Synthesis of water soluble porphyrins and their applications

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Rhys Thomas Mitchell
May, 2016
Certification

I, Rhys Mitchell, declare that the work in this thesis, submitted for the award of Doctor of Philosophy in the School of Chemistry at the University of Wollongong, is entirely my own, unless otherwise stated, referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Rhys Mitchell,

May, 2016
Abstract

This thesis is focused on the generation of water soluble amphiphilic porphyrins for the creation of an artificial photosynthesis model. The development of functionalised porphyrins will allow for the molecules to be bound to protein maquettes and a study into energy and electron transfer undertaken. The investigation into these molecules will also allow for a study into porphyrin synthesis by flow chemistry and the creation of a water soluble porphyrin bound hydrogel.

An investigation into the synthesis of porphyrins by flow chemistry was successful with the new method producing most of the desired products in synthesised yields comparable to literature methods. The Adler-Longo flow chemistry synthetic method also proved to be applicable to scale up synthesis with tetrphenylporphyrin produced in gram quantities. Copper insertion and porphyrin formylation was also achieved but with little advantage over previously reported methods.

A series of amphiphilic porphyrin dyads were synthesised using standard porphyrin condensations and Wittig chemistry. Water solubilisation was achieved at the final synthetic step for all dyads, to ensure purification could be performed at each step by standard techniques. A sulfonic acid containing dyad was synthesised from a trimethylsilyl containing aryl porphyrin, while benzoic acid dyads were generated following hydrolysis of porphyrin esters. Benzoic acid containing dyads allowed for control of metal centres, with Zn-Zn, Zn-Fe and Zn-free-base derivatives synthesised. Hydrophobic porphyrin-fullerene conjugates were also synthesised, with a potential special pair mimic connected to a fullerene generated using Wittig and Prato reactions.

Knoevenagel condensation using formylporphyrins and phenylacetonitriles was investigated to assess its potential to produce amphiphilic porphyrin arrays. The new synthetic method was first used to produce hydrophobic functionalised porphyrins with electron rich and electron poor phenylacetonitrile substituents. These molecules were characterised by electrochemistry, while solar cell studies were performed for a surface binding derivative. Subsequently, hydrophobic porphyrin dyads were successfully synthesised, with control of the metal centres achievable. Amphiphilic porphyrin dyad synthesis was however unsuccessful using Knoevenagel condensation.

A new porphyrin hydrogel was synthesised and its use for binding as a heavy metals was explored. The covalently linked porphyrin hydrogel, was generated using a two-step method
with a benzoic acid containing porphyrin linked to a branched Jeffamine polymer. Purification of the polymer appended porphyrin then reaction with poly(ethylene glycol) diglycidyl ether gave the highly cross-linked porphyrin hydrogel. Swelling of the gel in water followed by exposure to mercury and cadmium salts gave differently coloured porphyrin hydrogels with shifted fluorescence spectra.

The work performed in this thesis lays the basis for future porphyrin syntheses, leading to an expansion on existing porphyrin based applications and development of porphyrin based devices. Following on from Adler styled porphyrin syntheses, flow chemistry could be used to achieve further large scale Lindsey-style porphyrin syntheses. The successfully synthesised amphiphilic dyads will allow for a binding study to determine if a dyad can be inserted into a protein maquette. The library of porphyrins functionalised using Knoevenagel condensation can also be expanded to generate both amphiphilic dyads and arrays larger than two porphyrins. Lastly, the success of heavy metal sensors using a highly cross-linked porphyrin hydrogel could allow an investigation into the development of electrospun gels that could be combined with electrochemistry to achieve a highly sensitive sensor.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>ADP</td>
<td>adenosine diphosphate</td>
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<tr>
<td>aq.</td>
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<td>ATP</td>
<td>adenosine triphosphate</td>
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<tr>
<td>br s</td>
<td>broad singlet</td>
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<tr>
<td>CHES</td>
<td>( N)-cyclohexyl-2-aminoethanesulfonic acid</td>
</tr>
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<td>COSY</td>
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<td>Cytb(_{6f})</td>
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<td>Fc</td>
<td>ferrocene</td>
</tr>
<tr>
<td>Fc(^+)</td>
<td>ferrocenium</td>
</tr>
<tr>
<td>G(^{'})</td>
<td>elastic or storage modulus</td>
</tr>
<tr>
<td>G(^{''})</td>
<td>viscous or loss modulus</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>HPLC</td>
<td>high pressure liquid chromatography</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
</tr>
<tr>
<td>IPRI</td>
<td>Intelligent Polymer Research Institute</td>
</tr>
<tr>
<td>IR</td>
<td>infrared spectroscopy</td>
</tr>
<tr>
<td>Jeffamine</td>
<td>polyetheramine</td>
</tr>
<tr>
<td>KOtBu</td>
<td>potassium tert-butoxide</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>LVE</td>
<td>linear viscoelastic region</td>
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<tr>
<td>m</td>
<td>multiplet</td>
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<tr>
<td>M</td>
<td>mol L$^{-1}$</td>
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<tr>
<td>MALDI</td>
<td>matrix assisted laser desorption ionisation spectroscopy</td>
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<tr>
<td>MeOH</td>
<td>methanol</td>
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<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>MM</td>
<td>molecular mechanics</td>
</tr>
<tr>
<td>MOF</td>
<td>metal organic framework</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectroscopy</td>
</tr>
<tr>
<td>NADP/NADPH</td>
<td>nicotinamide adenine dinucleotide phosphate</td>
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<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
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<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOE</td>
<td>nuclear Overhauser effect</td>
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<tr>
<td>NOESY</td>
<td>2D nuclear Overhauser effect spectroscopy</td>
</tr>
<tr>
<td>PEG</td>
<td>poly(ethyleneglycol)</td>
</tr>
<tr>
<td>PEGDGE</td>
<td>poly(ethylene glycol) diglycidyl ether</td>
</tr>
<tr>
<td>pheo</td>
<td>pheophytin</td>
</tr>
<tr>
<td>POCl$_3$</td>
<td>phosphoryl chloride</td>
</tr>
<tr>
<td>PPM</td>
<td>parts per million</td>
</tr>
<tr>
<td>Q$_A$</td>
<td>quinone A</td>
</tr>
<tr>
<td>Q$_B$</td>
<td>quinone B</td>
</tr>
<tr>
<td>Rf</td>
<td>retention factor</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>RuBisCO</td>
<td>ribulose-1,5-bisphosphate carboxylase/oxygenase</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>TAP</td>
<td>tetra-arylporphyrins</td>
</tr>
<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<td>thin layer chromatography</td>
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<td>TMPyP</td>
<td>tetramethylpyridiniumporphyrin</td>
</tr>
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<td>tetraphenylporphyrin</td>
</tr>
<tr>
<td>TPPS</td>
<td>tetra(4-sulfophenyl)porphyrin</td>
</tr>
<tr>
<td>TXP</td>
<td>tetraxylylporphyrin</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible spectroscopy</td>
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</tbody>
</table>
Chapter 1

Introduction
1.1 Introduction to Porphyrins

Tetra-pyrrolic macrocycles play important roles in nature, with this class of compound typically involved in processes such as light absorption, gas transport and catalysis. Two key biological molecules are chlorophyll and haem (Figure 1-1), which contain tetra-pyrrolic units known as chlorins and porphyrins, respectively.\textsuperscript{[1]} Consequently, the development of biologically inspired technologies such as artificial photosynthesis, requiring molecules with a range of photophysical and redox characteristics, can be achieved using synthetic chlorins or porphyrins. However, the ease of synthesis and versatility of the more oxidised porphyrin system and its chemistry has ensured porphyrin-based systems are more widely used in this regard.

![Figure 1-1. Structures of natural occurring tetra-pyrrolic molecules, chlorophyll a and haem A.](image)

Porphyrs are cyclic organic compounds that consist of 4 pyrrole rings connected by methylene groups at the \( \alpha \) pyrrolic positions. The pyrrolic carbons in the porphyrin macrocycle are assigned \( \alpha \) and \( \beta \), while the methylene carbon is termed the meso position. The simplest porphyrin is known as porphin, with all other porphyrin derivatives having substituents in the \( \beta \)-pyrrolic and/or meso positions (Figure 1-2).\textsuperscript{[2]}
In porphyrins, the planar aromatic core contains 22 π-electrons, however only 18 are required for the aromatic system. The conjugated porphyrin ring allows for tautomerisation, with the free-base porphyrin I (Figure 1-3) having equivalent pyrrolic nitrogens. The free-base porphyrin which has 2 protons bound to pyrrolic nitrogens is able to accept 2 protons to form a dicationic species II. Basic conditions are able to produce a dianionic species III, with this open cage capable of coordinating to metal ions to form metalloporphyrins IV.

The aromaticity of the porphyrin ring, as a result of the delocalisation of electrons around the large ring system, is responsible for high chemical and thermal stability, the dyes characteristic electronic absorption spectra and their unique $^1$H nuclear magnetic resonance (NMR) spectra.

Porphyrins high molar extinction coefficients can be explained by the 4-orbital model, in which transitions between 2 highest occupied molecular orbitals (HOMO) and 2 lowest unoccupied molecular orbitals (LUMO) give rise to the unique electronic absorption porphyrin spectrum. Orbital mixing of the HOMOs, the $a_1u$ and $a_2u$ orbitals, and LUMOs, a set of degenerate $e_g$ orbitals, splits the energy states and therefore gives rise to 2 distinct spectral regions. A high energy state is formed that creates the dominating porphyrin Soret band between 380-420 nm ($\varepsilon > 200\,000\,\text{L mol}^{-1}\text{cm}^{-1}$), and the low energy state gives rise to the less intense Q bands. A free-
base porphyrin generates 4 Q bands between 500 and 700 nm (< 30 000 L mol\(^{-1}\) cm\(^{-1}\)), while the added symmetry of metalloporphyrins typically alters the absorption spectra by forming 2 Q bands (Figure 1-4).\[^{[6]}\] The energy transitions between the HOMO and LUMO can be affected not only by metal centre, but also substituents on the porphrin core which in turn alters the electronic absorption spectra.

![UV-vis absorption spectra of free-base (solid line) and metallated (Erbium) (dotted line) appended tetraarylporphyrins, with expanded Q band region.\[^{[7]}\)](image)

**Figure 1-4.** UV-vis absorption spectra of free-base (solid line) and metallated (Erbium) (dotted line) appended tetraarylporphyrins, with expanded Q band region.\[^{[7]}\]

The aromatic ring system drastically affects the \(^1\)H NMR spectrum. The major effect is the position of the pyrrolic NH signal, which due to the shielding of the induced ring current, is shifted from a highly deshielded region to approximately -2.7 ppm in porphyrins (Figure 1-5).\[^{[8]}\] The \(\beta\)-pyrrolic and meso phenyl protons are also affected by the porphyrins ring current, with a downfield shift of these protons observed relative to pyrrole and benzene.
Figure 1-5. $^1$H NMR chemical shifts of tetraphenylporphyrin (TPP) in CDCl$_3$ (Ph= phenyl).

Synthesis of functionalised porphyrins has enabled chemists to influence the chemical and physical properties of the macrocycle. Electron withdrawing and electron donating aromatic substituents are commonly placed at the meso position of porphyrins to increase the light harvesting capabilities of the dye. Surface binding substituents are also commonly incorporated onto the porphyrin core to assist with light harvesting applications.

1.1.1 Porphyrin Synthesis

The first functionalised porphyrin was synthesised by Rothmund in 1936 by reacting benzaldehyde and pyrrole in a sealed tube at 150°C for 24 hours (h) to produce TPP. Due to the harsh conditions, it meant that only small yields were obtained and the use of more sensitive aldehydes could not be investigated due to aldehyde decomposition. In 1967, Adler and Longo were able to develop a milder methodology in which benzaldehyde and pyrrole were reacted in refluxing propionic acid for 30 minutes (min) (Scheme 1-1). Molecular oxygen was the oxidant required for porphyrin oxidation, with TPP being synthesised at around 20% yields. The new reaction conditions not only produced higher yields, but also allowed for greater numbers of substituted aldehydes to be used. The ease of reaction allows it to be used for large multi gram scale reactions, however the method does not allow for the use of acid sensitive aldehydes. Purification can also be problematic for porphyrins that do not precipitate out of the reaction solution.
In 1987, Lindsey developed a method of porphyrin synthesis that overcame the problems observed with the Adler-Lungo synthesis. The method is performed under inert conditions with an acid catalyst (boron trifluoride etherate or trifluoroacetic acid (TFA)), to produce a high concentration of the porphyrinogen intermediate. To ensure that high concentrations of the cyclic porphyrinogen are produced, the reaction is performed at low concentrations ($10^{-2}$ mol L$^{-1}$ (M)). This low concentration reduces the amount of high molecular weight polymer, however it also results in large scale reaction limitations. Following completion of the formation of porphyrinogen, a chemical oxidant (p-chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)) is added to form the porphyrin. The main advantages of the Lindsey synthesis are the ability to produce porphyrins using acid sensitive aldehydes, while also producing yields of up to 50%.\cite{11}

(i) Propionic acid, O$_2$, reflux, 30 min. (ii) CH$_2$Cl$_2$, boron trifluoride etherate or TFA, room temperature (RT), 3 h. (iii) p-chloranil or DDQ, 30 min.

**Scheme 1-1.** Adler-Longo and Lindsey porphyrin syntheses.\cite{11-12}
1.1.2 Porphyrin Applications

The ability to incorporate differing levels of functionality, bind metals and form highly ordered complex structures had made porphyrins one of the most adaptable molecules in chemistry. A significant use of porphyrins has been for the catalysis of organic reactions, specifically oxidation and reduction reactions. Manganese(III) porphyrins have showed selectivity towards the epoxidation of alkenes, with activated hydrocarbons also undergoing selective oxidation reactions.\textsuperscript{[13]} Iron and ruthenium porphyrins have also shown promise for organic oxidation reactions.\textsuperscript{[14]} Furthermore, cobalt porphyrins have been used in the 4 electron reduction of molecular $O_2$ to $H_2O$. Face-to-face cobalt porphyrin dyads have been designed to facilitate the electroreduction of $H_2O$, with alterations to porphyrin design capable of producing hydrogen peroxide.\textsuperscript{[15]}

Porphyrins have been used extensively in dye sensitised solar cells (DSSCs) due to their high light absorption characteristics and the synthetic variability that can be incorporated onto the porphyrin core.\textsuperscript{[16]} Synthesis of porphyrin dyes have been developed to include a linker that connects a binding group to the highly aromatic porphyrin core. Carboxylic acid binding groups are commonly used to bind the porphyrin to semi-conductor surfaces. Push-pull functionality is also able to be incorporated into the porphyrins structure to ensure efficient charge injection from the porphyrin excited state into the conduction band of a semi-conductor (Figure 1-6).\textsuperscript{[17]}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{porphyrin_chromophore.png}
\caption{Porphyrin chromophore for DSSC applications, with electron-donating and surface binding moieties highlighted.\textsuperscript{[17]}}
\end{figure}

Another major field for porphyrin use is in medical treatment, particularly the treatment of cancer by photodynamic therapy. Photodynamic therapy is a treatment of tumours by using a
drug capable of sensitisation. Due to porphyrins high energy absorption characteristics, sensitisation can bring about a cytotoxic effect and potentially destroy the unwanted tissue. To concentrate a porphyrin in tumour tissue, organic chemists have had to incorporate water solubility into the drug to ensure solubility in biological conditions. Once bound to cancer cells, sensitisation allows for singlet \( \text{O}_2 \) formation and subsequent oxidation of the cancerous cell.

