 15.9 Hz, 2H, C₂), 7.60-7.62 (d, Jₜ-H = 7.6 Hz, 4H, C₆H₄-H), 8.12-8.14 (d, Jₜ-H = 7.6 Hz, 4H, C₆H₄-H), 9.07 (m, 4H, Hₗ), 9.30-9.31 (d, Jₜ-H = 4.5 Hz, 2H, Hₗ), 9.61-9.62 (d, Jₜ-H = 4.7 Hz, 2H, Hₗ), 10.09 (s, 1H, Hmeso) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 [C₃₈H₃₂N₄Zn](M⁺): 608.1918; found 608.1938.

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

Porphyrrin 62 (100 mg, 0.178 mmol) and Ni(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 CH₂Cl₂ as eluent. Recrystallisation of the product
using CH$_2$Cl$_2$/MeOH yielded red-purple crystals (199 mg, 90%). M.p. >300 °C; $R_f = 0.53$ (CH$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = 3.31$ (s, 1H, C=CH), 7.74 (m, 6H, Ph-H), 7.83-7.85 (d, $^3J_{H-H} = 7.9$ Hz, 2H, C$_6$H$_4$-H), 8.01-8.03 (d, $^3J_{H-H} = 8.0$ Hz, 2H, C$_6$H$_4$-H), 8.05-8.07 (d, $^3J_{H-H} = 7.0$ Hz, 2H, Ph-H), 8.77-8.78 (d, $^3J_{H-H} = 4.8$ Hz, 2H, H$_p$), 9.15-9.16 (d, $^3J_{H-H} = 4.8$ Hz, 2H, H$_p$), 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): $\lambda_{max}$ (log $\varepsilon$) = 407 (5.46), 521 (4.29), 557 (3.60) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{40}$H$_{24}$N$_4$Ni](M$^+$): 618.1354, found 618.1380.

7.2.5 Borylation

Porphyrrins 128, 129, 130, 132, and 133 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. Bromoporphyrin (1 equiv.) and Pd(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 °C. The reaction was followed by TLC using CH$_2$Cl$_2$ : n-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 CH$_2$Cl$_2$ : n-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 Pd(PPh₃)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 °C; Rf = 0.31 (CH₂Cl₂ : 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), PdCl₂(PPh₃)₂ (7 mg, 0.010 mmol), DCE (10 mL) and TEA (0.6 mL) dissolved in CHCl₃ (25 mL) according to standard procedure D to give a purple solid (89 mg, 0.113 mmol, 56%). M.p. >300 °C; Rf = 0.31 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz,
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CDCl₃, TMS): δ = 1.90 (s, 12H, CH₃), 3.95 (s, 6H, OCH₃), 7.30-7.32 (d, 3Jₕ-H = 8.3 Hz, 2H, C₆H₄-H), 7.65-7.69 (t, 3Jₕ-H = 15.7 Hz, 2H, C₆H₄-H), 7.77 (m, 5H, Ph/C₆H₄-H) 7.85-7.87 (d, 3Jₕ-H = 7.3 Hz, 2H, C₆H₄-H) 8.24-8.26 (d, 3Jₕ-H = 7.3 Hz, 2H, Ph-H), 8.99-9.00 (d, 3Jₕ-H = 4.6 Hz, 2H, H₈), 9.02-9.03 (d, 3Jₕ-H = 4.6 Hz, 2H, H₈), 9.16-9.17 (d, 3Jₕ-H = 4.6 Hz, 2H, H₈), 9.95-9.97 (d, 3Jₕ-H = 4.6 Hz, 2H, H₈) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 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): λmax (log ε) = 419 (5.58), 551 (4.17), 591 (3.39) nm; HRMS (MALDI) m/z calcd. for [C₄₆H₃₉N₄O₄ZnB](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 Pd(PPh₃)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; Rf = 0.32 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.65 (s, 2H, NH) 0.95 (m, 3Jₕ-H = 14.8 Hz, 12H, CH₃), 1.42 (m, 6H, CH₂), 1.53 (m, 6H, CH₂), 1.80 (m, 6H, CH₂), 1.87 (s, 12H, CH₃), 2.54 (m, 6H, CH₂), 4.95 (m, 6H, CH₂), 9.46 (d, 3Jₕ-H = 4.2 Hz, 2H, H₈), 9.58-9.48 (m, 4H, H₈), 9.84 (d, 3Jₕ-H = 4.2 Hz, 2H, H₈) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 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: λmax (log ε) = 421(5.46), 517 (4.11), 553 (3.76), 595 (3.57), 652 (3.47) nm; HRMS (ESI) m/z calcd. for [C₄₄H₆₂N₄O₄B](M+H)⁺ 689.4966, found 689.4977.
7.2.6 Suzuki coupling

Porphyrins 63, 138\textsuperscript{209} and 141\textsuperscript{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 K$_3$PO$_4$ (20 equiv.) and anhydrous THF (60 mL) under an argon atmosphere, then porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$. This mixture was washed with saturated NaHCO$_3$, H$_2$O, and brine, and then dried over Na$_2$SO$_4$. The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallisation from CH$_2$Cl$_2$/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), K$_3$PO$_4$ (1469 mg, 6.92 mmol), 4-nitrophenyl boronic pinacol ester 135 (862 mg, 3.462 mmol) and Pd(PPh$_3$)$_4$ (32 mg, 0.028 mmol) gave 138 mg (0.236 mmol, 85%) of a purple solid after recrystallisation from CH$_2$Cl$_2$/MeOH. M.p. >300 °C; $R_f = 0.42$ (CH$_2$Cl$_2$ : n-hexane = 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = -3.00$ (s, 2H, N//), 7.83 (m, 6H, Ph-//), 8.27 (d, $^3$J$_{H_{11}-H_{17}} = 8.8$ Hz, 4H, Ph-H), 8.42 (d, $^3$J$_{H_{11}-H_{17}} = 8.8$ Hz, 2H, C$_6$H$_4$-//), 8.65 (d, $^3$J$_{H_{11}-H_{17}} = 8.8$ Hz, 2H, C$_6$H$_4$-//), 8.79 (d, $^3$J$_{H_{11}-H_{17}} = 4.7$ Hz, 2H, $H_{11}$), 8.98 (d, $^3$J$_{H_{11}-H_{17}} = 4.7$ Hz, 2H, $H_{11}$), 9.07 (d, $^3$J$_{H_{11}-H_{17}} = 4.7$ Hz, 2H, $H_{11}$), 9.39 (d, $^3$J$_{H_{11}-H_{17}} = 4.7$ Hz, 2H, $H_{11}$), 10.29 (s, 1H, $H_{meso}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 105.2$, 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 (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) =
414 (4.88), 511 (3.66), 544 (3.22), 581 (3.23), 637 (2.71) nm; HRMS (ESI) \( m/z \) calcd.

\[
\text{for } [C_{38}H_{26}N_{5}O_{2}](M+H^+) : 584.2087, \text{found } 584.2093.
\]

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

Following the general procedure E, 105 (150 mg, 0.248 mmol), K\(_3\)PO\(_4\) (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\(_2\)Cl\(_2\)/MeOH. M.p. = 120-123 °C; \( R_f = 0.35 \) (CH\(_2\)Cl\(_2\) : n-hexane = 1 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \( \delta = 7.82 \) (m, 6H, Ph-H), 7.97-8.00 (d, \(^3\)\(J_{H-H} = 8.5\) Hz, 4H, Ph-H), 8.39-8.41 (d, \(^3\)\(J_{H-H} = 8.7\) Hz, 2H, C\(_6\)H\(_4\)-H), 8.64-8.66 (d, \(^3\)\(J_{H-H} = 8.7\) Hz, 2H, C\(_6\)H\(_4\)-H), 8.87-8.88 (d, \(^3\)\(J_{H-H} = 4.7\) Hz, 2H, \(H_\beta\)), 9.05-9.07 (d, \(^3\)\(J_{H-H} = 4.6\) Hz, 2H, \(H_\beta\)), 9.15-9.17 (d, \(^3\)\(J_{H-H} = 4.7\) Hz, 2H, \(H_\beta\)), 9.46-9.47 (d, \(^3\)\(J_{H-H} = 4.6\) Hz, 2H, \(H_\beta\)), 10.23 (s, 1H, \(H_{meso}\)) ppm; \(^13\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 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\(_2\)Cl\(_2\)): \( \lambda_{max} \) (log \( \varepsilon \)) = 416 (5.05), 546 (4.02), 585 (3.30) nm; HRMS (MALDI) \( m/z \) calcd. for 

\[ [C_{38}H_{23}N_{5}O_{2}Zn](M^+) : 645.1143, \text{found } 645.1157. \]

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 CH₂Cl₂/MeOH. M.p. >300 °C; Rf = 0.24 (CH₂Cl₂: n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.73 (s, 2H, NH), 7.82 (m, 6H, Ph-H), 8.21 (d, ³J = 7.0 Hz, 4H, Ph-H), 8.38 (d, ³J₁₁₁ = 4.4 Hz, 2H, H), 8.65 (d, ³J₁₁₁ = 8.8 Hz, 2H, C₆H₄-H), 8.72 (d, ³J₁₁₁ = 4.1 Hz, 2H, H), 8.87 (d, ³J₁₁₁ = 4.7 Hz, 2H, H), 8.94 (d, ³J₁₁₁ = 4.7 Hz, 2H, H), 9.71 (d, ³J₁₁₁ = 4.7 Hz, 2H, H), 10.36 (s, 1H, Hmeso) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 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 (CH₂Cl₂): λmax (log ε) = 421 (4.98), 518 (3.75), 555 (3.57), 599 (3.35), 651 (3.33) nm; HRMS (ESI) m/z calcd. for [C₃₈H₂₅NsO₂Br](M⁺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), K₃PO₄ (165 mg, 0.780 mmol), 4-nitrophenyl boronic pinacol ester 135 (78 mg, 0.314 mmol) and Pd(PPh₃)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 CH₂Cl₂ as eluent. M.p. = 189-191 °C; Rf = 0.54 (CH₂Cl₂: n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.57 (s, 36H, t-butyl-H), 7.86-7.87 (t, ³J₁₁₁ = 3.6 Hz, 2H, Ar-H), 8.14-8.15 (d, ³J₁₁₁ = 1.8 Hz, 4H, Ar-H), 8.43-8.44 (d, ³J₁₁₁ = 8.7 Hz, 2H, C₆H₄-H), 8.65-8.67 (d, ³J₁₁₁ = 8.7 Hz, 2H, C₆H₄-H), 8.90-8.91 (d, ³J₁₁₁ = 4.7 Hz, 2H, H), 9.11-9.13 (d, ³J₁₁₁ = 4.7 Hz, 2H, H), 9.20-9.21 (d, ³J₁₁₁ = 4.5 Hz, 2H, H), 9.47-9.48 (d, ³J₁₁₁ = 4.5 Hz, 2H, Hmeso), 10.36 (s, 1H, Hmeso) 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): $\lambda_{\text{max}}$ (log $\varepsilon$) = 418 (5.39), 550 (4.08), 591 (3.28) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{54}$H$_{55}$N$_{50}$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.), PdCl$_2$(PPh$_3$)$_2$ (0.2 equiv.) and Cul (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 CH$_2$Cl$_2$/MeOH.

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

![Diagram of 5,15-Bis(3,5-di-tert-butylphenyl)-10-trimethylsilylethynyl-20-phenylporphyrin](image)

Produced from 5-bromo-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrin 87 (180 mg, 0.214 mmol), PdCl$_2$(PPh$_3$)$_2$ (10.0 mg, 0.143 mmol), Cul (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, CH₂Cl₂ : n-hexane, 1 : 2, v/v) to yield a purple solid (154 mg, 0.179 mmol, 83%). M.p. >300 °C; Rᵣ = 0.55 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -2.32 (s, 2H, NH), 0.60 (s, 9H, TMS-CH₃), 1.54 (s, 36H, t-butyl-H), 7.76 (m, 3H, Ph-H), 7.84 (m, 2H, Ar-H), 8.09 (d, J₃H,1H = 1.5 Hz, 4H, Ar-H), 8.20-8.21 (d, J₃H,1H = 6.6 Hz, 2H, Ph-H), 8.78-8.79 (d, J₃H,1H = 4.4 Hz, 2H, H₈), 8.83-8.84 (d, J₃H,1H = 4.4 Hz, 2H, H₈), 9.69-9.70 (d, J₃H,1H = 4.4 Hz, 2H, H₈) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λₘₐₓ (log ε) = 428 (5.12), 529 (3.73), 566 (3.88), 602 (3.35), 663 (3.51) nm; HRMS (ESI) m/z calcd. for [C₅₉H₆₇N₄Si](M+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), PdCl₂(PPh₃)₂ (20.0 mg, 28.6 μmol), Cul (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, CH₂Cl₂ : n-hexane, 1 : 3, v/v) to yield a purple solid (23.2 mg, 0.254 mmol, 46%). M.p. >300 °C; Rᵣ = 0.52 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = 0.64 (s, 9H, TMS-CH₃), 1.58 (s, 36H, t-butyl-H), 7.77 (m, 3H, Ph-H), 7.85 (m, 2H, Ar-H), 8.10-8.11 (d, J₃H,1H = 1.7 Hz, 4H, Ar-H), 8.21-8.22 (d, J₃H,1H = 6.8 Hz, 2H, Ph-H), 8.90-8.91 (d, J₃H,1H = 4.4 Hz, 2H, H₈), 8.95-8.96 (d, J₃H,1H = 4.6 Hz, 2H, H₈), 9.06-9.07 (d, J₃H,1H = 4.6 Hz, 2H, H₈), 9.80-9.81 (d, J₃H,1H = 4.4 Hz, 2H, H₈) ppm; ¹³C NMR (150 MHz, CDCl₃): 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): $\lambda_{\text{max}}$ (log $\varepsilon$) = 433 (5.49), 569 (4.09), 613 (4.13) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{59}$H$_{64}$N$_4$SiZn](M$^+$) 920.4192, found 920.4191.

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

![Chemical Structure]

Following general procedure F, using bromoporphyrin 86 (65 mg, 0.076 mmol), PdCl$_2$(PPh$_3$)$_2$ (20 mg, 0.029 mmol), Cul (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$_2$Cl$_2$: 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$_2$Cl$_2$: n-hexane = 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = -2.29 (s, 2H, NH), 0.61 (s, 9H, TMS-CH$_3$), 0.94-0.98 (t, $^3$J$_{H-H}$ = 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, $^3$J$_{H-H}$ = 16.4 Hz, 2H, CH$_2$), 7.84 (m, 2H, Ar-H), 8.78-8.81 (d, $^3$J$_{H-H}$ = 4.7 Hz, 4H, C$_6$H$_3$-H), 8.90 (m, 4H, $H_\beta$), 9.44-9.45 (d, $^3$J$_{H-H}$ = 4.7 Hz, 2H, $H_\beta$), 9.60-9.61 (d, $^3$J$_{H-H}$ = 4.7 Hz, 2H, $H_\beta$) ppm; $^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta$ = 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): $\lambda_{\text{max}}$ (log $\varepsilon$) = 424 (5.15), 527 (3.71), 565 (3.78), 607 (3.33), 665 (3.53) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{59}$H$_{74}$N$_4$Si](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), PdCl₂(PPh₃)₂ (19.5 mg, 0.028 mmol), Cul (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, CH₂Cl₂ : 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; Rf = 0.48 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -2.39 (s, 2H, NH), 0.65 (s, 9H, TMS-CH₃) 4.00 (s, 3H, OCH₃), 7.34-7.36 (dd, ³J_H-H = 6.0, 2.5 Hz, 1H, C₆H₄-H), 7.64-7.67 (t, ³J_H-H = 15.8 Hz, 2H, C₆H₄-H), 7.81 (m, 8H, C₆H₄/Ph-H), 8.23-8.24 (d, ³J_H-H = 6.5 Hz, 4H, Ph-H), 8.79-8.80 (d, ³J_H-H = 4.6 Hz, 2H, H₈), 8.85-8.86 (d, ³J_H-H = 4.6 Hz, 2H, H₈), 8.92-8.93 (d, ³J_H-H = 4.6 Hz, 2H, H₈) ppm; ¹³C-NMR (150 MHz, CDCl₃): 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): λmax (log ε) = 427 (5.27), 525 (3.90), 563 (4.02), 602 (3.43), 654 (3.35) nm; HRMS (ESI) m/z calcd. for [C₄₄H₃₇N₄O₄Si](M+H)+: 665.2737, found 665.2759.

Deprotection of trimethylsilanylethynylporphyrins

Alkynyl porphyrins 152-155 and 157 were prepared from the corresponding trimethylsilanylethynylporphyrins via standard procedure. Spectroscopic data agreed with those in the literature.

General procedure G – Deprotection of trimethylsilyl alkynylporphyrins: Trimethylsilylalkynylporphyrin (1 equiv.) was dissolved in CH₂Cl₂ and TBAF (1M, 1 mL) was added. The reaction was followed by TLC using CH₂Cl₂ : n-hexane (1 : 1,
Upon completion, the solution was filtered through a plug of silica using CH$_2$Cl$_2$ as eluent. Solvent was removed \textit{in vacuo} and the residue recrystallised using CH$_2$Cl$_2$/MeOH.