Porphyrins with variable water solubility are also used biologically for deoxyribonucleic acid (DNA) intercalation for targeted cancer cell death and biological imaging of both tumours and lymph nodes.\textsuperscript{18}

The development of porphyrins with variable water solubility and the use of porphyrins as light harvesters opens the potential for porphyrins to be used in an artificial photosynthetic system, capable of interacting with an aqueous solvent that will allow conversion of \( \text{H}_2\text{O} \) to molecular \( \text{O}_2 \) and the reduction of \( \text{CO}_2 \) to a fuel.

1.2 Photosynthesis

Photosynthesis has enabled plants, algae and cyanobacteria to efficiently convert sunlight into chemical energy, with the energy responsible for sustaining life on earth for the last 3 billion years.\textsuperscript{19} Photosynthesis is overall described as the conversion of sunlight, \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) into carbohydrates and \( \text{O}_2 \); however the process is performed by one of the most complex systems found in nature. The biological machine that is responsible for photosynthesis can be divided into two components; Photosystem II and Photosystem I that are responsible for light absorption and \( \text{H}_2\text{O} \) splitting and carbon fixation, respectively.

1.2.1 Photosystem II

Photosystem II is a thylakoid membrane bound complex that is responsible for the absorption of light.\textsuperscript{20} The absorption of sunlight is achieved by an elaborate antenna system that comprises light harvesting complex I, light harvesting complex II and the reaction centre. Light harvesting complex I and II are transmembrane pigment-protein complexes, which contain predominately rings of chlorophyll a and chlorophyll b. The chlorophyll molecules are closely spaced within the ring structure to allow efficient energy transfer towards the reaction centre.\textsuperscript{21}
Once chlorophyll has been excited by light in photosystem II, the dye molecule is promoted to its excited state (π-π*). Upon returning to its ground state, the excited state energy is transferred to a neighbouring chlorophyll. The antenna system in photosystem II (Figure 1-7 A) is able to funnel energy towards the reaction centre due to the differing energy levels that are observed between light harvesting complex I, light harvesting complex II and the reaction centre. Once energy is absorbed, the energy gradient allows energy to be transferred from the distant chlorophylls to the reaction centre. It should be noted that all the chlorophyll components, however close to the reaction centre are capable of absorbing light.

Once energy has been funnelled to the reaction centre, electron transfer occurs. The reaction centre has a pair of chlorophyll molecules called the “special pair” or P680, which are the primary electron donors in the photosynthetic system. The adjacent special pair allow for π orbital overlap therefore enabling the units to act as a single entity. Upon excitation via the antenna complex, the special pair is able to transfer an electron to the primary electron acceptor via either of the special pair chlorophylls, which is a chlorophyll molecule known as pheophytin (pheo) (Figure 1-7 B). Due to the close proximity to each other, the P680++-Pheo− charge pair cannot be present for long, due to its potential for charge recombination.

The electron is transferred to an electron acceptor known as quinone A (QA) to form P680++-QA−, which is unable to perform a back reaction with the P680++ due to the distance between the two compounds. The stability of this newly formed state allows for the two electron transfer from QA to quinone B (QB) to take place. The process is two one electron transfer reactions and also incorporates two hydrogen ions from outside (stromal side) the thylakoid.

\[ 2Q_A^- + Q_B + 2H^+ \rightarrow 2Q_A + Q_BH_2 \]

Once QB is reduced, a proton gradient is established and QB is able to leave its binding site, with the proton gradient and QB being utilised in photosystem I for carbon fixation.
1.2.2 Oxygen Evolving Complex

The oxygen evolving complex is also a thylakoid membrane bound structure that is directly coupled to photosystem II. The electron transport from the special pair towards $Q_B$ results in a high redox potential at the dimer that is the driving force behind the oxidation of $H_2O$ and therefore generation of molecular $O_2$. The catalytic oxidation of $H_2O$ is achieved at the manganese cluster, which is a 4 manganese atom system which is able to extract 4 electrons from 2 $H_2O$ molecules (\(2H_2O \rightarrow O_2 + 4e^- + 4H^+\)).\(^{[20]}\) The thylakoid membrane is believed to contain a channel that is able uptake $H_2O$ to the manganese cluster, to ensure that the oxidation process is separate from the aqueous bulk of the thylakoid. The separation from the aqueous bulk allows for the 5 step process to be stabilised, as each step in the 4 step oxidation only occurs once the high redox potential at the dimer is established.\(^{[28]}\) An electron is transferred from $H_2O$ via the manganese cluster to a nearby tyrosine residue (Tyr$_Z$), which then reduces the special pair. The hydrogen is released to the inside side of the thylakoid (lumen) which reinforces the proton
gradient across the thylakoid membrane. After 4 reductions of the special pair, molecular O\textsubscript{2} is released from the manganese cluster and the process starts again.

### 1.2.3 Photosystem I

Photosystem II and photosystem I are connected in series by an electron transport chain (Figure 1-8). In a substantially more complex series of proton and electron transfers Photosystem I fixes CO\textsubscript{2} into storable energy sources through a 13 reaction sequence that is comprised of 11 differing enzymes, using NADPH and ATP from the light driven reactions of photosynthesis.\[^{[29]}\]

The reduction of CO\textsubscript{2} is achieved via ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) which converts ribulose-1,5-bisphosphate and CO\textsubscript{2} into two molecules of 3-phosphoglycerate.\[^{[30]}\] 3-Phosphoglycerate is then modified as it travels through the Calvin cycle and depending on feedback mechanisms can be converted back to ribulose-1,5-bisphosphate for further carbon fixation reactions or be converted into starch.\[^{[31]}\]

![Figure 1-8. Electron transport chain between photosystem II and photosystem I, with the end products of the system being used by the Calvin Benson cycle for carbon fixation.\[^{[32]}\)](image_url)

### 1.3 Artificial Photosynthesis

Nature’s ability to convert sunlight to a useable fuel, in the form of high energy chemical bonds has inspired scientists to try to mimic the highly efficient system. Artificial photosynthesis is the generic name established for the science around the use of sunlight to split H\textsubscript{2}O into H\textsubscript{2} and O\textsubscript{2}.\[^{[33]}\] Currently many research fronts have tackled artificial photosynthesis, with
photoelectrolysis of H₂O and protein and non-protein based charge separation reaction centres all considered viable approaches towards highly efficient systems. For this thesis photoelectrolysis applications will be ignored, with the majority of information based around charge separation reaction centres.

The objective of splitting H₂O into H₂ and O₂ with high efficiency is due to the great potential of H₂ as an energy source. H₂ is capable of directly producing energy with limited detrimental impacts on the earth. H₂ also has the potential to be coupled to specific catalysts to produce more complex products. As H₂ is explosive it is associated with handling and storage issues and therefore the coupling of a H₂O splitting process to a catalyst has greater potential. Coupling the two processes is able to facilitate the hydrogenation of CO₂ to produce methanol (MeOH), a chemical that is used as a safe, transportable fuel, and a starting reagent for the generation of thousands of chemicals.

Porphyrins, along with other molecules such as phthalocyanines and rylene-based molecules hold massive potential to produce artificial photosynthetic systems, due to their ability to absorb and transfer energy. Just as photosynthesis has light absorbing non-covalent chlorophyll arrays to funnel energy towards a reaction centre, an artificial system can mimic this to create energy transfer and a desired charge separated state. Due to advances in the synthetic capabilities of porphyrins the creation of an artificial photosynthetic system can utilise covalently bound porphyrin molecules to achieve a porphyrin array and not rely on the strategic positioning of individual porphyrin molecules. By selectively modifying a porphyrin array, directional energy transfer from high energy to low energy can be achieved from a peripheral porphyrin molecule towards a central porphyrin. The covalent linking of porphyrin molecules to create stable arrays, can be performed by either a linear one dimensional approach or by creating a branched system. Both systems are capable of transferring energy efficiently however due to the larger size of the branched system; a larger light harvesting efficiency is obtained. This absorbed light is then transferred from porphyrin to porphyrin by an energy transfer process until it reaches a reaction centre. The transfer of the excited state electron is known as singlet-singlet energy transfer and refers to the spin state of the excited electron. The singlet-singlet energy transfer can also occur through space for cofacial porphyrins, however due to the energy levels of the porphyrin arrays this three dimensional energy transfer will still overall be directed to the reaction centre.
The reaction centre is responsible for the electron transfer process and therefore generation of the charge separated state that can be used for oxidation and reduction reactions.\textsuperscript{[45]} The problems arise in artificial photosynthesis with the stability of this charge separated state and therefore the electron needs to be transferred to a suitable electron acceptor so that recombination and therefore loss of energy does not occur. One method employed by various researchers is to use a fullerene molecule to stabilise the charge separated state due to its ability to be an excellent electron acceptor.\textsuperscript{[46]} One example by Guldi \textit{et al.} uses a 6 component system to establish a charge separation state by using a 4 zinc porphyrin antenna complex linked to a free-base porphyrin-fullerene reaction centre. The 4 zinc porphyrins absorb light energy and then transfer the singlet excited state to the central zinc porphyrin, which then in turn transfers the energy to a free-base porphyrin. This precursor state is then able to perform electron transfer to the covalently linked fullerene to form a nanosecond long lived charge separated state (Figure 1-9).\textsuperscript{[47]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-9.png}
\caption{A) Artificial photosynthetic system showing a branched array that has the ability to transfer energy from 3 zinc porphyrins (S), to a zinc porphyrin acceptor (A\textsubscript{1}), to a free-base porphyrin (A\textsubscript{2}) which can then transfer energy to an electron acceptor fullerene.\textsuperscript{[47]} B) Energy diagram of the artificial system.\textsuperscript{[48]}}
\end{figure}

As reported in the literature, in order to mimic a photosynthetic system, it may be necessary for an artificial system to both have similar structures to natural photosynthetic systems for efficient light-harvesting and charge-separation, which can absorb photons, generate excited states and transfer the excitation energy to an interface, where photochemical charge separation takes place.\textsuperscript{[49]} While a large number of synthetic structures have been reported that harvest light and separate the resulting charge generated, none of these have light
harvesting and charge separation structures similar to the natural systems.\textsuperscript{[50]} Such a structure could be envisaged as containing an array of synthetic chlorophylls or porphyrins covalently or non-covalently connected to an energy-accepting porphyrin housed in a protein matrix with an embedded electron acceptor (Figure 1-10).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{model_covalent_porphyrin_array.png}
\caption{Model of covalent porphyrin array bound to a protein scaffold, known as a protein maquette.}
\end{figure}

### 1.3.1 Protein Maquettes

The structure of the photosynthetic array has inspired chemists to engineer artificial photosynthetic systems that utilise energy absorption molecules incorporated into a protein structure.\textsuperscript{[34d]} The complexity of the photosynthetic system has resulted in simplified protein structures that can be designed to bind specific molecules. One method that has been employed is the use of protein maquettes to bind natural dye molecules.\textsuperscript{[51]} Maquettes are synthetic proteins comprised of 4 $\alpha$-helix bundles that are currently used to mimic and study natural processes.\textsuperscript{[52]} The Dutton laboratory has engineered protein maquettes to contain histidine residues on the interior of their structure that are capable of binding natural iron(III) porphyrin molecules (haem).\textsuperscript{[53]} It is therefore believed that these maquettes have the potential to act as scaffolds for porphyrins and porphyrin arrays and with advanced engineering of the maquettes different electron acceptors. This would therefore mean stable charge separated states can be achieved between the bound porphyrin and bound electron acceptors. The charge separated state is potentially stable in the maquette as, just like the natural photosynthetic system, proteins are capable of insulating the charge from the bulk solution. The maquette also has the potential to allow incorporation of a catalytic $\text{H}_2\text{O}$ oxidising complex and carbon fixation catalyst, to produce a system that mimics photosynthesis in its entirety.
Currently the Dutton laboratory has various protein maquettes that can be utilised in the creation of an artificial photosynthetic system. The advantage of the protein maquette is the huge structural potential of the molecules, with hydrophilic, hydrophobic and amphiphilic functionality capable of being installed. The maquettes can also be designed to bind a variety of cofactors internally or externally. The positioning of histidine residues on the interior of the protein maquette can specifically bind both zinc(II) and iron(III) porphyrins and therefore opens the potential of generating a functional artificial photosynthetic system (Figure 1-11). Currently, the Dutton laboratory has shown various amphiphilic compounds are able to bind to protein maquettes including iron containing haems, bacteriochlorophylls and synthetic porphyrins such tetracarboxyphenyl porphyrin. Binding through maquette histine residues has also been promising for zinc containing porphyrins. Through these investigations it has been shown that molecules with a solubilisation component (carboxylic acids) are desired to allow for the large hydrophobic porphyrin core to bind in the hydrophobic interior of the protein maquette.

**Figure 1-11.** 4-α helix maquettes, tethered by differing chemical linkages, with co-factors and co-factor binding sites.
To generate a maquette based artificial photosynthetic system, the design of a series of amphiphilic porphyrin arrays is desired. It is proposed an amphiphilic porphyrin array would be capable of binding to the hydrophobic centre of the protein maquette through a hydrophobic zinc or iron porphyrin. The bound porphyrin would then allow for the hydrophilic portion of the porphyrin array to interact with the aqueous environment. The design will therefore allow for the harvesting of sunlight by the array and directional energy transfer towards the bound porphyrin (Figure 1-12). The development of the artificial photosynthetic system that incorporates porphyrin arrays will need to use a synthetic methodology that facilitates the step-by-step increase of array size. As photosynthesis uses 200-300 chlorophyll molecules to absorb and transfer energy to a reaction centre, we will need to determine how many covalently attached porphyrins are necessary for efficient light harvesting.[57] The end goal of an artificial photosynthetic system that is capable of oxidising H₂O means that the porphyrin arrays being inserted into the protein maquettes need to at least be able to interact with the aqueous environment, if not be water soluble.

![Figure 1-12. Model of proposed maquette-porphyrin artificial photosynthetic system.](image)

### 1.3.2 Water Soluble Porphyrins

Porphyrins are usually insoluble in H₂O due to their planar hydrophobic structure and their consequent ability to stack easily due to their large π-π interactions.[58] To solubilise porphyrins, a formal charge is commonly placed on the structure to allow for the compound to interact with H₂O.[59] Both anionic and cationic porphyrins are capable of solubilising the porphyrins, however these groups are usually positioned on aromatic substituents to ensure that aggregation is kept...
Meso substituted aromatic rings sit outside the plane of the porphyrin and therefore block face-to-face (H-type) aggregation; however side-by-side (J-type) aggregation is still possible.\textsuperscript{[58a, 60]} Currently benzoic acid, benzenesulfonic acid and aryl quaternary ammonium salts are used to make meso-substituted water soluble porphyrins (Figure 1-13).\textsuperscript{[61]} Due to the problems associated with purification of a formally charged porphyrin, the charge is usually masked until after porphyrin synthesis and purification is complete then a single reaction is employed to form the anion or cation.

![Figure 1-13. Aqueous solubilising groups for solubilisation of tetraarylporphyrins.](image)

### 1.3.3 Amphiphilic Porphyrins

The use of water solubilising groups in conjunction with hydrophobic groups and the hydrophobic porphyrin core has been a key area of research, due to the huge potential of the synthesised molecules. Specifically, the generation of amphiphilic molecules has been used extensively in the creation of supramolecular structures that can then be used as sensors, catalysts and for molecular electronics.\textsuperscript{[62]} The majority of synthetic work for amphiphilic molecules has been performed on single porphyrins, however the synthetic methodologies could be utilised for the creation of amphiphilic porphyrin arrays for binding to protein maquettes.\textsuperscript{[63]}

### 1.3.4 Non-Charged Amphiphilic Porphyrins

Non-charged functional groups have been used for the creation of amphiphilic porphyrin molecules, with hydroxyl, carbohydrate and polyethylene glycol (PEG) groups allowing differing levels of water solubility. Hydroxyl group containing porphyrins are usually directly synthesised through mixed aldehyde Adler-Lungo or Lindsey synthesis, with flash chromatography used to
separate the individual porphyrins.\[[64]\] Hydroxyl group porphyrin hydrophilicity is increased as pH is increased with deprotonation of the -OH groups occurring.\[[65]\]

Carbohydrate and PEGylated amphiphilic porphyrins are commonly synthesised by binding the water soluble group to an appropriate functional group present on a synthesised porphyrin.\[[66]\] PEG functionalised porphyrins have been used extensively in medical applications due to the PEG components stability in cells.\[[67]\] Scheme 1-2 shows the post synthesis modification of a PEGylated porphyrin, with solubility achieved in both aqueous and organic (CH\(_2\)Cl\(_2\), CHCl\(_3\)) solvents.\[[63, 68]\] As the synthesis of amphiphilic porphyrin arrays will need to solubilise a large hydrophobic unit, non-charged functional groups will be ignored for this thesis.

![](image.png)

**Scheme 1-2.** Synthesis of PEG containing amphiphilic porphyrin.\[[63]\]

### 1.3.5 Formally Charged Amphiphilic Porphyrins

Formally charged amphiphilic porphyrins are capable of producing molecules with high degrees of H\(_2\)O solubility. The majority of work towards formally charged amphiphilic porphyrins is based
around single, tetraarylporphyrins however alkyl derivatives have also been synthesised.\textsuperscript{[63]} Amphiphilic porphyrins are synthesised using one of two methodologies;

- Synthesis of mixed aldehyde porphyrin with precursor hydrophilic groups and hydrophobic groups. After purification and desired modifications (metalation) the formal charge is then exposed as the final step; and
- Synthesis of a porphyrin with a functional group capable of reacting with a specific hydrophilic or hydrophobic unit.

Carboxylic acid containing amphiphilic porphyrins have been studied extensively, with the simplest synthetic method being a mixed aldehyde condensation with a hydrophobic aldehyde and ester containing aldehyde.\textsuperscript{[69]} Purification by flash chromatography and subsequent hydrolysis is capable of producing 4 amphiphilic porphyrins, with differing aqueous solubility and aggregation characteristics.\textsuperscript{[70]} More complex carboxylic acid containing porphyrins can also be produced by linking ester containing groups to functionalised porphyrins. Small groups such as malonates and highly charged dendrons have been used to impart water solubility into hydrophobic porphyrins and porphyrin-fullerene conjugates (Figure 1-14).\textsuperscript{[71]} Solubility is limited for carboxylic acid containing amphiphilic porphyrins, with acidic conditions resulting in compound aggregation and subsequent insolubility.

![Figure 1-14. Benzoic acid containing amphiphilic porphyrin, synthesised by a mixed aldehyde synthesis.\textsuperscript{[63]} B) Malonic acid containing amphiphilic porphyrin synthesised by post porphyrin synthesis modification.\textsuperscript{[71b]} C) Porphyrin-fullerene conjugate with carboxylic acid containing dendron.\textsuperscript{[71a]}](image-url)
Sulfonic acid groups can also be used in the generation of amphiphilic porphyrin molecules. The addition of the sulfonic acid group is more synthetically challenging than carboxylic acid containing molecules, however the group has a wider aqueous solubility range with porphyrins commonly soluble in acidic conditions. Sulfonation of TPP is able to produce a series of amphiphilic porphyrins, however the problematic purification results in a mixture of inseparable sulfonated porphyrin products.\(^{72}\) The preferred method for creating sulfonated amphiphilic porphyrins, is a 2 step synthesis with a trimethylsilyl-substituted intermediate. The mixed aldehyde condensation of a hydrophobic aldehyde and trimethylsilyl-substituted aldehyde allows for porphyrin purification. Treatment with trimethylsilyl chlorosulfonic acid and hydrolysis with aqueous \(\text{NaOH}\), produces a single amphiphilic porphyrin at high yields (Scheme 1-3).\(^{73}\)

\[
\text{Scheme 1-3. Synthesis of sulfonic acid containing amphiphilic porphyrin.}^{63, 73a}
\]
Positively charged pyridinium and ammonium amphiphilic porphyrins are also synthesised using the same synthetic principles as their negatively charged counterparts. Similar to sulfonic acid porphyrins, positively charged porphyrins are soluble over a large pH range if more than 1 formal charge is present in the molecule. Pyridiniumporphyrins are most commonly prepared through mixed aldehyde Adler-Longo synthesis, with the isolated porphyrins subjected to N-alkylation with varying length alkyl bromides capable of producing high yielding products (Figure 1-15). 

![Figure 1-15. N-methylpyridiniumporphyrins synthesised by mixed aldehyde condensation.](image)

Problematic purification issues associated with amine based porphyrins has resulted in mixed aldehyde Lindsey porphyrin synthesis followed by alkylation or post porphyrin synthesis functionalisation being the main methods of ammonium containing amphiphilic porphyrins. The 2 methods are capable of producing highly varied amphiphilic molecules, with alkylation performed at high yields. Monti et al. introduced the ammonium group by Williamson ether synthesis, to place the positive charge away from the porphyrin core (Scheme 1-4).

![Scheme 1-4.](image)
Scheme 1-4. Williamson ether synthesis for generation of ammonium containing amphiphilic porphyrin.\textsuperscript{[77]}

The methodologies behind the synthesis of single amphiphilic porphyrins can be carried over to synthesis of amphiphilic porphyrin arrays, with the 2 major techniques applicable to array synthesis. Use of a precursor synthetic group that can be exposed as a last synthetic step or attachment of a water soluble unit, such as a dendron, to a functional group present on the porphyrin can be used towards the creation of maquette binding arrays.

1.4 Synthetic Strategy

The creation of a catalogue of amphiphilic porphyrin arrays for use in maquette-based artificial photosynthetic systems, will require specific synthetic strategies to enable the synthetically challenging structures to be created. The design of a synthetic strategy that can efficiently study maquette binding characteristics by easily changing between array size and composition, means
a building block technique is suited to the project. The design of a building block methodology can facilitate the easy interchange of array size and metal substitution pattern.\textsuperscript{[28]} Change in linker and subsequent reaction with the porphyrin building blocks can allow the step-by-step increase of array size (1→2→4→6→8). Currently both linear and branched covalent porphyrin arrays have been synthesised using porphyrin blocks and therefore these approaches can be utilised for creation of amphiphilic arrays. Both linear and branched approaches however have similar synthetic strategies with functionalised porphyrins being connected through a linker. Although the basic principles of array synthesis can be carried over to the design of amphiphilic arrays, specific challenges will require new approaches.

Amphiphilic arrays are designed to incorporate both a hydrophobic porphyrin connected to a H\textsubscript{2}O soluble region. This therefore requires the arrays to be synthesised by a step-by-step approach, to eliminate the potential of unwanted symmetrical side products. The connection of a hydrophobic porphyrin to a linker will enable purification of the intermediate and insertion of metal ligands to the porphyrin core, before the H\textsubscript{2}O soluble unit is incorporated.

The incorporation of the H\textsubscript{2}O soluble unit incorporates challenges, due to the issues associated with the purification of formally charged structures. To enable purification the synthetic strategy will need to incorporate a precursor H\textsubscript{2}O soluble unit that can expose a formal charge as a final single step. The use of the precursor unit will allow purification of the porphyrin array and subsequent metal insertion, to produce unsymmetrical porphyrin arrays with complete control of metal centre with hydrophobic and hydrophilic units (Figure 1-16).
Figure 1-16. A building block strategy for the synthesis of H₂O soluble amphiphilic porphyrin arrays.

The Officer laboratory has to date used Wittig chemistry to produce a series of amphiphilic dyads for surface binding studies in association to photovoltaics.[79] The synthesis of these structures has therefore proved the step-by-step approach to be successful for generation of amphiphilic dyads and allowed for a further investigation into a broad study for synthesis of maquette binding structures (Figure 1-17).

Figure 1-17. Structure of vinyl linked amphiphilic porphyrin dyad.[79]
1.5 Thesis Aims

The overarching aim of this thesis was to develop synthetic methods for the creation of a series of novel amphiphilic porphyrin based compounds and materials for applications in aqueous environments such as protein intercalation. More specifically, the individual aims of this thesis include:

- The aim of Chapter 1 was around the development of a flow chemistry methodology to allow for the synthesis of high yielding, large scale porphyrins. Future chapters involve the synthesis of amphiphilic porphyrins and therefore gram quantities of a series of tetraaryl porphyrins were required. Parameter and reaction concentration development was therefore required to allow for a porphyrin reaction to be set up and run for extended periods of time. Once perfected, gram quantities of porphyrins could be synthesised for the remaining thesis chapters.

- The artificial photosynthesis project between the Officer and Dutton laboratories required the synthesis of amphiphilic porphyrin arrays to bind to the protein maquettes. The Wittig reaction between porphyrin building blocks therefore needed development to allow for the linking of water soluble porphyrins to a hydrophobic porphyrin. Benzoic acids, N-methyl pyridinium and sulfonic acid amphiphilic arrays therefore were synthesised to allow Mr Christopher Hobbs to use the molecules in maquette binding studies and DSSC development.

- The Knoevenagel reaction between formyl porphyrins and phenylacetonitriles has shown promise for the synthesis of porphyrin arrays and therefore amphiphilic porphyrin arrays. The aim of Chapter 4 was therefore the development of porphyrin arrays for use in the protein maquette artificial photosynthesis project. The incorporation of water soluble units has previously been shown to introduce synthetic challenges and therefore it was believed a hydrophobic library should also be synthesised to understand the reaction and physical characteristics of the molecules.

- The interaction of porphyrins and solid supports such as protein maquettes indicates that binding of porphyrins to other structures should also open up exciting possibilities. Therefore, Chapter 5 aims to synthesise a porphyrin-hydrogel to determine its capabilities including the materials sensing potential.
1.6 Thesis Structure

The potential of porphyrins towards various applications has made the heterocycles targets for synthetic chemists. The Officer group over the years has been interested in the functionalisation of porphyrins by Wittig chemistry for various solar cell projects. The research has however been based consistently around hydrophobic structures, with amphiphilic or H$_2$O soluble compounds ignored. This thesis is structured around the synthesis of H$_2$O soluble porphyrins and the application of these H$_2$O soluble units.

Chapter 2 describes the synthesis and modification of porphyrins by flow chemistry with the aim of developing a new large scale porphyrin synthesis method suitable for amphiphilic porphyrin production. The new synthetic methodology utilises Adler-Longo styled synthesis to create a series of porphyrins in the flow chemistry apparatus. A resulting high yielding and large scale synthesis of tetraphenylporphyrin (TPP) enabled the porphyrin to be used in Chapters 3 and 4. Copper insertion and formylation of TPP were also performed by flow chemistry.

In Chapter 3, Wittig chemistry is utilised to create a series of amphiphilic porphyrin dyads. A sulfonic acid containing dyad was successfully prepared, while the preparation of pyridinium and 4-benzoic acid containing dyads were unsuccessful. 3-Benzoic acid containing dyads were also made, with metal substitution patterns controlled (Zn-Zn, Zn-Fe, Zn-Free-base) for maquette binding studies. The dyad product from the unsuccessful attempts to produce amphiphilic porphyrin trimers opened the way for the investigation into differing energy transfer molecules, with a hydrophobic porphyrin-fullerene conjugate being successfully made.

Chapter 4 introduces a new synthetic strategy for the functionalisation of porphyrins, in an attempt to produce amphiphilic porphyrin dyads for maquette binding studies. Knoevenagel chemistry was used to link to formylporphyrins, with functionalised monomers and dyads synthesised. Characterisation of the synthesised molecules was performed, with 2D NMR spectroscopy, electrochemistry and DSSC performance all extensively investigated. The synthetic methodology was however unsuccessful in the synthesis of amphiphilic porphyrins arrays.

Chapter 5 develops a new methodology for the synthesis of covalently bound porphyrin hydrogels. The 2 step synthesis links 4-carboxyphenylporphyrin to a Jeffamine polymer. Once purified the polymer appended porphyrin is then reacted with an epoxide containing polymer
to form a covalent network. The porphyrin hydrogel is then used to sense heavy metals, with mercury and cadmium both identified.
Chapter 2
Synthesis and Modification of Porphyrins by Flow Chemistry
2.1 Introduction

The overall aim of this thesis was to develop a series of amphiphilic porphyrin molecules for binding to protein maquettes to create an artificial photosynthetic system. It was determined at the outset of this thesis that multi-gram quantities of several tetraarylporphyrins would be required to generate the proposed amphiphilic porphyrin molecules. The requirement of high scale and high yield porphyrin synthesis, coupled to the introduction of a flow chemistry reactor into our synthetic labs, offered the potential to investigate a new approach to porphyrin synthesis. Chapter 2 is therefore based around the development of a new synthesis and functionalisation of tetraarylporphyrins by flow chemistry.

2.1.1 Porphyrin Synthesis

Adler-Longo, Lindsey and microwave synthesis are currently the most common high yielding porphyrin syntheses; however all have limitations in respect to large scale porphyrin synthesis as compared in Table 2-1. These reactions are commonly performed in high surface area to volume vessels (round bottom flask, microwave vessels), which are designed to maximise efficiency of heat transfer and stirring of reactions. As scale increases, there is a drop in both heat transfer and mixing efficiencies.\[80\]

To achieve optimum yields, heat transfer in a reaction needs to be finely controlled. In regards to exothermic reactions, highest yields will be produced when heat generated is equal to heat dissipated by removal of energy through reactor walls or reaction surroundings. Temperature control will avoid excess reaction heating, which with small temperature changes has the potential to lead to side reactions and degradation of reagents, products and catalytic material.\[81\] These aspects also affect endothermic reactions and therefore temperature control is necessary for both types of reactions. As scale increases, the control of reaction temperature is reduced as heat transfer rates between bulk solution and reactor wall and reaction surroundings decreases.