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

![5-Ethynyl-10,15,20-triphenylporphyrin](image)

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 °C; $R_f = 0.34$ (CH$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = -2.49$ (s, 2H, NH), 4.19 (s, 1H, C≡CH), 7.76 (m, 9H, Ph-H), 8.25-8.14 (m, 6H, Ph-H), 8.78 (d, $^{3}J_{H-H} = 4.7$ Hz, 4H, $H_{\beta}$), 8.91 (d, $^{3}J_{H-H} = 4.8$ Hz, 2H, $H_{\beta}$), 9.69 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, $H_{\beta}$) 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$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 425 (5.56), 525 (4.28), 560 (4.17), 599 (3.73), 655 (3.71) nm; HRMS (ESI) m/z calcd. for [C$_{40}$H$_{27}$N$_4$](M+H)$^+$: 563.2236, found 563.2231. Locos \textit{et al.} reported the synthesis of 152 but no experimental details were given.

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

![5-Ethynyl-10,20-diphenylporphyrin](image)

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$_2$Cl$_2$. The reaction mixture was stirred for 20 minutes. The solvent was removed under reduced pressure and the residue dissolved in
CH₂Cl₂ and filtered over a short silica gel column. Recrystallisation from CH₂Cl₂/MeOH gave purple crystals (60 mg, 0.123 mmol, 92%). M.p. > 300 °C; Rf = 0.52 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ= -2.70 (s, 2H, NH), 4.23 (s, 1H, C=CH₃), 7.83 (m, 6H, Ph-Η), 8.26 (m, 4H, Ph-Η), 8.98 (d, 3JHH = 4.1 Hz, 2H, H₆), 9.01 (d, 3JHH = 4.7 Hz, 2H, H₆), 9.33 (d, 3JHH = 4.7 Hz, 2H, H₆), 9.79 (d, 3JHH = 4.7 Hz, 2H, H₆), 10.27 (s, 1H, Hmeso) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 83.7, 85.7, 97.8, 106.3, 120.3, 126.7, 127.7, 130.5, 131.0, 131.4, 131.6, 134.4, 141.1 ppm; UV/vis (CH₂Cl₂); λmax (log ε) = 420 (4.76), 517 (3.38), 552 (3.28), 592 (3.28), 649 (2.98) nm; HRMS (ESI) m/z calcd. for [C₃₄H₂₃N₄](M+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 CH₂Cl₂ (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 CH₂Cl₂ (50 mL). All solvents were removed to yield a purple solid. Yield: 112 mg (0.142 mmol, 94%). M.p. >300 °C; Rf = 0.49 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ= -2.37 (s, 2H, NH), 1.51 (s, 36H, t-butyl-Η), 4.19 (s, 1H, C=CH₃), 7.70-7.80 (m, 3H, Ph-Η), 7.81-7.83 (m, 2H, Ar-Η), 8.05-8.09 (m, 4H, Ar-Η), 8.18-8.21 (m, 2H, Ph-Η), 8.79 (d, 3JHH = 4.7 Hz, 2H, H₆), 8.82 (d, 3JHH = 4.7 Hz, 2H, H₆), 8.97 (d, 3JHH = 4.7 Hz, 2H, H₆), 9.70 (d, 3JHH = 4.7 Hz, 2H, H₆) ppm; ¹³C NMR (150 MHz, CDCl₃): 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): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 427 (5.79), 527 (4.39), 562 (4.36), 602 (3.93), 659 (4.00) nm; HRMS (ESI) \( m/z \) calcld. for [C₅₆H₅₉N₄]⁺: 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 \textit{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); \(^1\)H NMR (600 MHz, CDCl₃, TMS): \( \delta = 1.59 \) (s, 36H, \( \sigma \)-butyl-\( \sigma \)), 4.09 (s, 1H, C=C-H), 7.78 (m, 3H, Ph-H), 7.86 (m, 2H, Ar-H), 8.12-8.13 (d, \( ^3J_{\text{H-H}} = 1.7 \) Hz, 4H, Ar-H), 8.22-8.23 (d, \( ^3J_{\text{H-H}} = 6.5 \) Hz, 2H, Ph-H), 8.93-8.94 (d, \( ^3J_{\text{H-H}} = 4.6 \) Hz, 2H, \( H_\beta \)), 8.97-8.98 (d, \( ^3J_{\text{H-H}} = 4.6 \) Hz, 2H, \( H_\beta \)), 9.08-9.09 (d, \( ^3J_{\text{H-H}} = 4.6 \) Hz, 2H, \( H_\beta \)), 8.96-9.12 (d, \( ^3J_{\text{H-H}} = 4.6 \) Hz, 2H, \( H_\beta \)) ppm; \(^{13}\)C NMR (150 MHz, CDCl₃): \( \delta = 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): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 429 (5.31), 566 (3.91), 608 (3.76) nm; HRMS (ESI) \( m/z \) calcld. for [C₅₆H₅₆N₄Zn]⁺: 848.3796, found 848.3836.
5,15-Bis(3,5-di-tert-butylphenyl)-10-ethynyl-20-hexylporphyrin (158):

![Structure of 5,15-Bis(3,5-di-tert-butylphenyl)-10-ethynyl-20-hexylporphyrin](image)

Produced from 149 (23 mg, 0.025 mmol) in CH$_2$Cl$_2$ (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$_2$Cl$_2$ (50 mL). All solvents were removed to yield a purple solid. Yield: 20 mg (0.023 mmol, 93%). M.p. >300 °C; $R_f = 0.54$ (CH$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = -2.33 (s, 2H, NH), 0.94-0.98 (t, $^3$J$_{H-H} = 14.5$ 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, C≡CH), 5.00 (m, 2H, CH$_2$), 7.84 (s, 4H, Ar-H), 8.07 (m, 2H, Ar-H), 8.91 (m, 4H, H$_\beta$), 9.45-9.46 (d, $^3$J$_{H-H} = 4.7$ Hz, 2H, H$_\beta$), 9.63-9.64 (d, $^3$J$_{H-H} = 4.7$ Hz, 2H, H$_\beta$) 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): $\lambda_{\text{max}}$ (log $\varepsilon$) = 428 (5.48), 525 (4.10), 562 (4.14), 603 (3.69), 661 (3.79) nm; HRMS (ESI) m/z calcld. for [C$_{56}$H$_{67}$N$_4$](M+H)$^+$: 795.5366, found 795.5378.

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

![Structure of 5-Ethynyl-15-(3-methoxyphenyl)-10,20-diphenylporphyrin](image)
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; 
$R_f = 0.40 \ (CH_2Cl_2 : n$-hexane = 1 : 1, v/v); $^1H$ NMR (400 MHz, CDCl$_3$, TMS): $\delta = -2.45$ (s, 2H, NH), 4.00 (s, 3H, OCH$_3$), 4.22 (s, 1H, C=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, $^3J_{H-H} = 6.8$ Hz, 2H, Ph-H), 8.79-8.80 (d, $^3J_{H-H} = 4.7$ Hz, 2H, $H_\beta$), 8.85-8.86 (d, $^3J_{H-H} = 4.7$ Hz, 2H, $H_\beta$), 8.93-8.94 (d, $^3J_{H-H} = 4.1$ Hz, 2H, $H_\beta$), 9.71-9.72 (d, $^3J_{H-H} = 4.1$ Hz, 2H, $H_\beta$) ppm; $^{13}C$ NMR (150 MHz, CDCl$_3$): $\delta = 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 $\varepsilon$) = 423 (5.58), 523 (4.19), 558 (4.13), 601 (3.66), 662 (3.38) nm; HRMS (ESI) m/z calcd. for [C$_{41}$H$_{29}$N$_4$O](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 Cs$_2$CO$_3$ (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(PPh$_3$)$_4$ (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 MgSO$_4$, 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; 

Rᵣ = 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, 3Jₜ-H = 4.8 Hz, 4H, Hₜ), 8.24-8.26 (d, 3Jₜ-H = 6.8 Hz, 4H, aryl-H), 8.31-8.34 (d, 3Jₜ-H = 5.8 Hz, 4H, aryl-H), 8.61-8.62 (d, 3Jₜ-H = 4.8 Hz, 2H, Hₜ), 8.65-8.66 (d, 3Jₜ-H = 4.8 Hz, 2H, Hₜ), 8.97 (m, 8H, Hₜ) 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 [C₇₀H₅₆N₈O₃](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$_2$CO$_3$ (4 mg, 0.02 mmol) and Pd(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 °C; R$_f$ = 0.32 (CH$_2$Cl$_2$ : n-hexane = 2 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = -2.14 (s, 2H, NH), -2.05 (s, 2H, NH), 0.91-0.82 (t, $^3$J$_{HH}$ = 15.0 Hz, 12H, C$_3$H), 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, $^3$J$_{HH}$ = 15.6 Hz, 2H, CH$_2$), 7.24-7.25 (d, $^3$J$_{HH}$ = 8.3 Hz, 4H, C$_6$H$_4$-H), 7.38-7.39 (d, $^3$J$_{HH}$ = 8.3 Hz, 2H, C$_6$H$_4$-H), 8.05-8.06 (d, $^3$J$_{HH}$ = 4.9 Hz, 2H, H$_p$, 8.08-8.09 (d, $^3$J$_{HH}$ = 4.4 Hz, 2H, H$_p$), 8.16-8.18 (d, $^3$J$_{HH}$ = 8.8 Hz, 4H, C$_6$H$_4$-H) 8.25-8.26 (d, $^3$J$_{HH}$ = 8.3 Hz, 2H, C$_6$H$_4$-H) 8.63-8.64 (d, $^3$J$_{HH}$ = 4.9 Hz, 2H, H$_p$), 8.96-8.97 (d, $^3$J$_{HH}$ = 4.9 Hz, 2H, H$_p$), 9.00-9.01 (d, $^3$J$_{HH}$ = 4.9 Hz, 2H, H$_p$), 9.13-9.14 (d, $^3$J$_{HH}$ = 4.4 Hz, 2H, H$_p$), 9.58-9.60 (d, $^3$J$_{HH}$ = 4.4 Hz, 2H, H$_p$), 9.66-9.67 ppm (d, $^3$J$_{HH}$ = 4.9 Hz, 2H, H$_p$); $^{13}$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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 410 (5.67), 450 (5.01), 507 (4.48), 567 (3.95), 599 (3.87), 666 (3.49) nm; HRMS (MALDI) $m/z$ calcld. for [C$_{79}$H$_{81}$N$_8$O$_3$](M+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$_2$CO$_3$ (4 mg, 0.02 mmol) and Pd(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 °C; R$_f$ = 0.30 (CH$_2$Cl$_2$ : n-hexane = 2 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = -2.16 (s, 2H, N//) -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, $^3$J$_{H-1}$ = 8.6 Hz, 4H, C$_6$H$_4$-H), 8.03 (d, $^3$J$_{H-1}$ = 4.7 Hz, 2H, H$_2^\beta$), 8.07 (d, $^3$J$_{H-1}$ = 4.7 Hz, 2H, H$_2^\beta$), 8.14 (d, $^3$J$_{H-1}$ = 8.6 Hz, 4H, C$_6$H$_4$-H), 8.22 (d, $^3$J$_{H-1}$ = 8.3 Hz, 2H, C$_6$H$_4$-H), 8.61 (d, $^3$J$_{H-1}$ = 4.7 Hz, 2H, H$_2^\beta$), 8.96 (dd, $^3$J$_{H-1}$ = 13.2, 4.7 Hz, 4H, H$_2^\beta$), 9.11 (d, $^3$J$_{H-1}$ = 4.8 Hz, 2H, H$_2^\beta$), 9.56 (d, $^3$J$_{H-1}$ = 4.7 Hz, 2H, H$_2^\beta$), 9.63 (d, $^3$J$_{H-1}$ = 4.8 Hz, 2H, H$_2^\beta$) 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$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $e$) = 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 [C$_{78}$H$_{81}$N$_8$O$_3$](M+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. Bromoporphyrin (1 equiv.), ethynylporphyrin (1 equiv.), Pd$_2$(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 NEt₃ (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 CH₂Cl₂ : 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), AsPh₃ (4 mg, 0.013 mmol) and Pd₂(dbac)₃ (5 mg, 0.001 mmol) following procedure 1. After purification dark green crystals were isolated (5 mg, 0.004 mmol, 29%). M.p. >300 °C; Rₕ = 0.37 (CH₂Cl₂ : n-hexane = 4 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.02 (s, 2H, NH), -1.93 (s, 2H, NH), 1.15 (t, 3J_H-H = 15.4 Hz, 3H, C₃), 1.88-1.81 (m, 2H, CH₂), 2.57-2.51 (m, 2H, CH₂), 4.14 (s, 6H, OCH₃), 4.98 (m, 2H, CH₂), 7.35 (m, 4H, C₆H₄-H), 7.80 (m, 9H, Ph-H), 8.17 (m, 4H, C₆H₄-H), 8.22 (m, 2H, Ph-H), 8.29 (m, 4H, Ph-H), 8.80 (m, 4H, Hβ), 8.90-8.91 (d, 3J_H-H = 4.7 Hz, 2H, Hβ), 9.07 (m, 4H, Hβ), 9.44 (d, 3J_H-H = 4.7 Hz, 2H, Hβ), 10.24 (d, 3J_H-H = 4.7 Hz, 2H, Hβ), 10.32 (d, 3J_H-H = 4.7 Hz, 2H, Hβ), ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): 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 [C₇₈H₅₈N₮O₂](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), AsPh₃ (5 mg, 0.020 mmol) and Pd(PPh₃)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 °C; Rᵣ = 0.30 (CH₂Cl₂ : n-hexane = 4 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.03 (s, 2H, NH) -2.01(s, 2H, NH), 3.98 (s, 3H, OCH₃), 4.01 (s, 6H, OCH₃), 7.10 (d, ⃗J_H-H = 15.9 Hz, 4H, C₆H₄-H), 7.63 (m, 9H, Ph-H), 7.75 (d, ⃗J_H-H = 15.9 Hz, 4H, C₆H₄-H), 7.91-7.87 (m, 4H, C₆H₄-H), 8.24-8.20 (m, 2H, Ph-H), 8.32-8.27 (m, 4H, Ph-H), 8.83-8.81 (m, 2H, H₀), 8.87-8.85 (m, 2H, H₁), 8.95-8.90 (m, 2H, H₂), 9.11-9.08 (m, 2H, H₃), 9.15-9.12 (m, 2H, H₄), 9.35-9.32 (m, 2H, H₅), 10.37-10.32 (m, 4H, H₆) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 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 (CH₂Cl₂): λ_max (log ε) = 412 (4.91), 473 (4.88), 517 (4.01), 620 (4.09), 713 (4.19) nm; HRMS (MALDI) m/z calcd. for [C₈₁H₅₆N₈O₃]^⁺: 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), AsPh₃ (10 mg, 0.033 mmol) and Pd₂(dba)₃ (2 mg, 0.003 mmol) were dried in vacuo and dissolved in degassed NEt₃ (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, CH₂Cl₂ : 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; Rf = 0.33 (CH₂Cl₂ : n-hexane : TEA = 2 : 1 : 0.01, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -1.92 (s, 2H, NH), -1.89 (s, 2H, NH), 1.59 (s, 36H, t-butyl-H), 4.11 (s, 3H, O C /₃), 4.14 (s, 6H, OCH₃), 7.31 (d, 3J_H-H = 8.2 Hz, 2H, C₆H₄-H), 7.31 (d, 3J_H-H = 8.8 Hz, 4H, Ar-H), 7.74-7.80 (m, 5H, aryl-H), 7.85-7.89 (m, 2H, C₆H₄-H), 8.15 (d, 3J_H-H = 8.2 Hz, 2H, Ph-H), 8.17-8.21 (m, 4H, aryl-H), 8.23 (d, 3J_H-H = 8.8 Hz, 4H, Ph-H), 8.84-8.93 (m, 8H, Hᵦ), 9.17 (d, 3J_H-H = 4.7 Hz, 2H, Hᵦ), 9.20 (d, 3J_H-H = 4.7 Hz, 2H, Hᵦ) 10.40 (m, 4H, Hᵦ) ppm; ¹³C-NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): 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 (C₇₇H₅₈N₆O₃)⁺ 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), AsPh₃ (25 mg, 0.082 mmol) and Pd₂(dba)₃ (16 mg, 0.028 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 : 4 to 1 : 1, v/v) to yield a red-green solid. Yield: 16 mg (0.012 mmol, 45%).