Batch reaction mixing is also affected by increases in reaction scale. Changes in reaction volume will result in changes in reactor size, reaction stirring speed and type of impeller which all have the potential to impact reaction yield.\[82\] Optimum yields are achieved with complete reaction mixing, as it ensures required reaction stoichiometry is attained. Reaction mixing can be altered
by one order of magnitude by stirring rate, while type of impeller and ratio of impeller diameter to reactor diameter has the ability to alter reaction mixing by 4 orders of magnitude.\cite{81} If reaction parameters are not redeveloped from small scale reactions to large scale, which is an expensive and time consuming process, heating and mixing of large scale reactions will result in undesirably low yields and increases of side products.

**Table 2-1.** Comparison of porphyrin synthesis techniques with proposed large scale flow chemistry synthesis.

<table>
<thead>
<tr>
<th></th>
<th>Adler Synthesis</th>
<th>Lindsey Synthesis</th>
<th>Microwave Synthesis</th>
<th>Proposed Flow Chemistry Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction Concentration</strong></td>
<td>0.01 M</td>
<td>0.2 M</td>
<td>20 M</td>
<td>-</td>
</tr>
<tr>
<td><strong>Reaction Time</strong></td>
<td>30 min</td>
<td>180 min</td>
<td>3-5 min</td>
<td>-</td>
</tr>
<tr>
<td><strong>Yield (TPP)</strong></td>
<td>25%</td>
<td>50%</td>
<td>41%</td>
<td>-</td>
</tr>
<tr>
<td><strong>Heating Efficiency</strong></td>
<td>-Small Scale-High/Large Scale-Low</td>
<td>-Small Scale-High/Large Scale-Low</td>
<td>-Small Scale-High/Large Scale-Low</td>
<td>-Small Scale-High/Large Scale-High</td>
</tr>
<tr>
<td><strong>Mixing Efficiency</strong></td>
<td>-Small Scale-High/Large Scale-Low</td>
<td>-Small Scale-High/Large Scale-Low</td>
<td>-Small Scale-High/Large Scale-Low</td>
<td>-Small Scale-High/Large Scale-High</td>
</tr>
<tr>
<td><strong>Formation of Solids</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Problematic</td>
</tr>
<tr>
<td><strong>Human Involvement: Starting Material To Product</strong></td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Worker Exposure to Hazardous Materials</strong></td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Scale Up Potential</strong></td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

Microwave irradiation can overcome some of the problems associated with large scale synthesis, by using short reaction times to perform batch synthesis that give high yields repetitively. This is achieved due to microwave synthesis reducing reaction time from 30 min (Adler) and 3 h (Lindsey) to 4 min.\cite{10-11,83} Although successful in obtaining large quantities of high yielding product, the process increases the amount of post synthesis processing. Despite
literature reports of clean products from microwave synthesis, our groups experience is that product purification is more difficult following the microwave method due to problematic removal of polymeric tar from the desired porphyrin.\cite{83}

Recent advances in technology has allowed for investigation into potential large scale porphyrin synthesis by flow chemistry. The proposed flow chemistry porphyrin synthesis method can be compared to the common porphyrin synthetic methods, with the benefits being shown in large scale heating and mixing efficiencies (Table 2-1). Flow chemistry also reduced human exposure to harmful materials and therefore offers huge potential to porphyrin scale up reactions.

### 2.1.2 Flow Chemistry

Continuous flow reactors have been used by chemical engineers to perform large scale reactions in industries such as the petroleum, polymer and pharmaceutical industries. Chemical plants and refineries use piping to transport material between large processing units, with parameters such as temperature, pressure, flow rate and chemical composition monitored throughout the whole process.\cite{84} The continuous process is able to run for years, with exposure of hazardous materials to humans kept to a minimum due to containment of reactions within the series of tubing. The design of scaled down versions of continuous flow reactors has recently allowed for research chemists to explore a new method of laboratory synthesis to compete with round bottom flask and microwave reactions.\cite{85}

Flow chemistry systems are instruments that use flow channels that can withstand high and low temperatures, high pressures, varying flow rates and highly reactive reagents or intermediates to perform differing organic reactions.\cite{86} The system is comprised of a series of key units that are bridged by connective tubing and can be externally controlled to provide a programmable platform for organic synthesis. Pumps are used to establish the flow of reagent and solvent in the system, with flow rates established by computer control. Control of flow rates is necessary to ensure both reagent stoichiometry, reaction concentration and resolution times on the reaction platform are at an optimum. Introduction of reagents into the flow chemistry system can be performed by dissolving into solvent supply, or introduced independently by reagent coils. The use of multi-pump flow chemistry systems will result in the use of either a T-piece or mixing chip to ensure reagents from each pump are effectively combined. The flow stream is then moved along to the reaction coil in which the reaction can be exposed to high or low
temperatures throughout the retention time. As flow channels are in the mm dimension mixing efficiencies and temperature transfer at these points are extremely high. The installation of a back-pressure regulator after the reaction coil ensures reaction pressure is monitored. Product is then deposited in a collection vial for work up and purification (Figure 2-1). \[87\]

![Flow Chemistry Instrument](image)

1 Reagent/solvent stock; 2 Pumps; 3 Reagent coil; 4 Mixing chip; 5 Reaction coil; 6 Back pressure regulator; 7 Computer control.

**Figure 2-1.** Schematic of flow chemistry instrument, with primary units.

Along with benefits such as containment of hazardous or odorous materials and high mixing and temperature transfer, the main advantage to flow chemistry is the scale up potential.\[88\] Once optimisation of a reaction is reached the development required is small in comparison to batch processes, for large scale production. Only minor changes are necessary for increase in flow
diameter while no changes are necessary for parallel synthesis, with deposit of product into a general collection vial.

Flow chemistry has been utilised by research chemists to successfully perform various small molecule reactions, such as acylation, alkylation, and olefination. Small molecule chemistry can provide insight into flow chemistry, however the synthesis of functional materials is more attuned to flow chemistry porphyrin synthesis. A major limitation associated with synthesis by flow chemistry is how the instrument handles the movement of solids throughout the system, with blocking of tubing known to damage the instrument. Synthesis of porphyrins is coupled to aggregation resulting in the formation of solids during the reaction, specifically upon cooling, therefore the potential for clogging the instrument is high. It has been shown nonetheless, that with the correct parameters the flow of suspended solid materials can be maintained giving high yields of synthesised materials. The nucleated growth of nanomaterials such as quantum dots, nanoparticles (gold, silver, zinc oxide) and metal-organic frameworks (MOFs) have all been optimised for flow chemistry and show promising control of particle growth without blocking and damaging the flow chemistry unit.

2.2 Porphyrin Synthesis by Flow Chemistry

A Uniqsis FlowSyn flow chemistry apparatus was used for the synthesis and modification of porphyrins (Figure 2-2). The instrument was used as a two pump system with reagents and solvent combined in separate Schott bottles. A glass static mixer-reactor chip was used primarily as a mixing unit, to combine reagents from pump A and B, with a reaction coil placed after for heating of the reaction mixture. A 2 mL reaction coil was used for the majority of reactions, with a 20 mL reaction coil only used for scale up investigations. A pressure regulator was used after reaction coil to ensure a constant pressure was maintained throughout the reaction. Reaction contents were then deposited into a Schott bottle, for reaction work up and analysis.
Porphyrin synthesis by flow chemistry allowed the investigation of both Adler-Lungo and Lindsey type syntheses. Initially it was decided that Alder-Lungo synthesis would be used, given the simpler reaction conditions with pyrrole and aryl aldehydes heated in propionic acid and dissolved O\(_2\) used as reaction oxidant. The one step reaction eliminates optimisation of porphyrinogen yield, followed by use of a third pump to inject a chemical oxidant for porphyrin formation (Lindsey synthesis).

To establish the reaction versatility of porphyrin flow chemistry synthesis, the targeted porphyrin series included electron withdrawing, electron donating and \(\text{ortho, meta and para}\) substituted aryl aldehydes. 4-methoxybenzaldehyde, benzaldehyde, 4-bromobenzaldehyde, 4-ethylbenzaldehyde, 3,5-di-tert-butylbenzaldehyde, methyl 4-formylbenzoate, 3,5-dimethoxybenzaldehyde and 4-nitrobenzaldehyde were therefore used to test electronic and steric effects (Figure 2-3).
To determine optimum conditions for Adler synthesis by flow chemistry, differing parameters were probed. An instrument heating limitation of 150°C meant reaction temperature could not be pushed to the high temperatures (200°C) that high yielding microwave irradiation porphyrin synthesis achieves and therefore reactions were performed at 141°C, the boiling point of propionic acid. The synthesis of 5,10,15,20-tetra(4-methoxyphenyl)porphyrin 1 was performed as the model for reaction optimisation, with flow rates examined for each porphyrin (Table 2-2).

Table 2-2. Yield of 1 at differing flow rates and concentrations.

<table>
<thead>
<tr>
<th>Flow Rate (mL min⁻¹)</th>
<th>0.1 M</th>
<th>0.2 M</th>
<th>0.3 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>6.2</td>
<td>4.3</td>
<td>3.0</td>
</tr>
<tr>
<td>0.10</td>
<td>6.5</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>0.08</td>
<td>6.8</td>
<td>9.6</td>
<td>-</td>
</tr>
<tr>
<td>0.06</td>
<td>5.4</td>
<td>5.9</td>
<td>-</td>
</tr>
<tr>
<td>Batch Conditions</td>
<td>14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Standard Adler-Lungo conditions are performed at a reaction concentration of ~0.2 M; therefore reactions were based around this and performed at 0.1 M, 0.2 M and 0.3 M. Both 0.1 M and 0.2 M showed similar trends with porphyrin yield increasing from 0.20 mL min⁻¹ to 0.08 mL min⁻¹ followed by a yield decline at the slowest flow rate of 0.06 mL min⁻¹. The 0.3 M reaction resulted in blocking of the flow chemistry apparatus, so full investigation into higher concentration reactions could not be performed. Highest yields of 9.6% at 0.2 M, coupled with risk of instrumentation damage by system blocking meant all porphyrin syntheses were performed at 0.2 M.
Table 2-3. Yields of 2-8 at differing flow rates, with all reactions performed at 0.2 M.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>0.20 mL min⁻¹</th>
<th>0.10 mL min⁻¹</th>
<th>0.08 mL min⁻¹</th>
<th>0.06 mL min⁻¹</th>
<th>Batch Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>7.11</td>
<td>15.0</td>
<td>29.0</td>
<td>21.6</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>8.0</td>
<td>17.5</td>
<td>19.5</td>
<td>11.5</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>3.5</td>
<td>5.8</td>
<td>7.4</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>3.8</td>
<td>4.2</td>
<td>4.5</td>
<td>3.9</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>7.0</td>
<td>10.5</td>
<td>12.5</td>
<td>9.0</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>8.5</td>
<td>12.5</td>
<td>13.0</td>
<td>14.5</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Porphyrin synthesis was performed for a further seven aryl aldehydes (Table 2-3). The syntheses of TPP 2, 5,10,15,20-tetra(4-bromophenyl)porphyrin 3 and 5,10,15,20-tetra(4-ethylphenyl)porphyrin 4 show yields similar to literature, with standard Adler-Longo conditions averaging around 25% for 2, 20% for 3 and 8% for 4. Literature precedents of 14% (5,10,15,20-tetra(4-methoxyphenyl)porphyrin 1), 30% (5,10,15,20-tetra(3,5-di-tert-butylphenyl)porphyrin 5) 20% (5,10,15,20-tetra(4-methylesterphenyl)porphyrin 6) and 22% (5,10,15,20-tetra(2,5-dimethoxyphenyl)porphyrin 7) showed remaining flow synthesis was below standard synthesis highest yields. Attempts to synthesise 5,10,15,20-tetra(4-nitrophenyl)porphyrin 8 resulted in blocking of the instrument, with a thick precipitate being formed in the instrument’s mixing chip (Table 2-3).

Poor yields of 4 could also be the result of incomplete reaction oxidation and therefore chlorin formation. Thin Layer Chromatography (TLC) analysis showed a large green spot of lower polarity (in comparison to porphyrin) indicative of chlorin formation. Addition of p-chloranil post porphyrin synthesis increased reaction yield to 9.0%. TLC comparison between each porphyrin synthesised showed that chlorin contamination was only problematic for 4 suggesting that further chemical oxidation was not required for other reactions.

The low yield observed for 4 of 9.0% led to an investigation of alternative conditions to determine if higher yields could be achieved. Campbell et al. showed that a 1:1 mixture of propionic acid:octanoic acid increased the yield of 4 to 20%. Flow chemistry yield for this solvent mixture however decreased to 5.4%. The high yield achieved by Campbell et al. was obtained at solvent reflux temperature, which, due to instrument limitations, was a temperature unachievable by flow chemistry. As pKa and polarity are very similar between propionic acid and
octanoic acid, it can be concluded that the high yield non-flow chemistry of 20% and low flow chemistry yield of 5.4% are due to the differing reaction temperatures.\cite{93a}

During characterisation of the synthesised porphyrin series it was noted that a complex $^1$H NMR spectrum was observed for porphyrin 7. As a simple tetraarylporphyrin spectrum was expected a high/low temperature NMR spectroscopy study was performed and can be found in Section 2.3.

Synthesis of the tetraarylporphyrin series proved that flow chemistry was a successful method for the synthesis of porphyrins. The yields were comparable to standard Alder synthesis conditions, however the value of the method was associated to the methods large scale synthesis potential (Section 2.2.2). Once optimal conditions are determined, the flow chemistry apparatus can then be left to run, with no operator input for h/days. Synthesis of large amounts of high yielding porphyrin can therefore be set up in the afternoon and run overnight, with the chemist returning in the morning for porphyrin purification.

### 2.2.1 Flow Chemistry Reaction Analysis

To determine porphyrin yields, the reaction mixture was analysed by UV-vis spectroscopy with the porphyrin’s soret band extinction compared against a standard curve. The spectroscopic analysis of porphyrin yield relative to reaction time shows similar trends for the majority of porphyrins. The general trend involved an increase in porphyrin yield over time, with a maximum yield observed for a 25 min reaction, followed by a yield reduction (Figure 2-4 a). Similar trends are observed for both Adler-Lungo metalloporphyrin synthesis and microwave porphyrin synthesis (see Figure 2-4 b).\cite{12, 83} Porphyrins 4 and 7 were the exception with maximum yields observed at a 33 min retention time. Reactions were attempted at 0.04 mL min$^{-1}$ (50 min retention) to determine if higher yields were achievable however blocking of the reactor tubing occurred for all reactions, as was typically experienced for this reactor at low flow rates.
Figure 2-4. A) Flow chemistry yield of tetraarylporphyrins 1-7 from this work. B) Microwave synthesis (from reference 82) yield of tetraarylporphyrins 3a-h.\textsuperscript{[83]}

2.2.2 Large Scale Synthesis

To assess the scale up potential of porphyrin synthesis by flow chemistry, the use of a larger reaction coil for multi gram synthesis was investigated. An increase in the reaction coil length from 2 mL to 20 mL would determine if retention time was the major effect upon reaction yield or if reaction flow rates had significant influence. As flow chemistry tubing diameter is the same between the 2 mL and 20 mL reaction coil, to maintain the reactions retention time on the reactor coil, flow rates will need to be adjusted. Using the highest yielding TPP 2 synthesis to
compare yields, a 10 fold increase in flow rate accompanied the 10 fold increase in reaction coil length. The 0.8 mL min$^{-1}$ flow rate produced TPP in 28.2% yield. Comparison between the 2 mL and 20 mL reaction coil showed a negligible yield difference, indicating that a 10 fold scale up of porphyrin synthesis can be performed with little redevelopment of reaction conditions. High yields, increased flow rate and the use of a 20 mL reaction coil meant TPP 2 synthesis could be performed continually for multi gram porphyrin production. Repeated and extended TPP synthesis was able to produce 5.2 g of porphyrin, demonstrating that multi gram production was achievable by flow chemistry.

2.2.3 Porphyrin Modification by Flow Chemistry

Porphyrin modification is typically necessary for most porphyrin-based applications to alter their electronic properties for the specific application. Porphyrin synthesis by flow chemistry has opened the door for further chemistry to be developed with these materials.

2.2.4 Copper Insertion

The use of metal salts to produce metalloporphyrins is one of the most commonly performed porphyrin reactions. Metalations are usually performed by reacting a metal salt in an organic solvent such as CHCl$_3$, toluene or dimethylformamide (DMF), with solvents such as MeOH used to dissolve or suspend the metal salt (Scheme 2-1).

\[(i) \text{1.2-1.3 eq. Cu(OAc)$_2$·H$_2$O, CHCl$_3$, MeOH, reflux, 30 min.}^{93a} (ii) \text{1.4 eq. Cu(OAc)$_2$·H$_2$O, CHCl$_3$, MeOH, 30°C, 30 min.}^{93a}\]

Scheme 2-1. Copper insertion reaction.
Copper insertion was performed by preparing 0.001 M solutions of 2 in chloroform and copper(II) acetate in MeOH. An overall flow rate was established at 4 mL min\(^{-1}\) with pump A and B altered to achieve specific reagent ratios along with a variation in temperature (Table 2-4). Reagent mixing was performed in the chip reactor (4, Figure 2-1), while heating was performed in the 2 mL reaction coil (5, Figure 2-1) (also see Figure 2-2).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>TPP:Cu(AcO)(_2) 1:1.1</th>
<th>TPP:Cu(AcO)(_2) 1:1.2</th>
<th>TPP:Cu(AcO)(_2) 1:1.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Incomplete</td>
<td>Incomplete</td>
<td>Complete</td>
</tr>
<tr>
<td>40</td>
<td>Incomplete</td>
<td>Incomplete</td>
<td>Complete</td>
</tr>
<tr>
<td>50</td>
<td>Incomplete</td>
<td>Incomplete</td>
<td>Complete</td>
</tr>
<tr>
<td>60</td>
<td>Incomplete</td>
<td>Incomplete</td>
<td>Complete</td>
</tr>
<tr>
<td>70</td>
<td>Incomplete</td>
<td>Incomplete</td>
<td>-</td>
</tr>
</tbody>
</table>

A less than 50% excess of copper(II) acetate (1.4 eq.) was able to achieve complete copper insertion for all temperatures, with conversion monitored by both TLC and matrix assisted laser desorption ionisation (MALDI) mass spectrometry. Comparison of flow chemistry and round bottom flask copper insertion over 30 min indicated that flow chemistry could produce 0.025 g of CuTPP while multi gram quantities could be produced in a round bottom flask.\(^{[96]}\) This was due to the solubility of copper(II) acetate in MeOH, which was the limiting factor in the flow chemistry reaction. To overcome this type of problem, the use of solid support-filled cartridges for catalytic flow chemistry reactions such as hydrogenation have been successful.\(^{[97]}\) The use of copper(II) acetate filled cartridges was investigated by Dr Ashley Walker in our laboratories, however he showed that the copper(II) acetate formed a solid block, causing reactor blocking. This demonstrated that flow chemistry was not always a suitable replacement methodology for some syntheses.

### 2.2.5 Porphyrin Formylation

The formylation of porphyrins is a reaction that our group performs regularly, with the reaction an early and key step in the formation of DSSC dyes and porphyrin arrays.\(^{[98]}\) Porphyrin formylation requires a Vilsmeier-Haack formylation, with the Vilsmeier reagent (DMF/phosphoryl chloride (POCl\(_3\))) added to a metalloporphyrin. This allows for electrophilic attack of the porphyrin core and single addition of a formyl group to the β-pyrrolic position. As
reported in the literature our group uses copper porphyrins for Vilsmeier-Haack formylation, with copper removal prior to reaction hydrolysis (Scheme 2-2).\(^9\) However, the addition of concentrated (conc.) H\(_2\)SO\(_4\) for copper removal produces a series of challenges. The hydrolysis of the Vilsmeier product 10 (Scheme 2-2) from the formylation affords the aldehyde 11 that forms a cyclic ketone 12 during the acid catalysed removal of the copper from the porphyrin. However, removal of copper prior to hydrolysis of the Vilsmeier product allows the isolation of the free-base porphyrin aldehyde 14. Following the addition of H\(_2\)SO\(_4\) and subsequent hydrolysis, litres of solvent are required to extract the desired formylporphyrin. Based on this reaction protocol, we were interested in determining if porphyrin formylation could be achieved by flow chemistry, with the desired free-base formylporphyrin isolated in high yields and a reduced solvent requirement.

Scheme 2-2. Porphyrin formylation showing successful and unsuccessful synthetic methodologies.
The initial experiments were performed without removal of copper, giving copper porphyrin aldehyde 11. Pumps A and B were again used, with TPP (0.004 M) and Vilsmeier reagent (0.400 M) prepared in 1,2-dichloroethane (DCE) in separate dry Schott bottles. Vilsmeier complex was pumped at 2X rate to ensure >100 equivalents (eq.) were reacting with porphyrin throughout the whole reaction.

Flow rates were varied to determine optimum conditions, with flow rates established to produce reaction coil residence times of 22, 33 and 67 min. The reaction coil was heated to 120°C for all formylation experiments. In order to analyse the product mixture, the crude reaction mixture was hydrolysed, neutralised and the organic phase filtered through a syringe filter. HPLC indicated best yields of 63.9% were achieved at 33 min residence time, with 22 min and 67 min producing yields of 9.1% and 9.9% respectively.

The assumption that highest conversion would be achieved by an increase in retention time was dismissed by the 67 min reaction. HPLC, MALDI mass spectrometry and TLC analysis showed the presence of TPP 2 and CuTPP 9. A third porphyrin compound and baseline material was also present in the reaction mixture. HPLC analysis showed the presence of 3 peaks (see C in Figure 2-5), with standards run against the reaction to conclude the mixture contained TPP 2 and CuTPP 9. The third peak which was assumed to be the copper formylporphyrin 11 (MALDI mass spectrometry analysis) had a different HPLC retention time compared to the previous reactions and formylporphyrin standard. The third product was therefore concluded to be the cyclic ketone product 12, that was being produced due to competing reactions present in the flow chemistry reactor. As the flow chemistry reactor cannot be dried as simply as a round bottom flask, it was assumed that during the 67 min reaction, H₂O present in the reactor was producing highly acidic conditions. These acidic conditions were therefore able to remove copper from the porphyrin core to produce 2 and also facilitate the cyclisation of any present formylporphyrins.
Multi gram scale synthesis of free-base porphyrin aldehyde was performed by extended running of the 33 min reaction, followed post synthesis addition of conc. H$_2$SO$_4$. The reaction was deposited into a dry round bottom flask and once complete, conc. H$_2$SO$_4$ was added and stirred for 20 min. Hydrolysis and purification produced 14 (0.140 g), however higher amounts were
not produced due to the highly acidic conditions produced in situ that resulted in instrumentation damage.

2.3 Analysis of the NMR Spectra of 5,10,15,20-Tetra(2,5-dimethoxyphenyl)porphyrin

During the flow chemistry porphyrin analysis, the $^1$H NMR signal of 5,10,15,20-tetra(2,5-methoxyphenyl)porphyrin 7 showed a series of signals for both methoxy groups (Figure 2-6). Due to porphyrin symmetry and assumed equivalent methoxy group environments it was expected singlets would be observed. The observed multiplet suggested the ortho-substituents were restricted in their rotation, giving rise to atropisomers. To our knowledge, the $^1$H NMR spectrum of 7 has not been reported in the literature. High and low temperature analysis was therefore performed to determine if rotation barriers could be overcome and the simplification of the $^1$H NMR spectra achieved.

![Figure 2-6. $^1$H NMR spectrum of porphyrin 7 in CDCl$_3$.](image)

To collect high temperature NMR spectra, chloroform-$d$ was replaced by toluene-$d_8$. Comparison of $^1$H NMR spectra between the two solvents at RT showed changes in both pyrrolic NH (Figure 2-7) and methoxy (Figure 2-8) signals. The broad pyrrolic NH singlet observed in
chloroform was replaced by 4 NH peaks, while the methoxy signals also increased in number. The 2-methoxy signals changed from a multiplet to 6 distinct signals, while the 5-methoxy remained as a closely grouped multiplet (Figure 2-8).

**Figure 2-7.** Solvent effects of pyrrolic NH peaks in chloroform-d and toluene-d8 of 7 at RT.

Structural investigations into ortho substituted arylporphyrins show that the observed $^1$H NMR spectra are characteristic of the formation of atropisomers. Crystal structures of 5,10,15,20-tetraarylporphyrins indicate that the aryl rings are rotated from the plane of the porphyrin ring by 60-90°. Restricted rotation of phenyl rings by ortho substituents mean the ortho methoxy groups can either sit above (α) or below (β) the porphyrin core. Porphyrin synthesis will therefore create a mixture of $\alpha\alpha\alpha\alpha$, $\alpha\alpha\alpha\beta$, $\alpha\alpha\beta\beta$ and $\alpha\beta\alpha\beta$ atropisomers (Figure 2-9). The 4 atropisomers can therefore explain the presence of 4 pyrrolic NH peaks in spectra obtained in toluene-d8. Solvation would appear to have a significant affect on chemical shift of the NH peaks of the atropisomers with the aromatic solvent that can π-π interact with the porphyrin and aryl substituents dramatically affecting the chemical shift in contrast to CDCl₃.
Chapter 2 - Synthesis and Modification of Porphyrins by Flow Chemistry

Figure 2-8. Low (-10°C) to high (90°C) temperature $^1$H NMR spectroscopy study of 2-methoxy and 5-methoxy signals.

Figure 2-9. Atropisomers of 7.
Crossley et al. have shown for similar 2-substituted porphyrins that atropisomer isolation produced $\alpha\beta\alpha\beta$, $\alpha\alpha\beta\beta$, $\alpha\alpha\alpha\beta$ and $\alpha\alpha\alpha\alpha$ in a ratio of 1:2:4:1. Four atropisomers are present; however molecule symmetry results in the presence of 6 methoxy peaks. This is highlighted by the 2-methoxy $^1$H NMR signals (Figure 2-8). $\alpha\beta\alpha\beta$, $\alpha\alpha\beta\beta$ and $\alpha\alpha\alpha\alpha$ produce one type of methoxy environment each, while $\alpha\alpha\alpha\beta$ produces 3 environments. Integration of the 25°C 2-methoxy $^1$H NMR signal shows that the 6 singlets integrate in a 1:2:1:2:1 pattern (Figure 2-8). Peak assignment can be performed through integration pattern, with $\alpha\beta\alpha\beta$ and $\alpha\alpha\alpha\alpha$ having an integration of 1 (3.12 parts per million (ppm) and 3.10 ppm), $\alpha\alpha\beta\beta$ having an integration of 2 (3.11 ppm) the lowest field singlets. The remaining 3 high field singlets (3.07 ppm, 3.04 ppm, 3.02 ppm) are the 3 signals for $\alpha\alpha\alpha\beta$. Increases in temperature from -10°C to 90°C resulted in a closing up of the chemical shifts of the 3-methoxy peaks from 52 Hz to 35 Hz across the 6 singlets (Figure 2-8) but there appears to be no change in the atropisomer ratio. It would be expected that with further increase of temperature, rotational barriers could be overcome and the porphyrin $^1$H NMR spectrum simplified.$^{[100]}

2.4 Conclusion and Future Directions

Flow chemistry technology was used to synthesise a series of arylporphyrins. Investigation into reaction parameters showed that highest yields could be observed at 141°C, 0.2M and retention times of 25 or 33 min. Yields were never observed above Adler-Lungo literature yields however the scale up potential of the process was observed. A 10 fold increase in both reactor size and reaction flow rates showed little change in reaction yield, with 5.2 g of TPP 2 collected. The synthesis of TPP 2 was used throughout the thesis, towards the generation of amphiphilic porphyrin molecules however the remaining required tetraarylporphyrins for Chapter 3, Chapter 4 and Chapter 5 were synthesised using standard Adler conditions. Blocking of instrumentation at low flow rates and instrument heating restrictions meant the Adler styled synthesis could not be examined in full. To increase reaction yields a future plan for flow chemistry porphyrin synthesis could involve Lindsey styled synthesis, with a third pump used to introduce the oxidant (p-chloranil, DDQ).

Porphyrin modification was also performed by flow chemistry, with formylation of Cu-TPP 9 successful. Flow chemistry was able to reduce the reaction from 16 h to 33 min, with HPLC indicating yields of 63.9% of copper formylporphyrin 11. Scale up and copper removal was able
to produce 0.14 g of formyl TPP 14 however instrumentation damage associated to the highly acidic conditions created by formylation resulted in abandonment of flow chemistry formylation. Copper insertion was also abandoned due to solubility issues associated with copper acetate in MeOH. Further trials associated to copper acetate filled cartridges could potentially improve flow chemistry copper insertion.

During porphyrin synthesis the characterisation of 5,10,15,20-tetra(2,5-dimethoxyphenyl)porphyrin 7 indicated multiple signals were present in the $^1$H NMR spectrum for pyrrolic NHs and both methoxy signals. It was concluded that due to the restriction of aryl ring rotation by the ortho substituents 4 atropisomers ($\alpha\alpha\alpha\alpha$, $\alpha\alpha\beta\beta$, $\alpha\beta\alpha\beta$ and $\alpha\beta\beta\beta$) were formed and identified by NMR spectroscopy.
Chapter 3
Synthesis of Vinyl Linked Amphiphilic Porphyrin Molecules
3.1 Amphiphilic Porphyrins

The use of protein maquettes in the design of an artificial photosynthetic system requires the binding dye, such as a porphyrin or porphyrin array, to be amphiphilic. This is to ensure the porphyrin has similar characteristics to Haem A and Haem B which have shown good binding affinity for the protein maquettes designed by the Dutton laboratory (Chapter 1). It is therefore hoped that the amphiphilic porphyrin or porphyrin array can be housed in the hydrophobic maquette, while also being soluble in an aqueous environment.