M.p. >300 °C; Rᵣ = 0.32 (CH₂Cl₂ : n-hexane = 2 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -1.93 (s, 2H, NH), -1.89 (s, 2H, NH), 0.94-1.00 (t, $^{3}J_{H-H} = 14.7$ Hz, 9H, CH₃), 1.38-1.49 (m, 6H, CH₂), 1.51-1.60 (m, 6H, CH₂), 1.59 (s, 36H, tert-butyl-H), 1.81-1.91 (m, 6H, CH₂), 2.51-2.61 (m, 6H, CH₂), 4.91-4.98 (m, 6H, CH₂), 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, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ), 8.88 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ), 9.17 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ), 9.45 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ), 9.49 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ), 9.61 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ), 10.32 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ), 10.37 (d, $^{3}J_{H-H} = 4.7$ Hz, 2H, Hβ) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λₘₐₓ (log ε) = 410 (4.61), 473 (4.82), 522 (3.85), 623 (4.04), 723 (4.17) nm; HRMS (ESI) m/z calcd. for [C₉₄H₁₀₀N₈](M+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; Rf = 0.29 (CH₂Cl₂ : n-hexane = 2 : 1, v/v); ¹H-NMR (600 MHz, CDCl₃, TMS): δ = -2.00 (s, 2H, N/H), -1.94 (s, 2H, NH), 1.58 (s, 36H, i-butyl-CH), 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, Hₖ), 9.11 (d, J₃₃ = 4.7 Hz, 2H, Hₖ), 9.15 (d, J₃₃ = 4.7 Hz, 2H, Hₖ), 10.36 (d, J₃₃ = 4.7 Hz, 2H, Hₖ), 10.37 (d, J₃₃ = 4.7 Hz, 2H, Hₖ) 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; Rf = 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, 2J_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, 2J_H-H = 5.7 Hz, 2H, Ph-H), 8.84 (d, 2J_H-H = 5.7 Hz, 2H, Ph-H), 8.92 (d, 2J_H-H = 4.7 Hz, 2H, H₉β), 9.06 (s, 4H, H₈β), 9.33 (s, 4H, H₈β) 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, 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), AsPh₃ (10 mg, 0.033 mmol) and Pd₂(dba)₃ (1 mg, 0.002 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: 15 mg (0.010 mmol, 43%). M.p. >300 °C; Rₜ = 0.27 (CH₂Cl₂ : n-hexane = 3 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -1.93 (s, 4H, NH), 1.58 (s, 72H, t-butyl-Ph), 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, H₅), 8.86 (s, 4H, H₆), 9.14 (s, 4H, H₇), 10.36 (s, 4H, H₈) ppm; ¹³C-NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λₘₐₓ (log ε) = 413 (4.59), 474 (4.72), 523 (3.87), 622 (3.99), 718 (4.09) nm; HRMS (ESI) m/z calcd. for [C₁₁₀H₁₁₄N₈](M+H)⁺: 1547.9292, found 1547.9245.
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; Rf = 0.26 (CH₂Cl₂ : n-hexane : TEA = 1 : 1 : 0.01, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -1.93 (s, 2H, N //), 1.58 (s, 36H, -butyl- //), 7.70-7.83 (m, 12H, Ar/Ph- //), 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, 3JH-H = 4.7 Hz, 2H, Hf), 8.87 (d, 3JH-H = 4.7 Hz, 2H, Hf), 8.88 (d, 3JH-H = 4.7 Hz, 2H, Hf), 8.92 (d, 3JH-H = 4.7 Hz, 2H, Hf), 8.93 (d, 3JH-H = 4.7 Hz, 2H, Hf), 9.13 (d, 3JH-H = 4.7 Hz, 2H, Hf), 9.19 (d, 3JH-H = 4.7 Hz, 2H, Hf), 10.33 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): λmax (log ε) = 406 (4.86), 473 (4.99), 521 (4.31), 624 (4.37), 716 (4.42) nm; HRMS (ESI) m/z calcd. for [C₉₄H₆₁N₈Zn](M+H)⁺: 1385.5930, found 1385.5876.
{5-[(10',20'-Bis(3,5-di-tert-butyphenyl)-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), AsPh₃ (15 mg, 0.049 mmol) and Pd₂(dba)₃ (5 mg, 0.005 mmol) were dried in vacuo and dissolved in degassed NEt₃ (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, CH₂Cl₂ : 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; Rₜ = 0.29 (CH₂Cl₂ : n-hexane : TEA = 1 : 1 : 0.01, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = 1.59 (s, 36H, tert-butyl), 7.70-7.83 (m, 14H, Ar/Ph), 8.15-8.22 (m, 8H, Ar/Ph), 8.29-8.32 (m, 4H, Ar/Ph), 8.89 (s, 2H, H₀), 8.92 (s, 4H, H₀), 8.97 (s, 2H, H₀), 9.18 (s, 2H, H₀), 9.23 (s, 2H, H₀), 10.43 (s, 4H, H₀) ppm. ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λₘₐₓ (log ε) = 413 (4.63), 480 (4.92), 559 (4.22), 690 (4.35) nm; HRMS (ESI) m/z calcd. for [C₉₄H₇₈N₈Zn₂](M+H)⁺: 1447.4935, found 1447.5011.

Dimer 166 (11 mg, 0.008 mmol) was dissolved in CHCl₃ (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 CH₂Cl₂ (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 °C; Rf = 0.32 (CH₂Cl₂ : n-hexane : TEA = 1 : 1 : 0.01, v/v); ¹H NMR (600 MHz, THF-d₈, TMS): δ = 0.94-0.99 (m, 9H, CH₃), 1.42-1.48 (m, 6H, CH₂), 1.54-1.60 (m, 6H, CH₂), 1.61 (s, 36H, t-Bu-H), 1.86-1.94 (m, 6H, CH₂), 2.54-2.65 (m, 6H, CH₂), 5.03-5.12 (m, 6H, CH₂), 7.74-7.78 (m, 3H, Ar/Ph-∥), 7.93-7.95 (m, 2H, Ar/Ph-H), 8.19-8.25 (m, 6H, Ar/Ph-H), 8.78 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 8.84 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 9.16 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 9.57 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 9.59 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 9.77 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 10.43 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 10.49 (d, 3JH-H = 4.7 Hz, 2H, Hβ), 10.49 ppm; ¹³C NMR (150 MHz, THF-d₈): δ = 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, 15.1, 151.2, 151.6, 153.2, 153.7 ppm; UV/vis (CH₂Cl₂): λ₂₅ (log ε) = 432 (4.45), 479 (4.78), 557 (4.21), 696 (4.38) nm; HRMS (ESI) m/z calcd. for [C₉₄H₁₀₃N₈Zn₂](M+H)⁺: 1471.6903, found 1471.6889.
5-(5',10',20'-Triphenylporphyrin-5-yl)ethynyl-15-(3-methoxyphenyl)-10,20-diphenylporphyrin (173):

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; Rf = 0.37 (CH₂Cl₂ : n-hexane = 3 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -2.09 (s, 2H, N=N), -1.99 (s, 2H, N=N), 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, H₀), 9.03-9.04 (d, 3J₁-H₁ = 4.5 Hz, 2H, H₀), 9.11-9.12 (d, 3J₁-H₁ = 4.7 Hz, 2H, H₀), 9.95-9.96 (d, 3J₁-H₁ = 4.8 Hz, 2H, H₀), 10.36-10.37 (d, 3J₁-H₁ = 4.7 Hz, 2H, H₀) ppm; UV/vis (THF): λₘₐₓ (log ε) = 407 (4.89), 471 (5.13), 520 (4.22), 625 (4.40), 712 (4.48) nm; HRMS (ESI) m/z calcd. for (C₇₀H₅₂N₈O)⁺: 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), AsPh₃ (34 mg, 0.111 mmol) and Pd₂(dba)₃ (5 mg, 0.004 mmol) using general procedure I to yield a dark solid following column chromatography (silica, CH₂Cl₂ : n-hexane, 1 : 3, v/v) (23 mg, 0.340 mmol, 39%). M.p. >300 °C; Rᵣ = 0.29 (CH₂Cl₂ : n-hexane = 3 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -1.99 (s, 2H, NH) -1.93 (s, 2H, NH) 0.91 (t, ³JH-H = 15.3 Hz, 3H, CH₃), 1.76-1.81 (m, 4H, CH₂), 1.84-1.88 (m, 2H, CH₂), 2.58 (m, 2H, CH₂), 5.00 (m, 2H, CH₂), 7.82 (m, 16H, Ph-H), 8.30 (m, 12H, Ph-H), 8.23-8.36 (m, 4H, H₀), 8.90-8.91 (d, ³JH-H = 4.7 Hz, 2H, H₀), 9.05-9.06 (d, ³JH-H = 4.7 Hz, 2H, H₀), 9.09-9.11 (d, ³JH-H = 4.7 Hz, 2H, H₀), 9.46-9.48 (d, ³JH-H = 4.7 Hz, 2H, H₀) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 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 [C₇₈H₅₉N₅](M+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), AsPh₃ (48 mg, 0.156 mmol) and Pd₂(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 CH₂Cl₂ : TEA as eluent (99 : 1, v/v), giving a green fraction. After removal of the solvent and recrystallisation from CH₂Cl₂/MeOH a dark powder was obtained (75 mg, 0.068 mmol, 48%). M.p. >300 °C; Rᵣ = 0.37 (CH₂Cl₂ : n-hexane = 5 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = -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, H₀), 9.11-9.13 (d, ³JH-H = 4.8 Hz, 4H, H₀), 10.36-10.38 (d, ³JH-H = 4.8 Hz 4H, H₀) ppm; ¹³C NMR (150
MHz, THF-d₈): δ = 29.5, 53.3, 126.6, 126.9, 128.0, 134.2, 134.5 141.6 ppm; UV/vis (THF): λ_max (log ε) = 407 (5.04), 472 (5.24), 519 (5.29), 619 (4.44), 712 (4.53) nm; HRMS (ESI) m/z calcd. for [C₇₈H₅₁N₈]⁺(M+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), AsPh₃ (38 mg, 0.123 mmol) and Pd₂(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 CH₂Cl₂: TEA as eluent (99:1, v/v), to yield a green fraction. Recrystallisation from CH₂Cl₂/MeOH gave a dark powder (75 mg, 0.068 mmol, 47%). M.p. > 300 °C; Rₛ = 0.22 (CH₂Cl₂ : n-hexane : TEA = 1 : 1 : 0.01, v/v);¹H NMR (400 MHz, CDCl₃, TMS): δ = 7.83 (m, 20H, Ph-//), 8.26 (m, 4H, Ph-//), 8.33 (m, 6H, Ph-H), 8.95-8.96 (d, 3J_H-H = 4.8 Hz 8H, H₆), 9.23-9.24 (d, 3J_H-H = 4.6 Hz, 4H, H₆), 10.51-10.52 (d, 3J_H-H = 4.6 Hz 4H, H₆) ppm;¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λ_max (log ε) = 412 (5.18), 479 (5.44), 548 (4.36), 685 (4.74) nm; HRMS (ESI) m/z calcd. for [C₇₈H₄₆N₈Zn₂]⁺(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; Rᶠ = 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, Hβ), 9.08 (m, 6H, Hβ), 9.33 (d, 3J_H-H = 4.4 Hz, 2H, Hβ), 9.39 (d, 3J_H-H = 4.4 Hz,
2H, Hβ), 10.05 (d, 3J_H-H = 4.4 Hz, 2H, Hβ), 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): λmax (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; Rf = 0.27 (CH₂Cl₂ : n-hexane = 2 : 1, v/v); ¹H NMR (400 MHz CDCl₃/pyridine-d₅ 10:1, TMS): δ = 7.02 (d, 3JH-H = 7.3 Hz, 2H, C₆H₄-H), 7.54 (d, 3JH-H = 7.3 Hz, 2H, C₆H₄-H), 7.25 (m, 2H, Ph-H), 7.86 (10H, m, Ph-H), 8.32 (8H, m, Ph-H), 8.48 (s, 2H, H₇), 9.10 (m, 4H, H₆), 9.17 (m, 4H, H₆), 9.41-9.42 (d, 3JH-H = 4.3 Hz, 2H, H₆), 9.47-9.48 (d, 3JH-H = 4.3 Hz, 2H, H₇), 10.11-10.12 (d, 3JH-H = 4.6 Hz, 2H, H₇), 10.28 (s, 1H, H₇), 10.35 (s, 1H, H₇) ppm; UV/vis (CH₂Cl₂): λmax (log ε) = 419 (4.89), 440 (4.62), 552 (3.75), 617 (3.61) nm; HRMS (Maldi) m/z calcd. for [C₇₂H₄₃N₈Zn₂](M+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; $R_t = 0.32$ (CH$_2$Cl$_2$ : n-hexane = 1 : 1, v/v);

$^1$H NMR (600 MHz, CDCl$_3$, TMS): $\delta = -2.87$ (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, C$_6$H$_4$-H), 9.04-9.05 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, $H_\beta$), 9.09-9.12 (dd, $^3J_{\text{H-H}} = 13.2$, 4.7 Hz, 4H, $H_\beta$), 9.36 (m, 2H, $H_\beta$), 9.41-9.42 (d, $^3J_{\text{H-H}} = 4.6$ Hz, 2H, $H_\beta$), 9.67-9.68 (m, 2H, $H_\beta$), 9.78-9.79 (m, 2H, $H_\beta$), 10.14 (s, 1H, $H_\text{meso}$), 10.15 (s, 2H, $H_\beta$), 10.30 (s, 1H, $H_\text{meso}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 13.9$, 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): $\lambda_{\text{max}}$ (log $\varepsilon$) = 412 (6.05), 434 (5.99), 508 (4.97), 572 (5.07), 666 (4.71) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{76}$H$_{38}$N$_8$Zn$_2$](M$^+$) 1010.4784, found 1010.4736.

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

Homocoupled side product obtained as a purple powder from the synthesis of 189 (11 mg, 0.009 mmol, 21%). M.p. >300 °C; $R_t = 0.37$ (CH$_2$Cl$_2$ : n-hexane : MeOH = 2 : 1 : 0.1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.02$ (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, C$_6$H$_4$-H), 8.28-8.30 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 4H, C$_6$H$_4$-H), 9.13-9.14 (d, $^3J_{\text{H-H}} = 9.1$ Hz, 4H, $H_\beta$), 9.47-9.48 (m, 4H, $H_\beta$), 9.86 (m, 8H, $H_\beta$), 10.19 (s, 2H, $H_\text{meso}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 14.1$, 22.5, 29.5, 123.8, 128.5, 130.8, 130.9, 134.4 ppm; UV/vis: $\lambda_{\text{max}}$ (log $\varepsilon$) = 420 (5.63), 456 (4.75), 552 (4.40), 592 (3.86), 668 (4.00) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{76}$H$_{70}$N$_8$Zn$_2$](M$^+$) 1222.4306, found 1222.4417.
Bis[5,5’][5,15-bis(3,5-di-tert-buty]phenyl)-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; Rf = 0.38 (CH2Cl2 : n-hexane : TEA = 1 : 1 : 0.05, v/v); 1H NMR (600 MHz, CDC13, TMS): δ = -2.00 (s, 4H, NH), 1.59 (s, 72H, t-butyl-NH), 7.73-7.81 (m, 6H, Ph-H), 7.85-7.87 (m, 6H, Ph-H), 8.13-8.16 (m, 8H, Ph-H), 8.21-8.24 (m, 4H, Ph-H), 8.79 (d, 3JH-H = 4.7 Hz, 4H, Hβ), 8.84 (d, 3JH-H = 4.7 Hz, 4H, Hβ), 9.07 (d, 3JH-H = 4.7 Hz, 4H, Hβ), 9.96 (d, 3JH-H = 4.7 Hz, 4H, Hβ) ppm; 13C NMR (150 MHz, CDC13): 5 = 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): λmax (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 AsPh₃ (2.1 equiv.) and Pd₂(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 CH₂Cl₂ : 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; Rₖ = 0.17 (CH₂Cl₂ : n-hexane = 10 : 1, v/v); ¹H NMR (400 MHz, CDCl₃/CF₃COOD 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_H-H = 4.7, 2.0 Hz, 8H, H₉), 9.17-9.18 (d, 3J_H-H = 4.8 Hz, 4H, H₉), 9.54-9.55 (d, 3J_H-H = 4.7 Hz, 4H, H₉), 10.11-10.12 (d, 3J_H-H = 4.7 Hz, 4H, H₉), 10.20-10.22 (d, 3J_H-H = 4.7 Hz, 4H, H₉), 10.89 (s, 2H, Hmeso) ppm; ¹³C NMR (150 MHz, CDCl₃/CF₃COOD 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: λmax (log ε) = 410 (4.96), 479 (4.96), 634 (4.57), 673 (4.53), 787 (4.45) nm; HRMS (MALDI) m/z calcd. for [C₁₀₀H₆₃N₁₂]⁺(M+H)⁺: 1431.5236, found 1431.5240.
5,15-Bis\{4-(10',20'-diphenylporphyrin-5-yl)phenylethylene\}-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; \( R_f = 0.20 \) (CH\(_2\)Cl\(_2\) : n-hexane : MeOH = 2 : 1 : 0.1, v/v); \(^1\)H NMR (600 MHz, CDCl\(_3\)/CF\(_3\)COOD, 10:1, TMS): \( \delta = 8.10 \) (m, 18H, Ph-H), 8.60 (m, 12H, Ph-H), 8.79-8.80 (d, \(^3\)J\(_{1H-1H} = 7.6 \) Hz, 4H, C\(_6\)H\(_4\)-H), 8.83-8.85 (d, \(^3\)J\(_{1H-1H} = 7.6 \) Hz, 4H, C\(_6\)H\(_4\)-H), 8.88-8.90 (d, \(^3\)J\(_{1H-1H} = 4.7 \) Hz, 4H, H\(_\beta\)), 8.93-8.95 (m, 8H, H\(_\beta\)), 9.10-9.11 (d, \(^3\)J\(_{1H-1H} = 4.7 \) Hz, 4H, H\(_\beta\)), 9.50-9.51 (d, \(^3\)J\(_{1H-1H} = 4.5 \) Hz, 4H, H\(_\beta\)), 9.71-9.72 (d, \(^3\)J\(_{1H-1H} = 4.5 \) Hz, 4H, H\(_\beta\)), 10.75 (s, 2H, H\(_\text{meso}\)) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)/CF\(_3\)COOD 10:1): \( \delta = 128.2, 128.5, 128.6, 129.2, 130.2, 130.3, 130.4, 130.6, 130.8, 132.3, 138.1, 138.3, 138.9 \) ppm; UV/vis: \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 412 (5.10), 446 (5.02), 470 (4.70), 602 (4.60), 634 (4.56), 710 (4.51) nm; HRMS (MALDI) \( m/z \) calc. for \([\text{C}_{112}\text{H}_{70}\text{N}_{12}]^{(M^+)}\) 1582.5846, found 1582.5859.

\{5,15-Bis\{4-(10',20'-diphenylporphyrinato-5-yl)zinc(II)\}phenylethylene\}-10,20-diphenylporphyrinato-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; $R_f = 0.27$ (CH$_2$Cl$_2$ : $n$-hexane : TEA = 1 : 1, 0.05 v/v); $^1$H NMR (400 MHz, CDCl$_3$/pyridine-d$_5$ 10:1, TMS): $\delta$ = 7.78 (m, 18H, Ph-$\Pi$), 8.28 (d, $^3$J$_{H-H} = 7.3$ Hz, 12H, Ph-$\Pi$), 8.41 (m, 8H, C$_6$H$_4$-$H$), 8.98 (m, 8H, $H_{\beta}$), 9.07 (m, 8H, $H_{\beta}$), 9.36-9.37 (d, $^3$J$_{H-H} = 8.1$ Hz, 4H, $H_{\beta}$), 9.94-9.95 (d, $^3$J$_{H-H} = 4.6$ Hz, 4H, $H_{\beta}$), 10.19 (s, 2H, $H_{meso}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$/pyridine-d$_5$ 10:1): $\delta$ = 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, 143.6, 143.3, 149.3, 149.6 ppm; UV/vis: $\lambda_{max}$ (log $\varepsilon$) = 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 [C$_{22}$H$_{65}$N$_2$][M+H]$^+$ 1769.3372, found 1769.3369.

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

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 [C$_{112}$H$_{64}$N$_{12}$Ni$_{3}$(M$^+$)]$^{1750.3437}$, found 1750.3448.
\(\{5,15\text{-}\text{Bis}\{4\text{-}[(10',20'\text{-'diphenylporphyrinato})\text{zinc(II)}]\text{ph}\text{enylethynyl}]\text{-}10,20\text{-}\text{bis}(3,5\text{-}\text{di-\text{tert}-butylphenyl})\text{porphyrin}\ (188)\):

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\(_2\)Cl\(_2\) : n-hexane = 2 : 1, v/v); \(\text{\(^1\)H NMR}\) (400 MHz, CDCl\(_3\)/pyridine-d\(_5\) 10:1, TMS): \(\delta = -1.73\) (s, 2H, NH), 1.56 (s, 36H, \(t\)-butyl-H) 7.73 (m, 12H, Ph-H), 7.84 (m, 4H, C\(_6\)H\(_4\)-H), 8.12-8.13 (m, 4H, C\(_6\)H\(_4\)-H), 8.23 (m, 8H, Ar/Ph-H), 8.38 (m, 6H, Ar/Ph-H), 8.97 (m, 8H, \(H_\beta\)), 9.01-9.02 (d, \(J_{\text{H-H}} = 4.6\) Hz, 4H, \(H_\beta\)), 9.04-9.05 (d, \(J_{\text{H-H}} = 4.6\) Hz, 4H, \(H_\beta\)), 9.31-9.32 (d, \(J_{\text{H-H}} = 4.6\) Hz, 4H, \(H_\beta\)), 9.90-9.91 (d, \(J_{\text{H-H}} = 4.6\) Hz, 4H, \(H_\beta\)), 10.14 (s, 2H, \(H_{\text{meso}}\)) ppm; \(\text{\(^{13}\)C NMR}\) (150 MHz, CDCl\(_3\)/pyridine-d\(_5\), 10:1): \(\delta = 13.9, 22.4, 31.4, 34.9, 120.0, 126.2, 127.0, 129.4, 129.8, 131.2, 131.4, 131.6, 132.1, 134.5, 134.9, 143.2\) ppm; UV/vis: \(\lambda_{\text{max}} (\log \varepsilon) = 418\) (4.55), 447 (4.39), 551 (3.32), 610 (3.57), 698 (3.35) nm; HRMS (MALDI) \(m/z\) calcd. for [C\(_{128}\)H\(_{99}\)N\(_{12}\)Zn\(_3\)](M+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$_2$Cl$_2$ : n-hexane = 2 : 1, v/v); $^1$H NMR (600 MHz, THF-d$_8$, TMS): $\delta = 1.02$ (t, $^3J_{H-H} = 14.6$ 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, $^3J_{H-H} = 7.6$ Hz, 4H, C$_6$H$_4$-H), 8.54-8.55 (d, $^3J_{H-H} = 7.6$ Hz, 4H, C$_6$H$_4$-H), 9.12-9.14 (d, $^3J_{H-H} = 9.2$ Hz, 4H, $H_p$), 9.44 (m, 4H, $H_p$), 9.88-9.90 (m, 12H, $H_p$), 10.10 (m, 4H, $H_p$), 10.13 (s, 2H, $H_p$) ppm; $^{13}$C NMR (150 MHz, THF-d$_8$): $\delta = 13.3$, 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: $\lambda_{max}$ (log $\varepsilon$) = 418 (5.41), 454 (5.32), 554 (4.22), 668 (4.59) nm; HRMS (MALDI) m/z calcd. for [C$_{128}$H$_{98}$N$_{12}$Zn$_3$](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; Rf = 0.35 (CH₂Cl₂ : n-hexane = 2 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.98 (t, 12H, ³J_{H-H} = 14.6 Hz, CH₃), 2.89 (m, 4H, CH₂), 3.07 (m, 4H, CH₂), 5.16 (m, 2H, CH), 7.67 (s, 4H, C₆H₄-H), 7.80 (m, 12H, Ph-H), 8.29 (m, 8H, Ph-H), 8.43-8.44 (d, ³J_{H-H} = 3.5 Hz, 4H, C₆H₄-H), 9.03-9.04 (d, ³J_{H-H} = 4.6 Hz, 4H, H₈), 9.07-9.08 (d, ³J_{H-H} = 4.5 Hz, 4H, H₈), 9.11-9.13 (d, ³J_{H-H} = 4.6 Hz, 4H, H₈), 9.38-9.39 (d, ³J_{H-H} = 4.5 Hz, 4H, H₈), 9.79 (m, 4H, H₈), 10.00 (m, 4H, H₈), 10.20 (s, 2H, H₈ meso) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 ε) = 422 (5.63), 457 (5.20), 554 (4.14), 673 (4.20) nm; HRMS (MALDI) m/z calcd. for [C₁₁₀H₇₀N₁₂Zn₁₂]⁺ (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\(_2\)Cl\(_2\) : n-hexane = 1 : 1, v/v); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \( \delta = 1.02 \) (t, \( \text{J}_{	ext{H-H}} = 14.5 \) 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\(_6\)H\(_4\)-H), 7.72 (s, 1H, C\(_6\)H\(_4\)-H), 8.04-8.06 (d, \( \text{J}_{	ext{H-H}} = 8.1 \) Hz, 1H, C\(_6\)H\(_4\)-H), 8.28-8.30 (d, \( \text{J}_{	ext{H-H}} = 8.1 \) Hz, 1H, C\(_6\)H\(_4\)-H), 9.18-9.20 (m, 2H, H\(_\beta\)), 9.47-9.48 (m, 2H, H\(_\beta\)), 9.69-9.93 (m, 10H, H\(_\beta\)), 10.07 (m, 2H, H\(_\beta\)), 10.18 (s, 1H, H\(_\text{meso} \)) 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, 129.6, 130.7, 131.3, 131.6, 132.8, 134.3, 134.6, 143.7, 149.4, 152.3 ppm; UV/vis: \( \lambda_{\text{max}} \) (log \( \epsilon \)) = 418 (5.19), 444 (5.21), 554 (4.03), 640 (4.29) nm; HRMS (MALDI) \( m/z \) calcd. for [C\(_{68}\)H\(_{63}\)N\(_8\)Zn\(_2\)Br](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\(_2\)Cl\(_2\) : n-hexane = 1 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \( \delta = 0.97 \) (t, \( \text{J}_{	ext{H-H}} = 14.8 \) 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\(_\beta\)), 8.32 (m, 4H, Ph-H\(_\alpha\)), 8.45 (m, 4H, C\(_6\)H\(_4\)-H), 9.02-9.04 (d, \( \text{J}_{	ext{H-H}} = 4.6 \) Hz, 2H, H\(_\beta\)), 9.07-9.08 (d, \( \text{J}_{	ext{H-H}} = 4.4 \) Hz, 2H, H\(_\beta\)), 9.11-9.12 (d, \( \text{J}_{	ext{H-H}} = 4.6 \) Hz, 2H, H\(_\beta\)), 9.37-9.38 (d, \( \text{J}_{	ext{H-H}} = 4.4 \) Hz, 2H, H\(_\beta\)), 9.71 (m, 6H, H\(_\beta\)), 9.99 (s, 2H, H\(_\beta\)), 10.20 (s, 1H, H\(_\text{meso} \)) 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, 133.2, 134.8, 139.6, 143.7, 152.3 ppm; UV/vis: \( \lambda_{\text{max}} \) (log \( \epsilon \)) = 418 (5.19), 444 (5.21), 554 (4.03), 640 (4.29) nm; HRMS (MALDI) \( m/z \) calcd. for [C\(_{68}\)H\(_{63}\)N\(_8\)Zn\(_2\)Br](M\(^+\)): 1200.3098, found 1200.3135.
131.7, 132.3, 134.5, 134.8, 143.1, 149.1, 149.4, 149.7, 149.9, 150.1 ppm; UV/vis: $\lambda_{\text{max}}$ (log $\varepsilon$) = 420 (5.49), 444 (5.46), 552 (4.33), 640 (4.54) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{70}$H$_{53}$N$_8$Zn$_2$Br](M)$^+$: 1212.2159, found 1212.2184.

### 7.4 Fused arrays

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

Porphyrs 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-$t$-butylphenyl)porphyrin-15-yl} (196):**

![Chemical structure of Bis{(5-phenyl-10,20-bis(3,5-di-$t$-butylphenyl)porphyrin-15-yl} (196)](image)

Synthesised from 5,15-di(3,5-di-$t$-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$_2$Cl$_2$ as eluent. Solvents were removed and residue recrystallised from CH$_2$Cl$_2$/MeOH to yield 196 a dark solid (48 mg, 0.040 mmol, 79%). M.p. >300 °C; $R_f = 0.39$ (CH$_2$Cl$_2$ : n-hexane = 3 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = -2.13$ (s, 4H, N/$t$-$t$), 1.46 (s, 72H, $t$-butyl-$t$); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = -2.13$ (s, 4H, NH), 1.46 (s, 72H, $t$-butyl-$t$), 7.72 (s, 4H, C$_6$H$_3$-$H$), 7.83 (m, 6H, Ph-$H$) 8.09 (m, 12 H, C$_6$H$_3$-$H/H_β$), 8.32-8.34 (d, $^{3}J_{H-H} = 6.4$ Hz, 4H, Ph-$H$), 8.74 (d, $^{3}J_{H-H} = 4.5$ Hz, 4H, $H_β$), 8.94 (s, 8H, $H_β$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 31.5$, 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): \( \lambda_{\text{max}} \) (log \( e \)) = 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):**

![Bis{5-bromo-10,20-bis(3-methoxyphenyl)porphyrin-15-ylato}zinc(II)}](image)