Amphiphilic porphyrins and porphyrin arrays can be synthesised by a variety of approaches. Porphyrin condensation is able to produce single amphiphilic porphyrins, with charges placed at differing positions of the porphyrin. Single tetraaryl amphiphilic porphyrins are usually synthesised by mixed aldehyde condensation or from precursors such as dipyrrmethanes. To aid porphyrin purification, charges are commonly placed on the porphyrin at the last step by a single functional group transformation. Synthesis of single amphiphilic porphyrin molecules has shown promising results towards the binding to protein maquettes in both the Officer and Dutton laboratories. The research into single amphiphilic porphyrins is being undertaken by other researchers, however the push to increase both maquette binding affinity and energy absorption has resulted in differing porphyrin targets in this thesis.

Amphiphilic porphyrins and porphyrin arrays can also be produced by the addition and modification of functionality on hydrophobic and hydrophilic porphyrins. Ruppert et al. have used an ester containing dendron to modify a hydrophobic porphyrin fullerene conjugate and, following hydrolysis, obtain a highly H$_2$O soluble amphiphilic molecule. Dendrons can therefore be used to add aqueous solubility to a vinyl linked porphyrin to produce a series of dendron-containing amphiphilic porphyrins and arrays.

The main aim of this chapter was to functionalise precursor H$_2$O soluble porphyrins and enable them to be used in conjunction with hydrophobic functionalised porphyrins for the synthesis of amphiphilic porphyrin arrays. The Officer group has developed a facile methodology to allow for linking of single porphyrin units, successfully forming amphiphilic porphyrin dyads successful. Using Wittig chemistry (Section 1.4), a porphyrin phosphonium salt can be reacted with an aldehyde appended porphyrin to produce benzoic acid containing amphiphilic porphyrin dyads. The author therefore aims at expanding on this methodology to produce a series of
Chapter 3- Synthesis of Vinyl Linked Amphiphilic Porphyrin Molecules

vinyl linked amphiphilic porphyrin dyads/arrays with sulfonic acid, N-methyl pyridinium and benzoic acid aqueous solubilising functional groups present.

The synthetic methodology towards the creation of amphiphilic porphyrin dyads and arrays requires precursors to \( \text{H}_2\text{O} \) soluble functionality, to ensure the purification of the multistep reaction is successful. The \( \text{H}_2\text{O} \) soluble functionality is then formed as a single final step.

The successful synthesis of precursor \( \text{H}_2\text{O} \) soluble porphyrin phosphonium salts that are necessary for use in Wittig based chemistry has been limited due to the inability to formylate a range of tetraarylporphyrins. Vilsmeier-Haack formylation is an electrophilic aromatic substitution, meaning porphyrins with electron withdrawing substituents do not readily react with the Vilsmeier reagent (Figure 3-1). Many \( \text{H}_2\text{O} \) soluble groups, such as ester, pyridyl and bromo groups are electron withdrawing. To overcome this issue various approaches are necessary to achieve formylation and create a key intermediate for Wittig chemistry, the precursor \( \text{H}_2\text{O} \) soluble porphyrin phosphonium salt.

![Figure 3-1. Electron withdrawing effect on the Vilsmeier formylation of porphyrins.](image)

3.2 Porphyrin Functionalisation by Wittig Chemistry

The functionalisation of porphyrins has been necessary to alter and exploit the physical and chemical performance of these heterocycles. Meso and \( \beta \)-pyrrolic functionalisations have been performed by many synthetic reactions, including metal catalysed cross coupling (Pd, Ag), amide coupling and Friedel-Crafts acylation.\(^{[93a, 105]}\) The Officer group has used Wittig chemistry to synthesise a library of \( \beta \)-pyrrolic Wittig functionalised porphyrins and porphyrin arrays.\(^{[106]}\)

A Wittig reaction occurs between an aldehyde and phosphorous ylide and creates a carbon-carbon double bond.\(^{[107]}\) Due to ylide instability, phosphonium salts are commonly used in the presence of a weak base to create the ylide \textit{in situ} (Scheme 3-1).\(^{[108]}\) Phosphonates are also used
(Wittig-Horner reaction), however the resonance stabilised phosphonate requires a stronger base for carbanion formation.\cite{93a}

\[
\text{Cl}_2\text{Ph}_2\text{P} \xrightarrow{\text{Base}} \text{Ph}_3\text{P} \xrightarrow{\text{HCl}} \text{Ph}_3\text{P} \xrightarrow{\text{R}} \text{Ph}_3\text{P} \xrightarrow{\text{R'}} \text{R} + \text{PPh}_3\text{O}
\]

**Scheme 3-1.** Generalised Wittig mechanism between a phosphonium salt and aldehyde.

If both the aldehyde and phosphonium ylides are porphyrin-based, the resulting Wittig product is a porphyrin dyad or array. Officer and co-workers have successfully demonstrated that β-pyrrolic formylation of tetraarylporphyrins can provide a variety of aldehydes for Wittig chemistry, although reactions of aryl phosphonium salts with such aldehydes can be problematic.\cite{93a} The inability to produce the desired Wittig products from formylporphyrins, was overcome by the use of phosphonates. Phosphonates have been shown to react with porphyrin aldehydes to produce a series of symmetrical arrays (Scheme 3-2). The synthetic methodology, although successful, resulted in poor yields due to the isolation of mono-, di- and tri-substituted products and side products.\cite{109} Reaction versatility was also limited as more complex unsymmetrical arrays were difficult to purify. To increase reaction scope, the use of β-pyrrolic formylporphyrins was abandoned with the phosphorous ylide placed on the porphyrin core.
The successful Wittig synthesis of porphyrin compounds has been mainly due to the creation of porphyrin phosphonium salts. The formation of the porphyrin phosphonium salt requires a 3 step synthesis from β-pyrrolic formylporphyrins (Chapter 2), which are able to be reduced to the alcohol with NaBH₄ in near quantitative yields. The subsequent treatment with SOCl₂ to produce the chloromethyl product, followed by reaction of the chloride material with PPh₃ produces the porphyrin phosphonium salt in yields above 90% (Scheme 3-3).[111] As a result of the instability of the chloromethyl product, it is commonly not isolated and phosphonium salt formation is carried out from the crude chloromethyl porphyrin.[106]
Scheme 3-3. Generalised synthesis of porphyrin phosphonium salts 25, 26 and 27.[79]

The synthesis of porphyrin phosphonium salts has enabled the formation of a variety of electron donating and withdrawing aryl aldehydes, with their electrochemical and spectroscopic properties studied.[112] Porphyrin-based Wittig reactions were originally performed under liquid-liquid phase transfer conditions using aqueous NaOH; however the reaction yields and purities were increased by use of 1,8-diazabicycloundec-7-ene (DBU) under inert conditions.[106, 113] Once synthesised, the vinyl-linked porphyrins can undergo various modifications such as metalation and ester hydrolysis for use in applications including DSSCs (Figure 3-2).[114]
Porphyridium phosphonium salts have also been used extensively for the creation of porphyrin arrays with the largest porphyrin array synthesised by this method being a porphyrin nonamer (Figure 3-3).\cite{78a} The synthesis of porphyrin phosphonium salts has allowed for the creation of key aldehyde appended intermediates that therefore allows for array versatility. The aldehyde appended porphyrins have allowed for the step-by-step linking of units for creation of symmetrical, unsymmetrical and mixed-metal arrays.\cite{79}

**Figure 3-2.** Series of vinyl linked porphyrins synthesised by Wittig chemistry.

**Figure 3-3.** Porphyrin nonamer synthesised by Wittig chemistry.\cite{78a}
3.3 Synthesis and Characterisation of Amphiphilic Porphyrins and Porphyrin Dyads

3.3.1 Tetra 4-(trimethylsilyl)phenylporphyrin Phosphonium Salt

The 3-benzoic acid containing amphiphilic porphyrin dyads synthesised by Campbell et al. has aqueous solubility in basic conditions, with limited solubility observed below pH 5.\[115\] To therefore improve aqueous solubility, sulfonic acid precursor phosphonium salts were attempted. Sulfonic acid porphyrins are soluble in a much larger pH range with solubility expected in a range of pH 1 to pH 14.\[116\]

Sulfonic acid porphyrins are usually synthesised by reaction with conc. H$_2$SO$_4$. The substitution reaction occurs at the para position of tetraarylporphyrins and is coupled with poor yields and problematic purification.\[117\] Chlorosulfonic acid has also been used to sulfonate the para position of tetraarylporphyrins. The creation of a chlorosulfonyl intermediate aids purification, however the process is not selective for synthesis of amphiphilic molecules due to protection of specific porphyrin positions unachievable.\[118\]

Selective sulfonation is necessary for creation of amphiphilic porphyrin molecules, to ensure phenylene linkages or desired hydrophobic porphyrins are not susceptible to substitution reactions. Ye et al. have used trimethylsilyl chlorosulfonate to selectively create H$_2$O soluble porphyrins and porphyrin dyads from trimethylsilyl containing porphyrins (Figure 3-4).\[736\]
The ability to selectively sulfonate a porphyrin, meant investigation into phosphonium salt formation of a trimethyl silyl porphyrin was begun. 4-(Trimethylsilyl)benzaldehyde 30 was synthesised from 4-bromobenzaldehyde, with protection (90%), silylation (70%) and deprotection (96%) able to produce 6.4 g of 4-(trimethylsilyl)benzaldehyde 30.\textsuperscript{[119]} Standard Adler conditions produced porphyrin 31 in 15% yield, while copper insertion produced 32 in 96% yield (Scheme 3-4).

Figure 3-4. Synthesis of sulfonic acid containing porphyrin dyads by Ye \textit{et al.}\textsuperscript{[73b]}
(i) \( p \)-Toluenesulfonic acid, toluene, reflux. (ii) \( n \)-BuLi, trimethylsilyl chloride, THF, \(-90^\circ C\). (iii) TFA, \( \text{CH}_2\text{Cl}_2, \text{H}_2\text{O} \). (iv) Propionic acid. (v) \( \text{Cu(OAc)}_2, \text{CHCl}_3, \text{MeOH} \).

**Scheme 3-4.** Synthesis of copper porphyrin 32.

Vilsmeier formylation and copper removal with conc. \( \text{H}_2\text{SO}_4 \) did not, however, produce any desired formylated product. Reaction purification and characterisation by NMR spectroscopy and MALDI mass spectrometry indicated that formyl TPP 14 was the major fraction (Scheme 3-5). Formylation was repeated without copper removal to determine if the conc. \( \text{H}_2\text{SO}_4 \) was responsible for the ipso substitution of the trimethyl silyl group. Successful isolation of porphyrin 33 in 72% yield indicated that harsh acidic conditions could therefore not be used and a differing technique was necessary for copper removal (Section 3.3.2). Reduction of aldehyde 33 to alcohol 34 with \( \text{NaBH}_4 \) was performed in near quantitative yields, however poor conversion for chlorination and phosphonium salt synthesis produced 36 in 54% yield (Scheme 3-5).
(i) (a) DMF, POCl₃, DCE, reflux. (b) RT, H₂SO₄. (ii) DMF, POCl₃, DCE, reflux. (iii) NaBH₄, THF, H₂O, RT. (iv) SOCl₂/pyridine, CH₂Cl₂, 0°C to RT. (v) PPh₃, CHCl₃, reflux.

**Scheme 3-5.** Synthesis of porphyrin phosphonium salt 36 and the unsuccessful attempt to produce the free-base derivative.
3.3.2 Sulfonic Acid Amphiphilic Porphyrins

Phosphonium salt 36 was used in the creation of trimethly silyl functionalised porphyrins that could be converted to H\textsubscript{2}O soluble sulfonic acid derivatives. Synthesis of 37 was performed in 81% yield by reaction of 37 with benzaldehyde (Scheme 3.6). A porphyrin dyad was also synthesised by a step-by-step method, with phosphonium salt 36 reacted with porphyrin 39 in 52% yield.

The inability to remove copper during porphyrin formylation due to the ipso substitution of all trimethyl silyl groups meant copper removal was necessary under milder conditions. Work by Dr Ashley Walker in our laboratories indicated treatment of copper porphyrins with methane sulfonic acid was able to remove copper to give free-base material in quantitative yields.\textsuperscript{[120]} The new conditions were used with 37 and 40 stirred with 40 eq. of methane sulfonic acid in CH\textsubscript{2}Cl\textsubscript{2}. TLC analysis indicated reaction completion in 2-5 min, with neutralisation, washing and crystalisation giving 38 in 95% and 41 in 95% yields (Scheme 3-6). \textsuperscript{1}H NMR spectroscopy and MALDI spectra indicated that methane sulfonic acid was able to remove copper from the porphyrin while not affecting the trimethylsilyl groups.
(i) DBU, CHCl₃, reflux. (ii) Methanesulfonic acid, CH₂Cl₂, RT.

Scheme 3-6. Copper removal from porphyrins 37 and 40 to form free-base derivatives 38 and 41.

The removal of copper resulted in ¹H NMR spectroscopy being the primary characterisation technique for porphyrins 38 and 41. The similar electronic properties of TPP and tetra-(4-trimethylsilylphenyl)porphyrin resulted in peak overlap in the downfield region, with multiplets present for β-pyrrolic and ortho, meta and para meso-aryl groups. Two singlets are present for the β-pyrrolic protons adjacent to the vinyl linker, while the doublets of the vinyl linkers are
present at 7.34, 7.29, 7.05 and 7.01 ppm, with 16 Hz coupling constants indicative of *trans* geometry. \H_{AR}\ is present as a singlet at 7.20 ppm, while trimethyl silyl groups and a broad NH peak are present at 0.51 ppm and -2.54 ppm respectively. Correlated spectroscopy (COSY) spectra aided the assignment of all downfield peaks.

*Figure 3-5.* \(^1\text{H} \) NMR spectrum of porphyrin dyad 41.
Conversion from the trimethyl silyl group to the sulfonate derivative was performed by reaction with trimethylsilyl chlorosulfonate.[73b] Porphyrins 38 and 41 were reacted with excess trimethylsilyl chlorosulfonate, with purification being performed with dialysis tubing. Porphyrins 42 and 43 were collected in 92% and 91% yield respectively (Scheme 3-7).