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); \(^1\)H NMR (400 MHz, CDCl₃, TMS): \( \delta = 3.89 \) (s, 12H, OCH₃), 7.22-7.24 (d, \(^3\)J\( _{H-H} \) = 8.6 Hz, 4H, C₆H₄-H), 7.55-7.56 (t, \(^3\)J\( _{H-H} \) = 15.9 Hz, 4H, C₆H₄-H), 7.73 (m, 4H, C₆H₄-H), 7.79-7.80 (d, \(^3\)J\( _{H-H} \) = 7.8 Hz, 4H, C₆H₄-H), 8.07-8.08 (d, \(^3\)J\( _{H-H} \) = 4.7 Hz, 4H, \( H_β \)), 8.66-8.67 (d, \(^3\)J\( _{H-H} \) = 4.7 Hz, 4H, \( H_β \)), 9.09-9.10 (d, \(^3\)J\( _{H-H} \) = 4.7 Hz, 4H, \( H_β \)), 9.86-9.87 (d, \(^3\)J\( _{H-H} \) = 4.7 Hz, 4H, \( H_β \)) ppm; \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta = 55.4, 105.4, 113.5, 120.3, 122.3, 127.4, 127.5, 132.3, 133.2, 134.2, 143.5, 149.7, 150.0, 151.0, 155.2, 157.8 \) ppm; UV/vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( e \)) = 421 (5.26), 455 (5.16), 562 (4.52) nm; HRMS (MALDI) \( m/z \) calcd. for [C₆₈H₄₉Br₂N₈O₄Zn₂](M⁺): 1322.0435, found 1322.0432.
Produced from 133 (50 mg, 0.066 mmol), 103 (40 mg, 0.066 mmol), Cs₂CO₃ (45 mg, 0.139 mmol) and Pd(PPh₃)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; Rₓ = 0.53 (CH₂Cl₂ : n-hexane = 3 : 2, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 0.88-0.93 (t, ³Jₓ-Hₓ = 14.6 Hz, 9H, CH₃), 1.38 (m, 6H, CH₂), 1.59 (m, 6H, CH₂), 1.85 (m, 6H, CH₂), 2.57 (m, 6H, CH₂), 4.81-4.85 (t, ³Jₓ-Hₓ = 16.4 Hz, 2H, CH₂), 4.88-4.92 (t, ³Jₓ-Hₓ = 15.7 Hz, 4H, CH₂), 7.72 (m, 6H, Ph-H), 8.08-8.09 (d, ³Jₓ-Hₓ = 4.7 Hz, 2H, H₉), 8.21-8.23 (d, ³Jₓ-Hₓ = 4.7 Hz, 2H, H₉), 8.30 (m, 4H, Ph-H), 8.75-8.76 (d, ³Jₓ-Hₓ = 4.7 Hz, 2H, H₉), 9.17-9.18 (d, ³Jₓ-Hₓ = 4.7 Hz, 2H, H₉), 9.21-9.23 (d, ³Jₓ-Hₓ = 4.7 Hz, 2H, H₉), 9.43-9.44 (d, ³Jₓ-Hₓ = 4.7 Hz, 2H, H₉), 9.51 (m, 4H, H₉), 10.38 (s, 1H, Hₚₓ) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λ_max (log ε) = 413 (5.33), 450 (5.10), 559 (4.37) nm; HRMS (MALDI) m/z calcd. for [C₇₀H₆₆N₈Zn₂]⁺: 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$_2$CO$_3$ (90 mg, 0.275 mmol) and Pd(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$_2$Cl$_2$ : 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$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$/pyridine-d$_5$ 10:1): $\delta$ = 2.64 (s, 6H, tolyl-CH$_3$), 7.47-7.49 (d, $^3$J$_{H-H}$ = 8.0 Hz, 4H, C$_6$H$_4$-H), 7.64 (m, 9H, Ph-H), 7.80-7.81 (d, $^3$J$_{H-H}$ = 4.7 Hz, 2H, $H_b$), 7.86-7.87 (d, $^3$J$_{H-H}$ = 4.6 Hz, 2H, $H_b$), 8.12-8.14 (d, $^3$J$_{H-H}$ = 8.0 Hz, 4H, C$_6$H$_4$-H), 8.21 (m, 6H, Ph-H), 8.49-8.51 (d, $^3$J$_{H-H}$ = 4.7 Hz, 2H, $H_b$), 8.60-8.61 (d, $^3$J$_{H-H}$ = 4.6 Hz, 2H, $H_b$), 8.92-8.93 (d, $^3$J$_{H-H}$ = 4.6 Hz, 2H, $H_b$), 8.95-8.96 (d, $^3$J$_{H-H}$ = 4.6 Hz, 2H, $H_b$), 9.10-9.11 (d, $^3$J$_{H-H}$ = 4.4 Hz, 2H, $H_b$), 9.41-9.42 (d, $^3$J$_{H-H}$ = 4.5 Hz, 2H, $H_b$), 10.24 (s, 1H, $H_{meso}$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$/pyridine-d$_5$ 10:1): $\delta$ = 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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 413 (5.16), 449 (5.18), 555 (4.53) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{72}$H$_{46}$N$_8$Zn$_2$](M$^+$): 1150.2428, found 1150.2389.
Produced from bromoporphyrin 110 (73 mg, 0.110 mmol), borylated porphyrin 129 (80 mg, 0.110 mmol), Cs₂CO₃ (90 mg, 0.275 mmol) and Pd(PPh₃)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 °C; *R*ₖ = 0.46 (CH₂Cl₂ : *n*-hexane = 2 : 1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 3.91 (d, ⁴J_H-H = 1.8 Hz, 6H, OCH₃), 7.23-7.26 (dd, ³J_H-H = 8.2, 2.4 Hz, 2H, C₆H₄-H), 7.58-7.62 (t, ³J_H-H = 4.9 Hz, 2H, C₆H₄-H), 7.83 (m, 11H, Ph/ C₆H₄-H), 8.12-8.15 (q, ³J_H-H = 12.1 Hz, 2H, H₁), 8.18-8.19 (d, ³J_H-H = 4.7 Hz, 2H, H₀), 8.25 (m, 6H, Ph-H), 8.35 (m, 2H, C₆H₄-H), 8.78-8.80 (d, ³J_H-H = 4.7 Hz, 2H, H₁), 9.03-9.04 (d, ³J_H-H = 4.7 Hz, 2H, H₀), 9.06-9.07 (d, ³J_H-H = 4.7 Hz, 2H, H₁), 9.21-9.22 (d, ³J_H-H = 4.6 Hz, 2H, H₀), 9.50-9.51 (d, ³J_H-H = 4.7 Hz, 2H, H₁). ¹³C NMR (100 MHz, CDCl₃): δ = 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 (CH₂Cl₂): λₘₐₓ (log ε) = 417 (5.57), 450 (4.87), 549 (4.41) nm; HRMS (MALDI) m/z calcd. for [C₇₂H₄₆N₈O₂Zn₂](M⁺): 1182.2327, found 1182.2358.
Produced from bromoporphyrin 110 (71 mg, 0.097 mmol), borylated porphyrin 131 (80 mg, 0.102 mmol), Cs$_2$CO$_3$ (70 mg, 0.214 mmol) and Pd(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$_2$Cl$_2$: 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$_2$Cl$_2$: n-hexane = 3:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.92$ (s, 8H, OCH$_3$), 3.95 (s, 4H, OCH$_3$) 7.23 (m, 2H, C$_6$H$_4$-H), 7.25 (m, 2H, C$_6$H$_4$-H), 7.58 (m, 4H, C$_6$H$_4$-H), 7.84 (m, 11H, Ph/C$_6$H$_4$-H), 8.12 (m, 4H, H$_b$), 8.33 (m, 2H, Ph-H), 8.72 (m, 2H, H$_b$), 8.78 (m, 2H, H$_b$), 9.06 (m, 4H, H$_b$), 9.22-9.23 (d, $^3$J$_{H-H} = 4.5$ Hz, 2H, H$_b$), 9.52-9.53 (d, $^3$J$_{H-H} = 4.6$ Hz, 2H, H$_b$), 10.42 (s, 1H, $H_{meso}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 55.5$, 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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 420 (5.32), 455 (5.14), 558 (4.36) nm; HRMS (MALDI) m/z calced. for [C$_{74}$H$_{50}$N$_8$O$_4$Zn$_2$](M$^+$): 1242.2538, found 1242.2524.
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{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), Cs₂CO₃ (78 mg, 0.239 mmol) and Pd(PPh₃)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 CH₂Cl₂ as eluent. Solvents were removed in vacuo and the residue was subjected to column chromatography (silica, CH₂Cl₂ : 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; Rᵣ = 0.45 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = 0.89-0.93 (t, ³Jₐ-H = 14.7 Hz, 12H, C₃H₃), 2.66 (s, 6H, tolyl-CH₃), 2.80 (m, 8H, CH₂), 3.03 (m, 1H, CH), 5.14 (m, 1H, CH), 7.51-7.53 (d, ³Jₐ-H = 7.9 Hz, 4H, C₆H₄-H), 7.84 (m, 3H, Ph-H), 8.10 (m, 2H, H₆), 8.17-8.18 (d, ³Jₐ-H = 7.7 Hz, 6H, Ph/C₆H₄-H), 8.31-8.33 (d, ³Jₐ-H = 7.3 Hz, 2H, H₆), 8.77-8.78 (d, ³Jₐ-H = 8.2 Hz, 2H, H₆), 9.03-9.05 (d, ³Jₐ-H = 8.2 Hz, 2H, H₆), 9.22-9.23 (d, ³Jₐ-H = 4.6 Hz, 2H, H₆), 9.39-9.43 (d, ³Jₐ-H = 17.0 Hz, 2H, H₆), 9.52-9.54 (d, ³Jₐ-H = 4.5 Hz, 2H, H₆), 9.76-9.79 (d, ³Jₐ-H = 15.1 Hz, 2H, H₆), 10.60 (s, 1H, Hₐmeso) ppm; ¹³C NMR (100 MHz, CDCl₃): 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, 132.5, 134.0, 134.4, 137.1, 139.7, 143.5, 139.8, 150.0, 150.8, 154.6 ppm; UV/vis (CH₂Cl₂): λₘₐₓ (log ε) = 416 (5.42), 454 (5.37), 560 (4.64) nm; HRMS (MALDI) m/z calced. for [C₇₀H₈₈N₆Zn₂]⁺: 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$_2$CO$_3$ (107 mg, 0.330 mmol) and Pd(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 °C; $R_f = 0.54$ (CH$_2$Cl$_2$ : n-hexane = 2 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.65$ (s, 6H, tolyl-CH$_3$), 3.88 (s, 6H, OCH$_3$), 7.21-7.23 (dd, $^3$J$_{H-H} = 8.6$, 2.1 Hz, 2H, C$_6$H$_4$-H), 7.51-7.53 (d, $^3$J$_{H-H} = 7.6$ Hz, 4H, C$_6$H$_4$(toly1)-H), 7.54-7.56 (t, $^3$J$_{H-H} = 16.0$ Hz, 2H, C$_6$H$_4$-H), 7.78 (m, 7H, Ph/C$_6$H$_4$-H), 8.11-8.12 (d, $^3$J$_{H-H} = 4.7$ Hz, 2H, H$_\beta$) 8.14-8.16 (d, $^3$J$_{H-H} = 7.6$ Hz, 6H, C$_6$H$_4$(toly1)/H$_\beta$), 8.32-8.34 (d, $^3$J$_{H-H} = 6.6$ Hz, 2H, Ph-H), 8.71-8.72 (d, $^3$J$_{H-H} = 4.4$ Hz, 2H, H$_\beta$), 8.77-8.78 (d, $^3$J$_{H-H} = 4.4$ Hz, 2H, H$_\beta$), 9.05 (m, 4H, H$_\beta$), 9.19-9.20 (d, $^3$J$_{H-H} = 4.4$ Hz, 2H, H$_\beta$), 9.48-9.50 (d, $^3$J$_{H-H} = 4.3$ Hz, 2H, H$_\beta$), 10.37 (s, 1H, H$_{meso}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$/pyridine-d$_3$): $\delta = 21.5$, 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, 149.8, 149.8, 149.9, 150.2, 150.6, 150.7, 154.7, 155.0, 157.8 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 415 (5.54), 454 (5.32), 550 (4.68) nm; HRMS (MALDI) m/z calcd. for [C$_{74}$H$_{50}$N$_8$O$_2$Zn$_2$]$(M^+)$: 1210.2640, found 1210.2672.
{5-(10',20'-Bis(3-methoxyphenyl)porphyrin-15□-phenyl-5'-ylato)-10,15,20-
triphenyl)porphyrinato}zinc(II) (209)

Produced from bromoporphyrin 111 (102 mg, 0.137 mmol), borylated porphyrin 129
(100 mg, 0.137 mmol), Cs$_2$CO$_3$ (98 mg, 0.301 mmol) and Pd(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$_2$Cl$_2$ : 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$_2$Cl$_2$ : n-hexane = 3 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.89 (d,
$^3$J$_{H-H}$ = 1.8 Hz, 6H, OCH$_3$), 7.23-7.25 (dd, $^3$J$_{H-H}$ = 11.2 Hz, 2H, C$_6$H$_4$-H), 7.52-7.56 (t,
$^3$J$_{H-H}$ = 15.2 Hz, 2H, C$_6$H$_4$-H), 7.70-7.85 (m, 16H, Ph/C$_6$H$_4$-H), 8.22-8.23 (d, $^3$J$_{H-H}$ = 4.8
Hz, 2H, $H_\beta$) 8.28-8.29 (d, $^3$J$_{H-H}$ = 4.7 Hz, 2H, $H_\beta$), 8.25 (m, 6H, Ph-H), 8.35 (m, 2H,
$\alpha$-H), 7.70-7.85 (m, 16H, $\alpha$-H), 8.22-8.23 (d, $^3$J$_{H-H}$ = 4.8 Hz, 2H, $H_\beta$), 9.02-9.03 (d, $^3$J$_{H-H}$ = 4.7 Hz, 2H, $H_\beta$),
9.08-9.10 (d, $^3$J$_{H-H}$ = 4.8 Hz, 2H, $H_\beta$), 9.21-9.22 (d, $^3$J$_{H-H}$ = 4.6 Hz, 2H, $H_\beta$), 9.50-9.51
(d, $^3$J$_{H-H}$ = 4.7 Hz, 2H, $H_\beta$), 9.75-9.77 (d, $^3$J$_{H-H}$ = 4.8 Hz, 2H, $H_\beta$) ppm; $^{13}$C NMR (100
MHz, CDCl$_3$): $\delta$ = 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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 420 (5.20), 455
(5.02), 559 (4.41) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{78}$H$_{50}$N$_8$O$_2$Zn$_2$](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$_2$Cl$_2$: 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 °C; $R_f$ = 0.45 (CH$_2$Cl$_2$: n-hexane = 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$/pyridine-D$_5$, 20:1): $\delta$ = 2.58 (s, 12H, tolyl-CH$_3$), 7.42-7.44 (d, $^3J_{H-H}$ = 7.8 Hz, 8H, C$_6$H$_4$-H), 7.79-7.80 (d, $^3J_{H-H}$ = 4.6 Hz, 4H, $H_{\beta}$), 8.07-8.09 (d, $^3J_{H-H}$ = 7.8 Hz, 8H, C$_6$H$_4$-H), 8.54-8.55 (d, $^3J_{H-H}$ = 4.6 Hz, 4H, $H_{\beta}$), 9.06-9.07 (d, $^3J_{H-H}$ = 4.4 Hz, 4H, $H_{\beta}$), 9.36-9.37 (d, $^3J_{H-H}$ = 4.3 Hz, 4H, $H_{\beta}$), 10.2 (s, 2H, $H_{meso}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$/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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 415 (5.29), 446 (5.32), 552 (4.69) nm; HRMS (MALDI) m/z calcd. for [C$_6$H$_4$N$_8$Zn$_2$](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)ethyl-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 Pd2dba3 (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; Rf = 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-), 8.19 (m, 4H, Hβ) 8.25-8.27 (d, 3JH-H = 6.4 Hz, 8H, C6H4-H), 8.32 (m, 8H, Ph-H), 8.73 (m, 4H, Hδ), 8.95-8.96 (d, 3JH-H = 6.5 Hz, 8H, Hδ), 9.24-9.25 (d, 3JH-H = 4.1 Hz, 4H, Hβ), 9.28 (m, 4H, Hβ), 10.55-10.56 (d, 3JH-H = 4.3 Hz, 8H, Hδ) 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): λmax (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 undesired 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; Rᵣ = 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, ³J_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, ³J_H-H = 4.6 Hz,
2H, H₈), 9.04-9.05 (d, ³J_H-H = 4.4 Hz, 2H, H₈), 9.11-9.12 (d, ³J_H-H = 4.5 Hz, 2H, H₈),
9.20-9.22 (d, ³J_H-H = 4.5 Hz, 2H, H₈), 9.30-9.31 (d, ³J_H-H = 4.4 Hz, 2H, H₈), 9.96-9.97
(d, ³J_H-H = 4.6 Hz, 2H, H₈), 10.11 (s, 1H, H₉meso), 10.46-10.47 (d, ³J_H-H = 4.6 Hz, 2H,
H₈), 10.49-10.50 (d, ³J_H-H = 4.6 Hz, 2H, H₈) 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, 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):
$\lambda_{\text{max}}$ (log ε) = 452 (5.06), 481 (5.22), 568 (4.08), 696 (4.64) nm; HRMS (MALDI) m/z calcd. for [C_{74}H_{46}N_{8}O_{2}Zn_{2}]^{2+}(M^\text{+}): 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 CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$. 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. NaBH$_4$ (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)\textsuperscript{[174]}**

![Bis{5,10,15-triphenylporphyrin-13,15,17-triylato}zinc(II)} (214)
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 alox 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, Hₘ), 7.53 (m, 30H, Ph-H), 7.74 (m, 12H, Hₘ) 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): λₘₐₓ (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]⁺: 1194.2115, found 1194.2141. Spectroscopica 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 alox 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, Hₘ), 7.44-7.45 (d, 3J_H-H = 4.6 Hz, Hₘ), 7.54 (m, 18H, Ph-H/ Hₘ), 7.71-7.72 (d, 3J_H-H
Chapter 7: Experimental

= 6.0 Hz, 8H, Ph-H), 7.89-7.92 (d, \( J_{H-H} = 8.6 \text{ Hz}, 4H, C_6H_4-H \)), 8.39-8.41 (d, \( J_{H-H} = 8.6 \text{ Hz}, 4H, C_6H_4-H \)) ppm; UV/vis (THF): \( \lambda_{max} (\log \varepsilon) = 421 (5.07), 460 (4.76), 563 (5.18), 963 (4.31), 1105 (4.58) \) nm; HRMS (MALDI) \( m/z \) calcd. for [C_{76}H_{40}N_{10}O_{4}Zn_{2}](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): \( \delta = 1.48 (s, 72H, t\)-butyl-H), 7.37 (s, 4H, \( H_\beta \)), 7.60-7.62 (d, \( J_{H-H} = 4.5 \text{ Hz}, 4H, H_\beta \)), 7.67 (m, 12H, Ar-H), 7.75-7.76 (d, \( J_{H-H} = 4.6 \text{ Hz}, 4H, H_\beta \)), 8.00-8.02 (d, \( J_{H-H} = 8.2 \text{ Hz}, 4H, C_6H_4-H \)), 8.11-8.13 (d, \( J_{H-H} = 8.2 \text{ Hz}, 4H, C_6H_4-H \)) ppm; \(^13C\) NMR (150 MHz, CDCl₃): \( \delta = 31.5, 106.2, 107.5, 120.9, 122.2, 124.2, 127.7, 128.1, 130.1, 131.9, 133.4, 135.9, 139.5, 147.3, 147.8, 151.6, 153.5, 153.9, 154.1 \) ppm; UV/vis (THF): \( \lambda_{max} (\log \varepsilon) = 423 (5.12), 566 (5.17), 886 (4.00), 967 (4.33), 1110 (4.63) \) nm; HRMS (MALDI) \( m/z \) calcd. for [C_{108}H_{104}N_{10}O_{4}Zn_{2}](M^+): 1732.6825, found 1732.6816.
Bis\{(5-butyl-10,20-bis(4-methoxyphenyl)porphyrin-13,15,17-triylato)zinc(II)\} (217):