Scheme 3-7. Synthesis of sulfonic acid porphyrins 42 and 43.
Characterisation of the sulfonic acid porphyrins was performed by NMR spectroscopy, electrospray (ES) mass spectrometry and UV. The $^1$H NMR spectra were not well resolved under a variety of deuterated solvent conditions and not improved with variable temperature NMR spectroscopy experiments. Electrospray mass spectrometry was necessary for porphyrin characterisation with MALDI mass spectrometry unable to detect any porphyrin signal using different matrices such as 1,8,9-anthracenetriol, trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and trans-3-indoleacrylic acid. Positive mode ES mass spectrometry gave a single peak chromatogram (Figure 3-5A) with the mass spectrum showing a parent ion minus sodium counterions at 1034 m/z (Figure 3-5B).

![Figure 3-6. Chromatogram and positive mode electrospray mass spectrum of 42.](image)
3.3.3 Aqueous Solubility of Amphiphilic Sulfonic Acid Containing Dyad

The incorporation of sulfonic acid groups into an amphiphilic porphyrin dyad was designed to improve aqueous solubility, in comparison to their benzoic acid counter parts. Aggregation studies of benzoic acid porphyrin dyads showed that aqueous solubility was lost at pH 4 (Section 3.3.10). Porphyrin dyad 43 was exposed to the same pH 4 conditions, with UV-vis spectra taken every 30 min for 15 h (Figure 3-6). A comparison between 0 h and 15 h showed a broad Soret peak that is characteristic of vinyl linked dyads and no major changes in spectrum over the 15 h run time. The stability of the porphyrin spectrum indicates aqueous solubility is achieved in acidic pH 4 conditions.

![Figure 3-7. UV-vis spectra of dyad 43 at pH 4.](image-url)

Despite the successful synthesis of amphiphilic porphyrins 42 and 43 and their excellent solubility, this approach to water soluble porphyrins dyads is limited. While free-base porphyrins can be prepared, the introduction of zinc or iron for maquette binding cannot be selectively achieved using this methodology. Consequently, the approach was abandoned and synthesis of tetrapyridylporphyrins investigated.
3.3.4 Attempted Synthesis of Tetra-4-pyridylporphyrin Phosphonium Salt

The abandonment of the sulfonic acid containing amphiphilic porphyrin molecules allowed for investigation into a positively charged amphiphilic porphyrin system that would provide H$_2$O solubility from pH 0 to pH 14. The synthesis of N-methylpyridiniumporphyrin containing porphyrin arrays were attempted by way of formylation of tetra-(4-pyridyl)porphyrin 44. Formylation of pyridylporphyrin 44, by formation of N-oxides on the pyridyl ring, was unsuccessful. It was hoped that with oxidation of the pyridyl group, the strongly electron withdrawing group would be reversed and therefore allow for β-pyrrolic formylation. Oxidation with m-chloroperoxybenzoic acid using stoichiometric equivalents, excess and differing temperatures never resulted in full oxidation and was therefore abandoned along with the creation of a positively charged amphiphilic porphyrin system (Scheme 3-8).

![Scheme 3-8. Unsuccessful synthesis of tetra N-oxidepyridylporphyrin.](image)

(i) m-Chloroperoxybenzoic acid, CHCl$_3$.

3.3.5 Tetra-(4-carboxymethyl)phenylporphyrin Phosphonium Salt

The partially successful synthesis of sulfonic acid containing amphiphilic dyads and failure of the N-methyl pyridinium based system resulted in experimentation to be directed at benzoic acid containing molecules. The synthesis of 3-benzoic acid containing amphiphilic porphyrin dyads by Campbell et al. although successful has various synthetic issues including the multi-step
reaction required to generate phosphonium salt 18 (Scheme 3-3) for porphyrin synthesis. The formation of 18 is dependent on the formation of methyl 3-formylbenzoate 45, the benzaldehyde required for porphyrin formation. The 3 step synthesis used to form 45 from 3-methylbenzoic acid involved an esterification, bromination and Sommelet reaction and could produce 45 in multigram quantities (49.1 g) (Scheme 3-9). In an attempt to simplify phosphonium salt synthesis, it was decided to purify the synthesis of the *para* analogue of porphyrin phosphonium salt 45 by attempting formylation of tetra-(4-carboxymethylphenyl)porphyrin 6. The commercial availability of methyl 4-formylbenzoate 46 in large quantities was also an advantage.

(i) \( \text{H}_2\text{SO}_4\), MeOH, reflux. (ii) N-bromosuccinimide (NBS), \( \text{CH}_2\text{Cl}_2\), \( \text{hv} \). (iii) (a) Hexamethylenetetramine, \( \text{H}_2\text{O}\), glacial acetic acid, reflux. (b) HCl, RT.


Formation of carboxyporphyrin 6 was undertaken using standard Adler conditions, with copper insertion performed by refluxing with copper acetate to obtain 47 (Scheme 3-10) in 95% yield.\textsuperscript{[121]} The increased deactivating effect of the *para* ester meant standard refluxing of the porphyrin did not result in successful Vilsmeier formylation. Microwave synthesis was therefore chosen due to the increased reaction rate and successful formylation of deactivated porphyrins by Moura et al.\textsuperscript{[122]} The microwave reaction was performed by the addition of excess pre-made Vilsmeier complex to 100 mg of 47 dissolved in 5 mL of \( \text{o}-\text{dichlorobenzene} \). The reaction was irradiated twice to 100°C, 160 Watts for 30 min in a microwave reactor, with excess pre-made...
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Vilsmeier complex added between the two runs. Vigorous stirring in the presence of conc. H$_2$SO$_4$, followed by reaction quenching and purification gave 48 in 38% yield (Scheme 3-6). Several reactions were performed to build up enough material for phosphonium salt synthesis.

Reduction from aldehyde to alcohol had solubility problems, which resulted in the use of tetrahydrofuran (THF) and CH$_2$Cl$_2$. Reduction is commonly performed at near quantitative yields, however 49 was collected in 86% yield. Subsequent chlorination and phosphonium salt synthesis was performed, with the 2 step process producing the desired phosphonium salt 51 in 88% yield (Scheme 3-10). Only 64 mg of porphyrin 51 was collected due to the limited microwave vessel size during porphyrin formylation. The successful synthesis of 51 was promising; however simplification of phosphonium salt synthesis was not achieved. The knowledge that multi gram quantities of the analogous 3-carboxyphenylporphyrin 27 could be produced and the decreased solubility of para substituted porphyrins meant the use of phosphonium salt 51 was not investigated further.[59]

(i) (a) DMF, POCl$_3$, DCE, reflux. (b) RT, H$_2$SO$_4$. (ii) NaBH$_4$, THF, CH$_2$Cl$_2$, H$_2$O, RT. (iii) SOCl$_2$/pyridine, CH$_2$Cl$_2$, 0°C to RT. (iv) PPh$_3$, CHCl$_3$, reflux.

Scheme 3-10. Synthesis of porphyrin phosphonium salt 51.
3.3.6 Tetra 3-(carboxymethyl)phenylporphyrin Phosphonium Salt

Despite the attempts to design new synthetic routes to amphiphilic porphyrin dyads and arrays using differing synthetic approaches to Campbell et al., none of the methods could compete with the Campbell approach using meta-substituted carboxylporphyrins. Therefore it was decided that the Campbell approach should be pursued to obtain the required arrays for maquette binding studies.\cite{79}

As shown in Scheme 3-11, the synthesis of the required phosphonium salt 27 was successfully achieved with a number of variations to Campbell’s synthetic procedures. The generation of 27 was successful due to the meta functionality reducing the electron withdrawing effect of the ester and allowing for porphyrin formylation.\cite{79} The deactivating effect of the ester still impacts the reaction, with slow and incomplete conversion to 18 experienced. Standard Vilsmeier formylation conditions on 16 produced 18 in 63% yield, with free-base starting material also collected.

The formylated material was then treated in 1 of 2 ways to achieve the synthesis of porphyrin phosphonium salt 27. Multi-gram synthesis of 18 resulted in problematic purification due to the similar retention factor (Rf) values of the product 18 and free-base starting material 52. Multiple purifications were performed to achieve pure 18, which could be reduced with NaBH₄ to give near quantitative yields of 21. Chlorination with SOCl₂ was then performed and due to product instability was taken directly to phosphonium salt synthesis by treatment with PPh₃ (Scheme 3-11). Phosphonium salt 27 (65% yield) was regularly produced throughout this thesis with largest scale being 1.94 g.

The time consuming purification of 18 meant attempts to make phosphonium salt 27 were performed without purification. It was hoped that the remaining starting material would be relatively unreactive towards reduction, chlorination and phosphonium salt formation and the vastly different Rf values (52 and 27) would then allow for simple purification by flash chromatography. The process was successful and resulted in quicker synthesis of desired phosphonium salt 27. Overall yields of 24% from copper porphyrin 16 to phosphonium salt 27, however, were below the previously reported standard procedures, which were consistently observed to be around 40%. Consequently, this resulted in preparing 27 predominantly by purification of aldehyde 18 as initially described.
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![Chemical structures andScheme 3-11. Synthesis of porphyrin phosphonium salt 27.](image)

(i) Cu(OAc)$_2$, CHCl$_3$, MeOH. (ii) (a) DMF, POCl$_3$, DCE, reflux. (b) RT, H$_2$SO$_4$. (iii) NaBH$_4$, THF, H$_2$O, RT. (iv) SOCl$_2$/pyridine, CH$_2$Cl$_2$, 0°C to RT. (v) PPh$_3$, CHCl$_3$, reflux.

3.3.7 3-Benzonic Acid Amphiphilic Porphyrins

The successful synthesis of 27 allowed for the creation of a series of amphiphilic porphyrins for use in maquette binding studies. A series of Zn-Zn, Fe-Zn and free-base-Zn porphyrin dyads were identified as synthetic targets to show the effects that differing substituents and metals would have upon the maquette binding affinity.

Initially a single amphiphilic porphyrin was synthesised as a model reaction to determine the most appropriate reaction conditions for both the Wittig reaction and subsequent hydrolysis. Phosphonium salt 27 was reacted with benzaldehyde to give 53 as the all $E$-isomer in 86% yield (Scheme 3-12). Base hydrolysis was performed by refluxing overnight in the presence of KOH. Once cooled to RT, solvent was removed and the reaction was redissolved in H$_2$O and acidified with H$_3$PO$_4$.[79] The resulting precipitate was filtered and washed with H$_2$O to give 54 in 89% yield.

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72
(i) DBU, CHCl₃, reflux. (ii) (a) KOH, THF, MeOH, H₂O. (b) H₃PO₄.

Scheme 3-12. Synthesis of amphiphilic porphyrin 54.

Following from the work established by Dr Wayne Campbell, aldehyde appended porphyrins were synthesised by reaction with terephthalaldehyde for use in the step-by-step synthesis of amphiphilic dyads.[79] Porphyrins 39, 55 and 56 were synthesised by refluxing porphyrin phosphonium salts in degassed CHCl₃ with DBU in 82%, 91% and 66% yields respectively. Single broad NH peaks and 2 doublets of 16 Hz (vinyl signals) in the ¹H NMR spectra indicated that the E-isomer was produced for all porphyrins.

The insertion of iron and zinc into the porphyrin core was necessary at this stage, for the creation of mixed metal porphyrin dyads. Iron insertion is performed by reacting free-base porphyrin with iron(II) and once insertion was successful the metal was oxidised to produce iron(III) porphyrin.[123] Successful iron insertions were performed by refluxing iron(II) chloride in dry, degassed acetonitrile with the slow addition of porphyrins 39 and 55 performed under an argon atmosphere.[110, 124] Reaction times of 3 h were followed by exposure to air for overnight oxidation of iron(II). Iron(III) porphyrins Fe39 and Fe55 were isolated by flash chromatography in 82% and 87% yield respectively. Zinc insertions were performed by standard zinc acetate conditions to afford Zn39 (89%) and Zn55 (74%) (Scheme 3-13). All the metallated porphyrins gave characteristic UV-vis spectra and mass spectral data consistent with metal insertion.
(i) DBU, CHCl₃, reflux. (ii) (a) FeCl₂, acetonitrile. (b) O₂. (iii) Zn(OAc)₂, CH₂Cl₂, MeOH.


3.3.8 Zinc-Zinc Dyads

Zinc-Zinc amphiphilic porphyrin dyads were synthesised by firstly linking free-base phosphonium salt 27 with porphyrin aldehydes 39 and 55. The Wittig reactions were performed using dry, degassed CHCl₃ with DBU added slowly to ensure unwanted side products (methyl porphyrin) were kept to a minimum. Purification and subsequent analysis by ¹H NMR spectrum showed the porphyrin dyads had multiple pyrrolic NH peaks and a complicated downfield region, indicating the presence of E/Z isomers. Overnight iodine treatment afforded 57 (62%) and 58 (64%) as the all E isomers (Figure 3-14).
(i) DBU, CHCl$_3$, reflux. (ii) Zn(OAc)$_2$, CH$_2$Cl$_2$, MeOH. (iii) (a) KOH, THF, MeOH, H$_2$O. (b) H$_3$PO$_4$.

**Scheme 3-14.** Synthesis of amphiphilic porphyrin dyads 61 and 62.

The $^1$H NMR spectrum of the porphyrin dyads look complex, however most peaks can be assigned with reference to the individual porphyrins and COSY spectra largely shown for 58 in Figure 3-7 and given in the experimental data. The porphyrin dyad 58 spectrum shows the two sets of pyrrolic NH protons as a single broad 4H singlet, while dyad 57 displays 2 closely spaced NH peaks. The downfield region shows closely grouped multiplets, although two sets of 16 Hz coupled AB quartets/doublets can be resolved associated with the vinyl linker (Figure 3-7) that
indicate trans vinyl geometry. COSY was used for the identification of the downfield aromatic region containing overlapping signals for the aromatic groups and β-pyrrolic protons.

**Figure 3-8.** $^1$H NMR spectrum of porphyrin dyad 58.
Zinc insertion was carried out by reaction of the free base dyads with zinc acetate, to give 59 and 60. The $^1$H NMR spectra were similar to the free-base dyads, with the only major spectral change being the disappearance of the pyrrolic NH signal.

The ultraviolet-visible (UV-vis) spectra of the dyads are similar to those previously reported for this type of phenylene-linked dyad. As reported by Burrell et al.$^{[125]}$ for the analogous symmetrical free base and zinc xylyl dyads, the dyad spectra observed are similar to their constituent porphyrin monomers albeit with a strong shoulder present on the low-energy side of the Soret band at ~ 490 nm that leads to a broadening of the Soret band, as can be seen in Figure 3-8 for Zn dyad 60. This shoulder and the related band broadening has been attributed to the beginning of a split Soret band as a result of limited electronic coupling between the two porphyrins of the dyad; dyads with strong coupling such as those with acetylene$^{[126]}$ or butadiyne$^{[127]}$ bridges have two Soret bands due to splitting.