\[
\begin{align*}
\text{Synthesised from } & 120 \text{ (20 mg, 0.031 mmol), DDQ (35 mg, 0.156 mmol), Sc(OTf)\textsubscript{3} (77 mg, 0.156 mmol) in dry toluene (20 mL), heated at 50 °C for 3 h, according to general procedure K. THF (6 mL) was added and reaction stirred for a further 1 h at room tempertaure. The reaction mixture was filtered through a short plug of alox using CH\textsubscript{2}Cl\textsubscript{2} as eluent to give side product 226 and using CH\textsubscript{2}Cl\textsubscript{2} : THF (1 : 1, v/v) as eluent to give fraction containg dimer 217. Solvents were removed \textit{in vacuo} and the residue was subjected to column chromatography using CH\textsubscript{2}Cl\textsubscript{2} as eluent to give two fractions, the first being side product 226, the second being desired dimer 217. Solvents were removed and 217 isolated as a dark solid (14 mg, 0.011 mmol, 70%). M.p. >300 °C; } ^1\text{H NMR (400 MHz, CDCl\textsubscript{3}/pyridine-D\textsubscript{5}, 10:1, TMS): } \delta = 0.82 \text{ (m, 6H, CH\textsubscript{3})}, 1.46 \text{ (m, 4H, CH\textsubscript{2})}, 1.95 \text{ (m, 4H, CH\textsubscript{2})}, 3.78 \text{ (s, 12H, OCH\textsubscript{3})}, 5.17 \text{ (m, 4H, CH\textsubscript{2})}, 6.99 \text{ (m, 6H, H\textsubscript{p}/C\textsubscript{6}H\textsubscript{4}-H)}, 7.14 \text{ (m, 8H, C\textsubscript{6}H\textsubscript{4}-H)}, 7.32 \text{ (m, 4H, C\textsubscript{6}H\textsubscript{4}-H)}, 7.53 \text{ (m, 8H, H\textsubscript{p})}, 8.15 \text{ (m, 2H, C\textsubscript{6}H\textsubscript{4}-H) ppm; UV/vis (THF): } \lambda_{\text{max}} (\log \varepsilon) = 422 \text{ (5.20), 459 (4.89), 559 (4.95), 949 (4.14), 1092 (4.41), 1094 (4.41) nm; HRMS (MALDI) } m/z \text{ calcd. for [C\textsubscript{76}H\textsubscript{58}N\textsubscript{8}O\textsubscript{4}Zn\textsubscript{2}](M\textsuperscript{+}): 1274.3164, found 1274.3123.}
\end{align*}
\]
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 CH$_2$Cl$_2$ as eluent giving one fraction which was discarded as no fusing product was detected via UV/vis/NIR analysis. Using CH$_2$Cl$_2$ : 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; $^1$H NMR (400 MHz, CDCl$_3$/pyridine-D$_5$, 10 : 1, TMS): $\delta = 3.88$ (s, 12H, OCH$_3$), 3.94 (s, 6H, OCH$_3$), 7.01 (s, 4H, $H_0$), 7.02 (d, $^3J_{H-H} = 8.3$ Hz, 6H, C$_6$H$_4$-$H$), 7.08-7.10 (dd, $^3J_{H-H} = 8.3$, 2.4 Hz, 4H, C$_6$H$_4$-$H$), 7.27-7.28 (m, 2H, C$_6$H$_4$-$H$), 7.29 (m, 2H, C$_6$H$_4$-$H$), 7.37-7.42 (t, $^3J_{H-H} = 15.6$ Hz, 6H, C$_6$H$_4$-$H$), 7.51-7.52 (d, $^3J_{H-H} = 4.6$ Hz, 4H, $H_0$), 7.55-7.57 (d, $^3J_{H-H} = 4.6$ Hz, 4H, $H_0$), 7.62-7.64 (d, $^3J_{H-H} = 8.3$ Hz, 4H, C$_6$H$_4$-$H$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$/pyridine-D$_5$, 10 : 1): $\delta = 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): $\lambda_{max}$ (log $\varepsilon$) = 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 [C$_{82}$H$_{54}$N$_8$O$_6$Zn$_2$]$^+$: 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, H₀), 7.50 (m, 20H, Ph-H), 7.66-7.67 (d, ³J_H-H = 8.0 Hz, 8H, H₇), 7.71 (m, 8H, H₈) 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): λₘₐₓ (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 [C₈₀H₄₀N₈Zn₂](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 alox 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; Rᵣ = 0.42 (CH₂Cl₂ : CH₃OH, 40:1, v/v); 'H NMR (600 MHz, CDCl₃, TMS): δ = 0.90 (t, 3Jₗ-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, 3Jₗ-H = 14.3 Hz, 4H, CH₂), 7.00 (s, 4H, Ar-H), 7.56 (m, 20H, Ar-H), 7.74 (m, 4H, Ar-H), 8.23 (m, 4H, Ar-H), 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):**

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

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 alox 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; \(^1\)H NMR (400 MHz, CDCl\(_3\)/pyridine-D\(_5\), 10 : 1, TMS): \(\delta = 0.96-0.99\) (t, \(^3\)J\(_{HH}\) = 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\(_{p}\)), 7.31-7.33 (d, \(^3\)J\(_{HH}\) = 7.2 Hz, 8H, C\(_6\)H\(_4\)-H), 7.59-7.60 (m, 4H, C\(_6\)H\(_4\)-H), 7.59-7.61 (m, 4H, H\(_{p}\)), 8.21-8.22 (d, \(^3\)J\(_{HH}\) = 4.3 Hz, 4H, H\(_{p}\)) ppm; \(^1\)C NMR (150 MHz, CDCl\(_3\)/pyridine-D\(_5\), 10 : 1): \(\delta = 14.0, 20.9, 22.7, 35.0, 40.7, 117.5, 122.3, 126.8, 127.5, 135.7, 139.9, 148.4, 154.9\) ppm; UV/vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) (log \(\varepsilon\)) = 406 (4.99), 460 (4.70), 555 (4.89), 976 (4.16), 1044 (4.22) nm; HRMS (MALDI) m/z calcd. for [C\(_{76}H_{58}N_{8}Zn\(_2\)](M\(^+\)): 1210.3367, found 1210.3375.

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

(225):

![Chemical structure](image)

Synthesised according to general procedure L from {5-bromo-10,20-(3-methoxyphenyl)porphyrinato}zinc(II) 110 (20 mg, 0.030 mmol) in CH\(_2\)Cl\(_2\) (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\(_2\)O (100 mL) and organic layer extracted using CH\(_2\)Cl\(_2\) : THF (1 : 1, v/v). The organic layer was then washed with NaHCO\(_3\) (2 \( \times \) 50 mL), H\(_2\)O (30 mL) and dried over Na\(_2\)SO\(_4\), 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 CH$_2$Cl$_2$/n-hexane to give a dark purple solid (3 mg, 0.002 mmol, 14%). M.p. >300 °C; $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 3.93 (s, 12H, OCH$_3$), 7.04 (s, 4H, H$_{5}$), 7.16 (m, 4H, C$_6$H$_4$$\cdot$H), 7.70 (m, 6H, C$_6$H$_4$$\cdot$H), 7.73 (m, 10H, C$_6$H$_4$$\cdot$H/H$_{6}$), 8.45 (m, 2H, H$_{6}$), 8.61 (m, 2H, H$_{6}$) ppm; UV/vis (CH$_2$Cl$_2$: THF, 1:1, v/v): $\lambda_{\text{max}}$ (log $\varepsilon$) = 425 (5.01), 459 (4.66), 566 (4.68), 871 (3.98), 1110 (4.17) nm; HRMS (MALDI) m/z calcd. for [C$_{68}$H$_{40}$Br$_2$N$_8$O$_4$Zn$_2$](M$^+$): 1318.0122, found 1318.0150.

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

Isolated as a side product from the synthesis of 217. The reaction mixture was filtered through a short plug of alox using CH$_2$Cl$_2$ 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 °C; $R_f$ = 0.53 (CH$_2$Cl$_2$: n-hexane = 2:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 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, $^3$J$_{H-H}$ = 15.9 Hz, 4H, CH$_2$), 7.24-7.27 (d, $^3$J$_{H-H}$ = 8.6 Hz, 4H, C$_6$H$_4$$\cdot$H), 7.56-7.60 (t, $^3$J$_{H-H}$ = 15.8 Hz, 4H, C$_6$H$_4$$\cdot$H), 7.82 (m, 8H, C$_6$H$_4$$\cdot$H), 8.08 (m, 4H, H$_{5}$), 8.67 (m, 4H, H$_{5}$), 9.12-9.13 (d, $^3$J$_{H-H}$ = 4.8 Hz, 4H, H$_{6}$), 9.71-9.72 (d, $^3$J$_{H-H}$ = 4.8 Hz, 4H, H$_{6}$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 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$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 424 (5.35), 457 (5.27), 568 (4.59) nm; HRMS (MALDI) m/z calcd. for [C$_{76}$H$_{62}$N$_8$O$_4$Zn$_2$](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$_2$Cl$_2$ 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 °C. $R_f = 0.55$ (n-hexane : CH$_2$Cl$_2$ = 1 : 2, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.98-1.01 (t, $^3J_{H1-H1}$ = 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, $^3J_{H1-H1}$ = 15.3 Hz, 4H, CH$_2$), 7.70 (s, 12H, Ph), 8.08-8.09 (d, $J = ^3J_{H1-H1}$ = 4.5 Hz, 4H, $H_\beta$), 8.25 (m, 8H, Ph), 8.62-8.63 (d, $^3J_{H1-H1}$ = 4.5 Hz, 4H, $H_\beta$), 9.07-9.08 (d, $^3J_{H1-H1}$ = 4.6 Hz, 4H, $H_\beta$), 9.69-9.70 (d, $^3J_{H1-H1}$ = 4.7 Hz, 4H, $H_\beta$) 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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 421 (5.48), 454 (5.41), 561 (4.88) nm; HRMS (MALDI) m/z calcd. for [C$_{76}$H$_{62}$N$_8$Zn$_2$]($^+$): 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$_2$Cl$_2$ as eluent. Solvents were removed to give a red-purple solid 228 (8 mg, 0.007 mmol, 27%) M.p. >300 °C; $R_f = 0.45$ (CH$_2$Cl$_2$ : n-hexane = 3 : 2, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta =$ 0.89-0.93 (t, $^3J_{H-H} = 16.2$ 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, $^3J_{H-H} = 15.6$ Hz, 4H, CH$_2$), 7.49-7.51 (d, $^3J_{H-H} = 7.8$ Hz, 8H, C$_6$H$_4$-H), 8.07-8.08 (d, $^3J_{H-H} = 4.9$ Hz, 4H, $H_{b}$), 8.11-8.13 (d, $^3J_{H-H} = 7.8$ Hz, 8H, C$_6$H$_4$-H), 8.65-8.66 (d, $^3J_{H-H} = 4.7$ Hz, 4H, $H_{b}$) 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, 122.0, 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$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 423 (5.54), 456 (5.45), 566 (4.80) nm; HRMS (MALDI) m/z calcd. for [C$_{76}$H$_{62}$N$_8$Zn$_2$$]^+$: 1214.3680, found 1214.3663.
{(5,10,15-Trihexyl-20-(10',20'-diphenylporphyrin-5'-yl)-13,17-triyato)zinc(II)} (229):

Synthesised from directly linked dimer 203 (20 mg, 0.019 mmol), DDQ (22 mg, 0.096 mmol), Sc(O Tf)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): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 416 (4.97), 578 (4.70), 672 (4.56), 987 (3.87), 1106 (4.09) nm; HRMS (MALDI) \( m/z \) calcd. for \([C_{70}H_{62}N_8Zn_2](M^+)\): 1142.3680, found 1142.3625.
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 alox using CH$_2$Cl$_2$, then CH$_2$Cl$_2$ : THF (1 : 1, v/v) as eluent. Solvents were removed in vacuo to give a dark residue which was redissolved in CH$_2$Cl$_2$ 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; $^1$H NMR (400 MHz, CDCl$_3$/pyridine-D$_5$, 20 : 1, TMS): $\delta$ = 3.93 (s, 6H, OCH$_3$), 7.03 (m, 4H, H$_6$), 7.13 (m, 4H, C$_6$H$_4$-H), 7.23 (m, 2H, C$_6$H$_4$-H), 7.43 (m, 2H, C$_6$H$_4$-H), 7.49-7.62 (m, 20H, Ph-H/Ph$_2$), 7.70-7.83 (m, 8H, Ph-H/Ph$_2$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$/pyridine-D$_5$, 20 : 1): $\delta$ = 55.4, 112.9, 126.5, 126.9, 127.3, 128.8, 130.6, 130.9, 157.8 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 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 [C$_{78}$H$_{46}$N$_8$O$_2$Zn$_2$](M$^+$): 1254.2327, found 1254.2286.

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, 3JH-H = 8.6 Hz, 8H, C6H4-H), 6.92 (s, 4H, Hp), 7.12-7.14 (d, 3JH-H = 8.6 Hz, 8H, Ph-H), 7.43 (m, 10H, Ph-H/Hp), 7.54-7.56 (t, 3JH-H = 14.6 Hz, 12H, C6H4-H), 7.65 (t, 3JH-H = 14.6 Hz, 8H, C6H4-H), 7.73-7.90 (m, 24H, Ph-Ph), 7.95-7.96 (d, 3JH-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): λmax (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), CHCl₃ (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 CH₂Cl₂ as eluent. Solvents were removed in vacuo to give a purple solid 235 (120 mg, 0.091 mmol, 76%). M.p. >300 °C; Rᶠ = 0.54 (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.91 (s, 12H, OCH₃), 7.23 (m, 4H, C₆H₄-H), 7.56 (m, 4H, C₆H₄-H), 7.80 (m, 11H, Ph/C₆H₄-H), 8.03 (m, 4H, H₆), 8.11-8.13 (d, ²J_H-H = 5.3 Hz, 2H, Ph-H), 8.64 (m, 2H, H₈), 8.68 (m, 2H, H₈), 9.02-9.06 (q, ³J_H-H = 12.1 Hz, 4H, H₆), 9.08-9.09 (d, ³J_H-H = 4.7 Hz, 2H, H₈), 9.84-9.86 (d, ³J_H-H = 4.7 Hz, 2H, H₈) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 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 (CH₂Cl₂): λ_max (log ε) = 418 (5.21), 450 (5.17), 558 (4.55) nm.¹³³
{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), CHCl₃ (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 CH₂Cl₂ as eluent. Solvents were removed *in vacuo* to give a purple solid 236 (29 mg, 0.024 mmol, 91%). M.p. >300 °C; *Rf* = 0.48 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.97-1.00 (t, ³J_H-H = 13.9 Hz, 12H, CH₃), 2.66 (s, 6H, tolyl-CH₃), 2.80 (m, 8H, CH₂), 5.05 (m, 1H, CH), 5.16 (m, 1H, CH), 7.50-7.52 (d, ³J_H-H = 7.6 Hz, 4H, C₆H₄-H), 7.83 (m, 3H, Ph-H), 8.08 (m, 4H, Ph-H/Hp), 8.12-8.14 (d, ³J_H-H = 7.6 Hz, 4H, C₆H₄-H), 8.32-8.33 (d, ³J_H-H = 6.6 Hz, 2H, Hp), 8.66-8.67 (d, ³J_H-H = 4.6 Hz, 2H, Hp), 9.04 (m, 2H, Hp), 9.10-9.11 (d, ³J_H-H = 4.5 Hz, 2H, Hp), 9.39-9.43 (d, ³J_H-H = 17.3 Hz, 2H, Hp), 9.76-9.79 (d, ³J_H-H = 12.8 Hz, 2H, Hp), 9.87-9.88 (d, ³J_H-H = 4.5 Hz, 2H, Hp) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 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 (CH₂Cl₂): *λmax* (log ε) = 414 (5.32), 450 (5.27), 554 (4.54) nm; HRMS (MALDI) *m/z* calcd. for [C₇₀H₅₇N₈Zn₂Br]⁺: 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 CH₂Cl₂ (60 mL). The reaction was stirred at room temperature for 3 h. NaBH₄ (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 H₂O (50 mL) and extracted with CH₂Cl₂. The organic layer was washed with NaHCO₃ (2 × 50 mL) and H₂O (50 mL), dried over Na₂SO₄ and filtered. Solvents were removed to give a dark green residue which was redissolved in CH₂Cl₂ 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, CDCl₃/pyridine-d₅, 10 : 1, TMS): δ = 3.86-3.93 (m, 12H, OCH₃), 6.55 (d, 3J₁-H₁ = 4.3 Hz, 2H, H₈), 6.95 (m, 2H, aryl-H), 7.04 (m, 4H, C₆H₄-H), 7.12 (d, 3J₁-H₁ = 4.3 Hz, 2H, H₈), 7.16 (m, 4H, C₆H₄-H), 7.35 (m, 2H, aryl-H), 7.45 (m, 4H, aryl-H), 7.64 (d, 3J₁-H₁ = 4.3 Hz, 2H, H₈), 7.75 (m, 4H, C₆H₄-H), 8.44 (d, 3J₁-H₁ = 4.3 Hz, 2H, H₈), 9.09-9.11 (d, 3J₁-H₁ = 4.7 Hz, 4H, H₈), 9.68-9.69 (d, 3J₁-H₁ = 4.7 Hz, 4H, H₈) ppm; ¹³C NMR (C-H COSY 150 MHz, CDCl₃): 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): λmax (log ε) = 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 CH$_2$Cl$_2$ as eluent to give fraction one, which contained starting material 236 and CH$_2$Cl$_2$: THF (1:1, v/v) as eluent to give fused dimer 238. Solvents were removed \textit{in vacuo} to give a dark green solid 238 (12 mg, 0.010 mmol, 65%). M.p. >300 °C; $^1$H NMR (400 MHz, CDCl$_3$, TMS): δ = 0.92 (m, 12H, CH$_3$), 2.31 (m, 8H, CH$_2$), 2.53 (s, 6H, tolyl-CH$_3$), 5.44 (m, 2H, CH$_2$), 6.84 (m, 2H, H$_{p}$), 7.16 (m, 2H, H$_{p}$), 7.39-7.87 (m, 21H, Ph-//p); UV/vis (THF): $\lambda_{\text{max}}$ (log $\varepsilon$) = 422 (5.18), 565 (5.04), 965 (4.32) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{70}$H$_{53}$N$_{8}$Zn$_{2}$Br](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). NaNO₂ (300 mg, 4.347 mmol) was added and the reaction was stirred for 1 h at room temperature. H₂O (70 mL) was added and extracted with CH₂Cl₂. The organic layer was washed with sat. NaHCO₃ and H₂O, dried over Na₂SO₄ and filtered. The solvents were removed and the residue was redissolved in CH₂Cl₂ and filtered through a plug of silica. Solvents removed to give a purple solid 240 (22 mg, 0.018 mmol, 38%). M.p. >300 °C; Rᵣ = 0.29 (CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, TMS): δ = -2.13 (s, 4H, N //), 7.72 (m, 6H, Ph-//γ), 8.12 (m, 4H, Hᵣ), 8.23-8.24 (d, 4H, ³Jᵣ-H = 6.8 Hz, Ph-//γ), 8.42-8.44 (d, 4H, ³Jᵣ-H = 7.7 Hz, C₆H₄-H), 8.50-8.52 (m, 4H, Hᵣ), 8.59-8.61 (d, 4H, ³Jᵣ-H = 7.7 Hz, C₆H₄-H), 8.72-8.73 (d, 4H, ³Jᵣ-H = 7.7 Hz, C₆H₄-H), 8.95-8.88 (m, 8H, Hᵣ) ppm; UV/vis (CH₂Cl₂): λ_max (log ε) = 424 (5.34), 458 (5.19), 532 (4.54), 590 (4.12), 656 (3.97) nm; HRMS (MALDI) m/z calcd. for [C₇₆H₄₆N₁₂O₈]⁺(M⁺): 1254.3562, found 1254.3580.
7,8-dehydropurpurin (245) and

\[ \text{3,5-Diphenylmethane-10,20-bis(3-methoxy)phenylporphyrinato} \text{Zn(II) (249):} \]

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. Pd₂dba₃ (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; Rf = 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, J_H-H = 15.2 Hz, 2H, C₆H₄-H), 7.24-7.27 (t, 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, H₆), 9.09 (m, 2H, H₇), 9.38 (m, 2H, H₈), 10.28 (s, 1H, Hmeso) ppm; ¹³C
NMR (100 MHz, CDCl$_3$): $\delta = 55.4, 55.5, 108.0, 113.5, 120.5, 122.3, 127.4, 127.6, 127.7, 128.0, 130.4, 131.6, 132.2, 132.4, 132.7, 132.8, 135.5, 138.0, 141.1, 142.8, 143.3, 143.6, 144.2, 144.9, 148.8, 150.3, 150.4, 151.0, 151.8, 157.8, 157.9, 194.4, 198.9$ ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 415 (5.47), 479 (4.15) 543 (4.15) nm; HRMS (MALDI) m/z calcd. for [C$_{48}$H$_{32}$N$_4$O$_4$Zn](M$^+$): 792.1715, found 792.1732.

7,8-dehydropurpurin (246) and

3,5-Diphenylmethane-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. Pd$_2$(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$_2$Cl$_2$ as eluent. Solvents were removed to yield a dark orange solid 246, confirmed by UV/vis and HRMS analysis. UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 416 (5.33), 489 (5.18), 619 (4.02) nm; HRMS (MALDI) m/z calcd. for [C$_{54}$H$_{36}$N$_4$O$_2$Zn](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$_2$Cl$_2$ : 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 °C; $R_f = 0.32$ (n-hexane : EtOAc = 3 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = 3.97$ (s, 3H, OCH$_3$), 3.99 (s, 3H, OCH$_3$), 7.10 (m, 2H, C$_6$H$_4$-H), 7.25 (m, 2H, C$_6$H$_4$-H), 7.37 (m, 2H, Ph-H), 7.56 (m, 4H, C$_6$H$_4$-H), 7.63 (m, 2H, Ph-H), 7.75 (m, 7H, Ph-H), 7.97 (d, $^3$J$_{H\text{-}H} = 7.9$ Hz, 2H, Ph-H), 8.20 (d, $^3$J$_{H\text{-}H} = 8.0$ Hz, 2H, Ph-H), 8.87 (m, 5H, $H_\beta$), 8.96 (d, $^3$J$_{H\text{-}H} = 2.1$ Hz, 1H, $H_\beta$), 9.09-9.07 (dd, $^3$J$_{H\text{-}H} = 4.7$ Hz, 1H, $H_\delta$) 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$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 428 (5.22), 553 (4.07), 596 (3.64) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{54}$H$_{36}$N$_4$O$_4$Zn]$^+$: 868.2028, found 868.1988.

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

Porphyrrin 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$_2$Cl$_2$. The solution was washed with H$_2$O (2 x 10 mL), extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$ and filtered. The solvents were removed to yield a green solid which was redissolved in CH$_2$Cl$_2$ 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; \( R_f = 0.27 \) (CH\(_2\)Cl\(_2\) : EtOAc 10 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 3.93 \) (s, 3H, OCH\(_3\)), 3.95 (s, 3H, OCH\(_3\)), 7.16-7.18 (d, \( J_{H-H} = 15.7 \) Hz, 2H, C\(_6\)H\(_4\)-H), 7.24-7.27 (dd, \( J_{H-H} = 8.7, 2.5 \) Hz, 2H, C\(_6\)H\(_4\)-H), 7.35 (m, 2H, C\(_6\)H\(_4\)-H), 7.38-7.42 (t, \( J_{H-H} = 15.5 \) Hz, 2H, C\(_6\)H\(_4\)-H), 7.55-7.58 (t, \( J_{H-H} = 13.7 \) Hz, 2H, C\(_6\)H\(_4\)-H), 7.63 (m, 2H, Ph-H), 7.75 (m, 2H, Ph-H), 7.82 (m, 5H, Ph-H), 7.93-7.94 (d, \( J_{H-H} = 8.0 \) Hz, 2H, Ph-H), 8.23 (m, 2H, Ph-H), 8.90-8.91 (d, \( J_{H-H} = 4.8 \) Hz, 2H, H\(_9\)), 8.96 (m, 5H, H\(_9\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 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 (CH\(_2\)Cl\(_2\)): \( \lambda_{max} \) (log \( e \)) = 428 (5.01), 555 (3.95), 703 (3.80) nm; HRMS (MALDI) \( m/z \) calcd. for [C\(_{54}\)H\(_{36}\)N\(_6\)O\(_2\)Zn](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)P\(_3\) (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. Pd\(_2\)(dba)\(_3\) (2 mg, 0.002 mmol) and \( N,N\)-dicyclohexylmethyamine (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 CH\(_2\)Cl\(_2\) as eluent. Solvents were removed and the residue was subjected to column chromatography](image)
(silica, CH$_2$Cl$_2$: 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$_2$Cl$_2$: n-hexane = 3: 1, v/v); $^1$H NMR (600 MHz, CDCl$_3$, TMS): $\delta$ = 3.81 (s, 6H, OCH$_3$), 3.85 (s, 6H, OCH$_3$), 6.93 (s, 1H, $H_\beta$), 6.97 (s, 1H, $H_\beta$); 7.07-7.08 (d, $^3$$J_{H-H}$ = 8.2 Hz, 2H, C$_6$H$_4$-$H$), 7.12-7.13 (d, $^3$$J_{H-H}$ = 8.2 Hz, 2H, C$_6$H$_4$-$H$), 7.23-7.27 (m, 4H, aryl-$H$), 7.38-7.41 (m, 24H, aryl-$H$/$H_\beta$), 7.59-7.60 (d, $^3$$J_{H-H}$ = 7.2 Hz, 6H, aryl-$H$), 7.69-7.71 (m, 2H, $H_\beta$), 7.79-7.81 (d, $^3$$J_{H-H}$ = 6.8 Hz, 4H, aryl-$H$), 7.86-7.88 (m, 2H, aryl-$H$), 8.06-8.07 (d, $^3$$J_{H-H}$ = 4.8 Hz, 2H, $H_\beta$) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 55.2, 55.3, 113.1, 113.3, 119.1, 119.2, 119.5, 120.0, 123.9, 124.9, 125.5, 125.6, 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$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 410 (5.46), 513 (5.54) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{96}$H$_{62}$N$_8$O$_4$Zn$_2$](M$^+$): 1518.3477; found 1518.3505.

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

![Porphyrrin](image)

Porphyrrin 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$_2$O (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 redissovled
in CH$_2$Cl$_2$ 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 °C; $^1$H NMR (400 MHz, CDCl$_3$/pyridine-D$_5$, 10 : 1, TMS): $\delta$ = 0.68-0.73 (t, $^3J_{H-H}$ = 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, $^3J_{H-H}$ = 11.0 Hz, 2H, pyrrole-CH$_2$), 6.82 (m, 2H, $H_p$), 7.13 (m, 2H, $H_p$), 7.20 (m, 2H, $H_p$), 7.40-7.81 (m, 32H, Ph/$H_p$), 8.25 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, Ph-H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$/pyridine-D$_5$, 10 : 1): $\delta$ = 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$_2$Cl$_2$): $\lambda_{max} (\log e) =$ 418 (5.21), 564 (5.05), 808 (3.89), 910 (4.22), 1027 (4.41) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{80}$H$_{50}$N$_8$Zn$_2$][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):

\[
\text{\includegraphics[width=0.2\textwidth]{carbazole.png}}
\]

$n$-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$_2$SO$_4$. 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); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta =$
0.90-0.94 (t, $^3J_{H-H} = 13.8$ 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, $^3J_{H-H} = 14.6$ Hz, 2H, CH$_2$), 7.25-7.29 (t, $^3J_{H-H} = 14.5$ Hz, 1H, carbazole-H), 7.44-7.46 (d, $^3J_{H-H} = 8.2$ Hz, 1H, carbazole-H), 7.51-7.55 (t, $^3J_{H-H} = 15.1$ Hz, 1H, carbazole-H), 7.73-7.75 (d, 1H, $^3J_{H-H} = 7.8$ Hz, 1H, carbazole-H), 7.93 (s, 1H, carbazole-H), 8.15-8.16 (d, $^3J_{H-H} = 3.0$ Hz, 1H, carbazole-H), 8.17-8.18 (d, $^3J_{H-H} = 3.0$ 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 [C$_{24}$H$_{33}$BN$_0$$_2$](M+H)$^+$ 378.2604, found 378.2606.

7.5.2 Porphyrin-carbazole conjugates

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

Porphyrrin 83 (50 mg, 0.08 mmol), borylated carbazole 266 (61 mg, 0.16 mmol) and K$_3$PO$_4$ (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. Pd(PPh$_3$)$_4$ (9 mg, 0.01 mmol) was added, the reaction heated to 80 $^\circ$C under argon and left to stir at this temperature for 18 hrs. Solvents were removed in vacuo, the residue was dissolved in CH$_2$Cl$_2$ and washed with saturated NaHCO$_3$, brine and H$_2$O. The organic layers were dried over MgSO$_4$ and solvents were removed in vacuo. The residue was subjected to column chromatography (CH$_2$Cl$_2$ : n-hexane 1 : 1) to yield purple product 274 (49 mg, 0.06 mmol, 75%). M.p. = 201 $^\circ$C; $R_f = 0.68$ (CH$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = -2.68$ (s, 2H, NH), 0.76-0.80 (t, $^3J_{H-H} = 14.0$ 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, $^3J_{H-H} = 14.0$ Hz, 2H, CH$_2$),
7.40-7.43 (t, \( ^3J_{H-H} = 15.0 \) Hz, 1H, carbazole-\( H \)), 7.60 (m, 2H, carbazole-\( H \)), 7.79 (m, 9H, Ph-\( H \)), 8.14-8.17 (d, \( ^3J_{H-H} = 9.4 \) Hz, 1H, carbazole-\( H \)), 8.24-8.28 (d, \( ^3J_{H-H} = 6.6 \) Hz, 6H, Ph-\( H \)), 8.28 (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-\( H \)), 8.87 (m, 6H, \( H_p \)), 8.92-8.93 (d, \( ^3J_{H-H} = 4.7 \) Hz, 2H, \( H_p \)) 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\( _2 \)Cl\( _2 \)): \( \lambda_{\text{max}} (\log \varepsilon) = 422 (5.40), 517 (4.43), 522 (4.31) 591 (4.28), 646 (4.23) \) nm; HRMS (MALDI) \( m/z \) calcd. for [C\(_{56}\)H\(_{45}\)N\(_5\)](M\(^+\)) 787.3675, found 787.3652.

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

Porphyrrin 94 (50 mg, 0.09 mmol), borylated carbazole 266 (35 mg, 0.09 mmol) and K\(_3\)PO\(_4\) (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. Pd(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 \textit{in vacuo}, the residue dissolved in CH\(_2\)Cl\(_2\) and washed with saturated NaHCO\(_3\), brine and H\(_2\)O. The organic layers were dried over MgSO\(_4\) and solvents were removed \textit{in vacuo}. The residue was subjected to column chromatography (CH\(_2\)Cl\(_2\) : n-hexane 1 : 1) and the product recrystallised from CH\(_2\)Cl\(_2\)/MeOH to give purple crystals 275 (38 mg, 0.05 mmol, 61%). M.p. = 182 °C; \( R_f = 0.54 \) (CH\(_2\)Cl\(_2\) : n-hexane = 1 : 1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \( \delta = -2.91 \) (s, 2H, NH), 0.75-0.79 (t, \( ^3J_{H-H} = 13.4 \) 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, \( ^3J_{H-H} = 14.0 \) Hz, 2H, CH\(_2\)), 7.39-7.43 (t, \( ^3J_{H-H} = 12.8 \) Hz, 1H, carbazole-\( H \)), 7.61 (m, 2H, carbazole-\( H \)), 7.80 (m, 6H, Ph-\( H \)), 8.15-8.17 (d, \( ^3J_{H-H} = 7.6 \) Hz, 1H, carbazole-\( H \)), 8.27 (m, 4H, Ph-\( H \)), 8.30 (m, 1H, carbazole-\( H \)), 8.38-8.39 (d, \( ^3J_{H-H} = 4.7 \) Hz, 2H, \( H_p \)) 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\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} (\log \varepsilon) = 422 (5.40), 517 (4.43), 522 (4.31) 591 (4.28), 646 (4.23) \) nm; HRMS (MALDI) \( m/z \) calcd. for [C\(_{56}\)H\(_{45}\)N\(_5\)](M\(^+\)) 787.3675, found 787.3652.
$H = 7.6 \text{ Hz, 1H, carbazole-}H$, 8.43-8.45 (d, $^3J_{H-H} = 7.6 \text{ Hz, 1H, carbazole-}H$), 8.91-8.92 (d, $^3J_{H-H} = 4.6 \text{ Hz, 2H, } H_\beta$), 8.95-8.96 (d, $^3J_{H-H} = 4.6 \text{ Hz, 2H, } H_\beta$), 9.06-9.07 (d, $^3J_{H-H} = 4.6 \text{ Hz, 2H, } H_\beta$), 9.06-9.07 (d, $^3J_{H-H} = 4.7 \text{ Hz, 4H, } H_\beta$) 10.27 (s, 1H, $H_{meso}$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.9, 22.5, 27.1, 29.1, 31.5, 43.3, 109.1, 115.8, 117.9, 119.2, 119.7, 120.7, 121.6, 122.2, 122.8, 125.9, 126.7, 126.8, 126.9, 127.7, 130.7, 131.3, 131.4, 131.8, 134.6, 134.7, 136.6, 139.2, 140.1, 141.2, 141.8, 147.5 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max} (\log \epsilon) = 424 (5.43), 518 (4.48), 524 (4.33) 590 (4.30), 647 (4.26)$ nm; HRMS (MALDI) $m/z$ calcd. for [C$_{50}$H$_{41}$N$_5$](M$^+$) 711.3362, found 711.3362.

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

Porphyрин 274 (27 mg, 0.03 mmol) was dissolved in CHCl$_3$ (10 mL) and heated to 70 °C. Zn(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$_2$Cl$_2$ 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$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = 0.78-0.82$ (t, $^3J_{H-H} = 14.0 \text{ Hz, 3H, } C_3$), 1.27 (m, 4H, $CH_2$), 1.42 (m, 2H, $CH_2$), 1.98 (m, 2H, $CH_2$), 4.42-4.46 (t, $^3J_{H-H} = 14.6 \text{ Hz, 2H, } CH_2$), 7.38-7.42 (t, $^3J_{H-H} = 14.6 \text{ Hz, 1H, carbazole-}H$), 7.61 (m, 2H, carbazole-)$H$, 7.80 (m, 9H, Ph-$H$), 8.17-8.19 (d, $^3J_{H-H} = 7.6 \text{ Hz, 1H, carbazole-}H$), 8.27 (d, $^3J_{H-H} = 6.0 \text{ Hz, 6H, Ph-}H$), 8.30 (m, 1H, carbazole-)$H$, 8.36-8.38 (d, $^3J_{H-H} = 7.6 \text{ Hz, 1H, carbazole-}H$), 8.44-8.46 (d, $^3J_{H-H} = 7.6 \text{ Hz, 1H, carbazole-}H$), 8.95 (m, 8H, $H_\beta$), 9.00 (m, 6H, $H_\beta$), 9.06-9.07 (d, $^3J_{H-H} = 4.7 \text{ Hz, 2H, } H_\beta$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.9, 22.6, 27.1, 29.2, 31.6, 43.3, 109.1, 115.6, 117.9, 119.2, 120.7, 121.1, 121.2, 122.1, 122.9, 125.9, 126.5, 126.6, 127.5, 131.9, 132.3, 134.4, 139.2, 140.3, 141.2, 142.8, 150.2, 150.6 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max} (\log \epsilon) = 423 (5.42), 549 (4.45)$,
587 (4.28) nm; HRMS (MALDI) m/z calcd. for [C_{56}H_{43}N_{5}Zn](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$_3$PO$_4$ (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$_2$Cl$_2$ and washed with saturated NaHCO$_3$, brine and H$_2$O. The organic layers were dried over MgSO$_4$ and solvents were removed in vacuo. The residue was subjected to column chromatography (CH$_2$Cl$_2$: 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$_2$Cl$_2$: n-hexane = 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.66 (s, 2H, N//), 0.76-0.81 (t, $^3$J$_{H-H}$ = 13.9 Hz, 3H, C //), 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-C//), 2.75 (s, 3H, tolyl-C//), 4.42-4.46 (t, $^3$J$_{H-H}$ = 13.9 Hz, 2H, CH$_2$), 7.40-7.43 (t, $^3$J$_{H-H}$ = 14.0 Hz, 1H, carbazole-H), 7.50 (m, 6H, C$_6$H$_4$-H), 7.60 (m, 2H, carbazole-H), 8.13-8.15 (d, $^3$J$_{H-H}$ = 7.0 Hz, 6H, C$_6$H$_4$-H), 8.05 (m, 2H, carbazole-H), 8.29 (s, 1H, carbazole-H), 8.37-8.39 (d, $^3$J$_{H-H}$ = 7.6 Hz, 1H, carbazole-H), 8.44-8.45 (d, $^3$J$_{H-H}$ = 7.6 Hz, 1H, carbazole-H), 8.91 (m, 8H, $H_p$) 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$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 423 (5.50), 518 (4.61),
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554 (4.50), 591 (4.41), 650 (4.39) nm; HRMS (MALDI) m/z calcd. for [C_{59}H_{54}N_{5}Zn](M⁺) 828.4144, found 828.4121.

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

Porphyrrin 277 (50 mg, 0.06 mmol) was dissolved in CHCl₃ (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 CH₂Cl₂ 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; Rᵣ = 0.53 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.77-0.80 (t, 3J₃H-H = 14.4 Hz, 3H, C /3), 0.89 (m, 4H, CH₂), 1.19 (m, 2H, CH₂), 1.98 (m, 2H, CH₂), 2.47 (s, 6H, tolyl-CH₃), 2.75 (s, 3H, tolyl-CH₃), 4.43-4.45 (t, 3J₄H-H = 14.4 Hz, 2H, CH₂), 7.40-7.42 (t, 3J₅H-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, 3J₆H-H = 7.5 Hz, 1H, carbazole-H), 8.44-8.45 (d, 3J₇H-H = 7.5 Hz, 1H, carbazole-H), 9.00 (m, 8H, H₈) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): 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_{5}Zn](M⁺) calcd. 891.3279, found 891.3237.
2-[5',10',15'-Tris(4-methylphenyl)porphyrinato(palladium)(II)-20'-yl]-9-hexyl-carbazole (279):

Porphyrrin 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 \textit{in vacuo} and the residue was redissolved in CH$_2$Cl$_2$. The crude product was filtered through a plug of silica, solvents were removed \textit{in vacuo} to yield a red coloured solid 279 (30 mg, 0.03 mmol, 89%). M.p. = 130 °C; $R_f$ = 0.78 (CH$_2$Cl$_2$ : n-hexane, 1 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = 0.77$-0.81 (t, $^3$J$_{HH} = 14.4$ Hz, 3H, CH$_3$), 1.29 (m, 4H, CH$_2$), 1.65 (m, 2H, CH$_2$), 1.96 (m, 2H, CH$_2$), 2.71(s, 6H, toyl-CH$_3$), 2.73 (s, 3H, tolyl-CH$_3$), 4.40-4.44 (t, $^3$J$_{HH} = 14.4$ Hz, 2H, CH$_2$), 7.41 (m, 1H, carbazole-H), 7.47-7.49 (m, 1H, carbazole-H), 7.57 (m, 6H, C$_6$H$_4$-H), 8.08-8.09 (d, $^3$J$_{HH} = 7.8$ Hz, 6H, C$_6$H$_4$-H), 8.12 (m, 1H, carbazole-H), 8.24 (s, 1H, carbazole-H), 8.36-8.38 (d, $^3$J$_{HH} = 7.8$ Hz, 1H, carbazole-H), 8.42-8.44 (d, $^3$J$_{HH} = 7.8$ Hz, 1H, carbazole-H), 8.87 (m, 8H, H$_p$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.9$, 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 (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 421 (4.42), 526 (3.53) nm; HRMS (MALDI) $m/z$ calcd. for [C$_{59}$H$_{49}$N$_5$Pd](M$^+$) 933.3023, found 933.3058.
2-[5',10',15'-Tris(4methylphenyl)porphyrinato(indium chloride)-20'-yl]-9-hexyl-carbazole (280):

Porphyрин 277 (33 mg, 0.04 mmol), InCl₃ (88 mg, 0.40 mmol), CH₃COONa (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 CH₂Cl₂. The crude product was extracted from saturated NaHCO₃, organic phases washed with brine and dried over MgSO₄. Solvents were removed in vacuo to yield a purple-green coloured solid 280 (23 mg, 0.02 mmol, 59%). M.p. = 141 °C; Rᵣ = 0.27 (CH₂Cl₂ : n-hexane = 2 : 1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.81-0.85 (t, ³J_H-H = 12.9 Hz, 3H, CH₃), 0.91 (m, 2H, CH₂), 1.28 (m, 4H, CH₂), 1.48 (m, 2H, CH₂), 2.06 (m, 2H, CH₂), 2.74 (s, 6H, tolyl-C₃), 2.75 (s, 3H, tolyl-C₂), 4.45-4.49 (t, ³J_H-H = 13.8 Hz, 2H, CH₂), 7.40-7.44 (t, ³J_H-H = 14.0 Hz, 1H, carbazole-H), 7.58 (m, 4H, C₆H₄-H), 7.64 (m, 2H, carbazole-H), 8.03-8.05 (d, ³J_H-H = 7.6 Hz, 4H, C₆H₄-H), 8.27-8.29 (d, ³J_H-H = 7.6 Hz, 4H, C₆H₄-H), 8.37-8.39 (d, ³J_H-H = 7.6 Hz, 1H, carbazole-H), 8.44 (s, 2H, carbazole-H), 8.49-8.50 (d, ³J_H-H = 7.6 Hz, 1H, carbazole-H), 9.12 (m, 8H, CH₃) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λₒₘₐₓ (log ε) = 431 (5.45), 562 (4.47), 603 (4.32) nm; HRMS (MALDI) m/z calcd. for [C₅₉H₄₉N₅InCl](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$_3$PO$_4$ (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$_2$Cl$_2$ and washed with saturated NaHCO$_3$, brine and H$_2$O. 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$_2$Cl$_2$ as eluent. Solvents were removed and the purple solid was recrystallised from CH$_2$Cl$_2$/MeOH to yield purple crystals 281 (58 mg, 0.06 mmol, 76%). M.p. = 283-285 °C; $R_f = 0.57$ (CH$_2$Cl$_2$ : n-hexane = 1 : 1, v/v); $^1$H NMR (600 MHz, CDCl$_3$, TMS): δ = -2.61 (s, 2H, NH), 0.77-0.80 (t, $^3$J$_{H-H}$ = 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, $^3$J$_{H-H}$ = 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, $^3$J$_{H-H}$ = 7.6 Hz, 2H, carbazole-H), 8.25-8.26 (d, $^3$J$_{H-H}$ = 7.6 Hz, 4H, Ph-H), 8.29-8.30 (d, $^3$J$_{H-H}$ = 1.8 Hz, 2H, carbazole-H), 8.37-8.40 (d, $^3$J$_{H-H}$ = 7.7 Hz, 2H, carbazole-H), 8.44-8.46 (d, $^3$J$_{H-H}$ = 7.7 Hz, 2H, carbazole-H), 8.68-8.88 (d, $^3$J$_{H-H}$ = 4.7 Hz, 4H, H$_{\beta}$), 8.93-8.94 (d, $^3$J$_{H-H}$ = 4.7 Hz, 4H, H$_{\beta}$) 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$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 426 (5.49), 518 (4.47), 554 (4.36), 592 (4.30), 648 (4.29) nm; HRMS (MALDI) m/z calcld. 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 CHCl₃ (10 mL) and heated to 70°C. Zn(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 CH₂Cl₂ 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; Rf = 0.45 (CH₂Cl₂ : n-hexane, 1 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ = 0.78-0.80 (t, ³JH-H = 13.2 Hz, 6H, CH₃), 1.26 (m, 8H, CH₂), 1.43 (m, 4H, CH₂), 1.99 (m, 4H, CH₂), 4.44-4.46 (t, ³JH-H = 13.9 Hz, 4H, CH₂), 7.40-7.42 (t, ³JH-H = 13.9 Hz, 2H, carbazole-H), 7.60 (m, 4H, carbazole-H), 7.78 (m, 6H, Ph-H), 8.18-8.19 (d, ³JH-H = 7.3 Hz, 2H, carbazole-H), 8.27-8.28 (d, ³JH-H = 6.6 Hz, 4H, Ph-H), 8.31 (s, 2H, carbazole-H), 8.38-8.39 (d, ³JH-H = 7.4 Hz, 2H, carbazole-H), 8.45-8.46 (d, ³JH-H = 7.4 Hz, 2H, carbazole-H), 8.97-8.98 (d, ³JH-H = 4.4 Hz, 4H, Hβ), 9.04-9.05 (d, ³JH-H = 4.4 Hz, 4H, Hβ) ppm; ¹³C NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂): λ_{max} (log ε) = 424 (5.52), 548 (4.51), 590 (4.38) nm; HRMS (MALDI) m/z calcd. for [C₆₈H₅₈N₆Zn](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):

Porphyrrin 83 (50 mg, 0.08 mmol), borylated carbazole 273 (90 mg, 0.18 mmol) and
K₃PO₄ (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(PPh₃)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 CH₂Cl₂ and washed with saturated
NaHCO₃, brine and H₂O. The organic layers were dried over MgSO₄ and the solvents
were removed in vacuo. The residue was subjected to column chromatography (CH₂Cl₂
: n-hexane, 1 : 1, v/v) to yield purple product which was recrystallised from
CH₂Cl₂/MeOH to give purple crystals 283 (46 mg, 0.05 mmol, 62%). M.p. = 231-234
°C; Rf = 0.26 (CH₂Cl₂ : n-hexane = 1 : 1, v/v); ¹H NMR (600 MHz, CDCl₃, TMS): δ =
2.65 (s, 2H, NH), 0.77-0.79 (t, J₃H-H = 13.6 Hz, 3H, CH₃), 0.89 (m, 2H, CH₂), 1.26 (m,
2H, CH₂), 1.56 (s, 12H, CH₃), 2.01 (m, 4H, CH₂), 4.49 (m, 2H, CH₂), 7.62-7.63 (d, J₃H-
H = 7.8 Hz, 1H, carbazole-H), 7.78 (m, 9H, Ph-H), 7.87-7.88 (d, J₃H-H = 7.8 Hz, 1H,
carbazole-H), 8.16-8.18 (d, J₃H-H = 7.8 Hz, 2H, carbazole-H), 8.26 (d, J₃H-H = 7.6 Hz,
6H, Ph-H), 8.38-8.39 (d, J₃H-H = 7.8 Hz, 1H, carbazole-H), 8.45-8.47 (d, J₃H-H = 7.8 Hz,
1H, carbazole-H), 8.87 (m, 6H, Hβ), 8.93-8.94 (s, J₃H-H = 4.0 Hz, 2H, Hβ) ppm; ¹³C
NMR (150 MHz, CDCl₃): 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 (CH₂Cl₂):
λmax (log ε) = 422 (5.13), 515 (4.22), 552 (4.17), 592 (4.15), 655 (4.09) nm; HRMS
(MALDI) [C₆₂H₅₇N₅O₂B](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$_3$PO$_4$ (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$_2$Cl$_2$ and washed with saturated
NaHCO$_3$, brine and H$_2$O. 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$_2$Cl$_2$: n-
hexane (1 : 1, v/v) and CH$_2$Cl$_2$ 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$_2$Cl$_2$: n-hexane = 2 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = -2.67 (s, 2H,
NH), 0.77-0.80 (t, $^3$J$_{H-H}$ = 14.2 Hz, 3H, CH$_3$), 0.91 (m, 2H, CH$_2$), 1.29 (m, 4H, CH$_2$),
1.49 (s, 12H, C$_6$H$_4$), 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, $^3$J$_{H-H}$ = 14.2 Hz, 2H, CH$_2$), 7.58 (m, 6H, C$_6$H$_4$), 7.87-7.89 (d, $^3$J$_{H-H}$ = 7.8
Hz, 1H, carbazole-H), 8.07 (s, 1H, carbazole-H), 8.13-8.15 (d, $^3$J$_{H-H}$ = 8.3 Hz, 6H,
C$_6$H$_4$), 8.29 (s, 1H, carbazole-H), 8.36-8.40 (d, $^3$J$_{H-H}$ = 7.8 Hz, 1H, carbazole-H),
8.45-8.47 (d, $^3$J$_{H-H}$ = 7.8 Hz, 1H, carbazole-H), 8.90 (s, 8H, H$_{para}$) ppm; $^{13}$C NMR (100
MHz, CDCl$_3$): $\delta$ = 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$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 424 (5.60), 518 (4.49), 553
(4.36), 592 (4.27), 649 (4.26) nm; HRMS (ESI) m/z calcd. for [C_{65}H_{63}N_3O_2B](M+H)^+ calcd. 956.5075, found 956.5072.

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

Porphyrrin 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. Pd(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); \(^1\)H NMR (600 MHz, CDCl_3): \(\delta = -2.55\) (s, 2H, NH), 0.69-0.71 (t, \(^3J_{H-H} = 13.9\) 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, \(^3J_{H-H} = 7.9\) Hz, 2H, carbazole-\(H\)), 8.32 (m, 12H, Ph-\(H\)), 8.47 (s, 2H, carbazole-\(H\)), 8.66-8.68 (d, \(^3J_{H-H} = 7.9\) Hz, 2H, carbazole-\(H\)), 8.95 (m, 8H, H_9), 8.97-8.98 (d, \(^3J_{H-H} = 4.5\) Hz, 4H, H_9), 9.08-9.09 (d, \(^3J_{H-H} = 4.5\) Hz, 4H, H_9) ppm; \(^13\)C NMR (150 MHz, CDCl_3): \(\delta = 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): \(\lambda_{max} (\log \varepsilon) = 423\) (5.60), 517 (4.61), 554 (4.43), 592 (4.38), 647 (4.37) nm; HRMS (MALDI) m/z calcd. for [C_{94}H_{69}N_9](M^+) 1323.5676, found 1323.5653.
2,7-Bis[5',10',15'-tri(4-methylphenyl)porphyrin-20'-yl]-9-hexyl-carbazole (286):

Porphyrrin 284 (30 mg, 0.03 mmol), bromoporphyrin 93 (21 mg, 0.03 mmol) and K$_3$PO$_4$ (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$_2$Cl$_2$ and washed with saturated NaHCO$_3$, brine and H$_2$O. The organic layers were dried over MgSO$_4$ and solvents were removed in vacuo. The residue was subjected to column chromatography (CH$_2$Cl$_2$ : 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$_2$Cl$_2$ : n-hexane = 2 : 1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = -2.63 (s, 2H, NH), 0.67-0.70 (t, $^3$J$_{H-H}$ = 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, $^3$J$_{H-H}$ = 14.1 Hz, 2H, CH$_2$), 7.60-7.61 (d, $^3$J$_{H-H}$ = 6.2 Hz, 12H, C$_6$H$_4$-H), 8.16-8.17 (d, $^3$J$_{H-H}$ = 6.2 Hz, 12H, C$_6$H$_4$-H), 8.30-8.32 (d, $^3$J$_{H-H}$ = 8.2 Hz, 2H, carbazole-H), 8.44 (s, 2H, carbazole-H), 8.68-8.70 (d, $^3$J$_{H-H}$ = 8.2 Hz, 2H, carbazole-H), 8.92 (m, 2H, N), 9.02-9.03 (d, $^3$J$_{H-H}$ = 4.4 Hz, 4H, H$_6$) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 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$_2$Cl$_2$): $\lambda_{max}$(log $\varepsilon$) = 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


References


References


[329] Porphyrin crystals often form clathrate type structures, in compacting large numbers of solvent molecules. In many cases, these are so tightly bound as to make reliable elemental analysis impossible.


[331] *13C NMR spectra of 173 could not be obtained due to low solubility*.

[332] As a comparison for a mass spectrometry study the nickel trimer 187 was synthesised. Despite many attempts, purification of this array was unsuccessful, therefore a full characterisation was not obtained.

[333] HRMS was attained but value had a m/z of approximately 0.9 higher than the exact mass. This could be attributed to a solubility issue of the dimer.

[334] HRMS was attained but value had a m/z of approximately 0.9 higher than the exact mass. This could be attributed to a solubility issue of the dimer.