In contrast, the Q bands are largely unaffected. Analogous to the single tetra-arylporphyrins (TAPs) and zinc TAP starting materials, the free-base dimers show four Q bands and the metallated compounds only two as a result of the porphyrin unit $D_{2h}$ (TAPs) and $D_{4h}$ (zinc TAP) symmetries units.$^{[128]}$

![UV-vis spectra of porphyrin dyad 60 in DMF.](image)

**Figure 3-9.** UV-vis spectra of porphyrin dyad 60 in DMF.
Base (KOH) catalysed hydrolysis was performed on the zinc dyads to give 61 (50%) and 62 (75%). The purification of the H₂O soluble porphyrin salt was achieved by precipitation from basic solution with aqueous H₃PO₄, which converts the salt to the protonated benzoic acid and results in a loss of H₂O solubility. The addition of 2-5% excess aqueous H₃PO₄ in relation to KOH allows protonation of the benzoic acid groups without displacing zinc from the porphyrin core.⁷⁹ The fine precipitate can then be filtered and washed to remove remaining salt, although some product was lost during this process.

Hydrolysis and subsequent treatment with aqueous H₃PO₄ resulted in the porphyrin dyads being insoluble in CHCl₃ and H₂O while soluble in dimethyl sulfoxide (DMSO), acetone, DMF and basic aqueous solutions. ¹H NMR spectra analysis was attempted using DMSO-d₆, acetone-d₆ and aqueous NaOD, however only acetone-d₆ gave a suitable spectrum. The spectrum although identifiable was not well-resolved with multiplets recorded for the majority of downfield aromatic peaks. It is believed the strong intermolecular hydrogen bonding between benzoic acid moieties was responsible for this trend. Of note was the disappearance of methyl ester signals, while COSY was able to aid the identification of the molecule particularly the vinyl linker. MALDI mass spectrometry gave a weak signal for the parent ion.

### 3.3.9 Mixed Metal Dyads

The binding of amphiphilic porphyrin dyads to protein maquettes would be through histidine residues that have been engineered to sit in the hydrophobic core of the 4 α-helix bundle. Zinc porphyrins are able to ligate to one ε-nitrogen of histidine, however stronger binding is observed for iron porphyrins. Iron porphyrins preferentially form six coordinate complexes and therefore can ligate to two histidine residues.¹²⁹ Since electron transfer from zinc porphyrins to iron porphyrins is well established, an iron-zinc amphiphilic porphyrin dyad that would strongly bind to a maquette through a hydrophobic iron porphyrin appeared to be an ideal target. This would then require a zinc hydrophobic dyad component that would not bind to the maquette. However, at the time this work was being carried out, maquette binding results suggested this may be a problem.
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Figure 3-10. Structure of porphyrin 63, synthesised by Mr. Nicholas Roach.

Initial binding results of a single water soluble zinc porphyrin performed by Mr. Nick Roach and Mr. Chris Hobbs showed that zinc 5,10,15,20-carboxyphenylporphyrin 63 (Figure 3-8) gave a spectral shift (indication of porphyrin ligation) in the presence of a GL-maquette. This result was unexpected as it was believed the porphyrin needed a hydrophobic region, similar to Haem A and Haem B to interact with the hydrophobic region of the maquette. A second binding experiment to a different maquette, BT-maquette, showed no spectral shift. Nonetheless, these results suggested that not only should an iron-zinc dyad be prepared but also two zinc-free-base dyads; a dyad with zinc in either the hydrophobic or hydrophilic porphyrin. The synthesis of the two Zn-free-base dyads would provide models to probe competitive binding of the iron or zinc porphyrins. The mixed metal systems will also allow for studies to determine the directional energy transfer from the zinc porphyrin to the free-base or iron porphyrin.

The synthesis of mixed metal dyads was performed by the same step-by-step approach for dyads 61 and 62. Zinc or iron porphyrin aldehydes (Zn39, Zn56, Fe39 and Fe46) were reacted with free-base phosphonium salts to produce a series of metal-free-base dyads (Scheme 3-13). Yields of 57% for 64 and 61% for 65 were obtained for iron containing reactions, while lower yields of 52% and 36% were obtained for 70 and 71 respectively. Although the Wittig reactions containing zinc coordinating porphyrins gave poorer yields, Ishkov et al. had proposed that no product would be obtained in this type of reaction.\textsuperscript{130} While the reason for the reduced Wittig reaction
yields in the presence of zinc has not been determined, literature indicates coordination between phosphoryl-oxygen and zinc suppress the reaction.\textsuperscript{114}

Zinc insertion for iron containing dyads was achieved in 91% yield for 66 and 95% yield for 67. Base catalysed hydrolysis was performed on all porphyrins to give dyads 68, 69, 72 and 73 between 70% and 100% yields, with their salts having water solubility (Scheme 3-15).

\textbf{Scheme 3-15.} Synthesis of mixed metal dyads 68, 69, 72 and 73.
It was expected that the mild conditions used to form the iron-zinc ester dyads would lead to retention of the chloride ion on the iron porphyrin. However, the use of the strong hydroxide base to hydrolyse the dyad ester would almost certainly lead to the formation of the µ-oxo dimers that would form the phosphate salts 59 and 60 on treatment with phosphoric acid.[132]

The characterisation of iron containing dyads 64-69 was limited due to the paramagnetic nature of the metal ion. This meant NMR spectroscopy could not be performed and MALDI mass spectrometry and UV-vis spectroscopy were the major characterisation techniques used. MALDI spectra of iron containing dyads were dominated by the parent ion minus the chloride or hydrogen phosphate ion as shown in Figure 3-9. The chloride or hydrogen phosphate ion was never detected, and varying the matrix or the beam power did not lead to detection of the parent ion.

**Figure 3-11.** MALDI mass spectrum of 67 with 1,8,9-anthracenetriol as matrix.
As previously observed for the zinc-zinc dyads (see p. 76), the UV-vis spectra of the mixed metal dyads result from a linear combination of the spectra of the starting porphyrins with a broadened Soret band and shoulder at ~490 nm.

### 3.3.10 Aqueous Solubility

Benzoic acid groups are known to have a limited solubility range and therefore UV-vis studies were performed to determine the solubility of the amphiphilic porphyrins over a pH range. Dyad 61 was dissolved in a stock solution of DMSO and then diluted with either N-cyclohexyl-2-aminoethanesulfonic acid (CHES) buffer (pH 9), H₂O (pH 7) or sodium acetate: acetic acid buffer (pH 4). Solubility was tested by running spectra every 30 min over a 15 h period. Spectra at pH 7 and pH 9 were similar with the absorption maximum observed at 427.5 nm, with no changes in peak position or intensity over the 15 h period (Fig 3-10). For clarity only the pH 7 spectra is shown in Figure 3-9, with the spectra showing solubility is high above pH 7.

In comparison, the spectra observed for pH 4 had a 6 nm redshifted peak indicating the formation of J aggregates. The peak extinction coefficient also dropped by 82% over the 15 hour testing period, indicating that porphyrin 61 was forming large aggregates and dropping out of solution (see insert, Figure 3-10).

![Figure 3-12. UV-vis spectra of dyad 61 at pH 7 and pH 4 (inserted image shows porphyrin falling out of solution at pH 4).](image-url)
3.4 Porphyrin-Fullerene Conjugates

The successful synthesis of water soluble porphyrin dyads opened up the possibility of making other water soluble porphyrin arrays. As has been well established, the synthesis of porphyrin arrays using phosphonium salts has been successful for the formation of large porphyrin arrays.\cite{78a, 106} The synthesis of a porphyrin trimer with a 1,3,5 substitution pattern around a benzene ring has however been unsuccessful (Scheme 3-16). This reaction has been attempted using benzene-1,3,5-tricarbaldehyde reacted with porphyrin phosphonium salts and 1,3,5-tris((chlorotriphenylphosphoranyl)methyl)benzene reacted with formylporphyrins.\cite{110} Nonetheless, this failure has shifted attention to the possible synthesis of another variety of energy transfer molecules. Since the major fraction of the benzene-1,3,5-tricarbaldehyde reaction was the diporphyrin aldehyde, it gave a handle that could be used to attach a fullerene.

\[ \text{(i) DBU, CHCl}_3, \text{ reflux.} \]

**Scheme 3-16.** Generalised synthesis of porphyrin dyad from porphyrin phosphonium salt and benzene-1,3,5-tricarbaldehyde 74.

The Prato reaction is a 1,3-cycloaddition between an azomethine ylide and either a fullerene or nanotube. Once heated, the ylide is formed between sarcosine (N-methylglycine) and an aldehyde, that reacts in a 6-6 ring position to form a N-methylpyrrolidine derivative off the fullerene or nanotube (Scheme 3-17).\cite{134} The addition of $C_{60}$ fullerene to the di-substituted
material will provide an interesting molecule for energy transfer studies, as a special pair mimic will be placed next to a known electron acceptor.

![Scheme 3-17. Generalised Prato reaction mechanism to form functionalised fullerene-C60.](image)

**Scheme 3-17.** Generalised Prato reaction mechanism to form functionalised fullerene-C60.

### 3.4.1 Synthesis and Characterisation of Porphyrin-Fullerene Triad

Benzene-1,3,5-tricarbaldehyde 74 was prepared from mesitylene by bromination and a Sommelet reaction.\[^{[135]}\] The resulting mixture of brominated products meant isolation was not performed prior to aldehyde formation. The newly prepared reagent 74 and 3.5 eq. of phosphonium salt 26 were reacted with DBU in degassed and dry CHCl₃ for 45 min. Purification by flash chromatography and subsequent isomerisation led to the isolation of the porphyrin dyad 75 in 74\% yield (Scheme 3-18). The symmetry of 75 resulted in the all E-isomer being easily characterised by ¹H NMR spectroscopy with the aldehyde signal at 10.21 ppm and the typical β-pyrrolic H multiplets evident between 8.82 and 9.18 ppm. One characteristic 16 Hz vinyl doublet occurred at 7.24 ppm with the other masked in an aromatic proton multiplet around 7.40 ppm. A high resolution mass spectrometry protonated parent ion at m/z= 1607.7942 could be observed.
(i) N-Bromosuccinimide, CH₂Cl₂, hv. (ii) (a) Hexamethylenetetramine, H₂O, glacial acetic acid, reflux. (b) HCl, RT. (iii) DBU, CHCl₃, reflux.

**Scheme 3-18. Synthesis of porphyrin dyad 75.**

The formation of the porphyrin-fullerene triad was attempted using generalised Prato conditions. Dyad 75 was stirred at reflux with excess fullerene and sarcosine in toluene under argon, however no product was observed after a 16 h reaction. Excess fullerene is required due to fullerene’s ability to coordinate to the porphyrin core and therefore not sit in a position accessible for reaction.

The reaction was tried again with 20 eq. of fullerene under microwave irradiation. Microwave conditions of 150°C, 250 W for 60 min produced the desired porphyrin-fullerene triad 76 in 79% yield. Purification of the reaction was performed by flash chromatography with toluene used to flush out excess fullerene. Once no further bands of fullerene appeared, the solvent was changed to CH₂Cl₂:hexane (7:3) to elute the major fraction of the required porphyrin-fullerene triad 76. Zinc insertion was performed by stirring with zinc acetate to give zinc porphyrin-fullerene triad 77 (Scheme 3-19).
(i) Toluene, microwave. (ii) Zn(OAc)$_2$, CH$_2$Cl$_2$, MeOH.

**Scheme 3-19. Synthesis of porphyrin-fullerene conjugate 77.**

The tendency of porphyrin-fullerene conjugates to aggregate and the nature of fullerene in mass spectrometry, resulted in differing techniques being used for molecule characterisation. The solubility of 76 and 77 was problematic once the products were dried under vacuum. Sonication was required for CHCl$_3$ solubility, however overnight NMR spectroscopy experiments showed a pellet of compound present after acquisition. This poor solubility affected the resolution of NMR spectroscopy signals, and meant CS$_2$ was required to obtain an identifiable spectra. CS$_2$ itself was able to fully dissolve 76 and 77 however a 1:1 ratio with CDCl$_3$ provided sufficient solubility to allow spectra to be obtained. The downfield region consisted of 3 large multiplets of β-pyrrolic signals between 8.9-8.7 ppm, H$_{o-Xyl}$ and H$_{AR}$ between 7.9-7.7 ppm and H$_{p-Xyl}$, H$_{AR}$ and H$_{vinyl}$ between 7.5-7.3 ppm. The 3 N-methylpyrrolidine signals were observed at 5.0, 4.4 and 2.9 ppm with COSY spectra used for assignment of all signals. Methyl xylol signals were observed between 2.7 and 2.4 ppm, while free-base 76 has a broad NH singlet at -2.7 ppm.
MALDI mass analysis was attempted using 1,8,9-anthracenetiol as the matrix at differing concentrations. The parent ion was however never observed with 720 (fullerene) and the parent
ion minus 720 being the dominant peaks. The matrix was then changed to DCTB, with differing ratios of product to matrix tried. Ratios of porphyrin-fullerene to matrix were performed at 1:0, 1:10, 1:100 and 1:500, with the first 3 concentrations showing similar trends to 1,8,9-anthracenetriol. The 1:500 ratio was however able to give a parent ion, with little fragmentation observed (Figure 3-11).

The high tendency of porphyrin-fullerene conjugates 76 and 77 to aggregate in solution meant UV-vis spectra were recorded in CS₂, a solvent with high product solubility. The UV-vis spectra show a single broad Soret peak as exemplified by porphyrin 77 (Figure 3-13) without the strong shoulder at ~490 nm as observed for the para-substituted dyads (Section 3.3.8). This suggests a smaller degree of electronic coupling in the meta-dyad than the para-dyad, as observed by Burrell et al.\[125\]. However, it is notable that the Soret band in the zinc-zinc dyad fullerene is centered at 440 nm, significantly red shifted from that of the free-base dyad 76 (427 nm). This may be due to increased electronic coupling in the metallated dyad 77, although there is no apparent increase in the shoulder at 490 nm. A slight rise in the spectra between 380 and 400 nm is also seen indicative of the presence of the fullerene.

![Figure 3-14](image-url)  
Figure 3-14. UV-vis spectra of porphyrin dyad 77 in CS₂.
3.4.2 Synthesis and Characterisation of Porphyrin-Fullerene Dyad

The synthesis of porphyrin fullerene triads sparked the interest of the Guldi group at Friedrich-Alexander University Erlangen-Nuremberg to undertake photophysical characterisation of both triads 76 and 77. However, in order to do so, the German researchers requested the synthesis of the analogous porphyrin fullerene dyads for spectral comparison. Thus, the synthesis of dyads 79 and 80 (Scheme 3-20) were undertaken.

Porphyrin 26 was reacted with terephthaldehyde by standard Wittig conditions to give 78 as the all E isomer in 90% yield. Microwave Prato conditions and zinc insertion were performed under the same conditions as for the porphyrin-fullerene triad, to give 79 and 80 in 53% and 75% yields, respectively (Scheme 3-20).

The spectral characterisation of the dyads were very similar to those of the triads with only small chemical shift differences in the $^1$H NMR spectra.

3.4.3 Unsuccessful Synthesis of Water Soluble Porphyrin-Fullerene Trimer

Despite the success of making porphyrin dyads and triads, all attempts to produce a H₂O soluble porphyrin-fullerene triad were unsuccessful. The synthesis of the required dyad ester 81 was achieved in a 47% yield by reacting 3 eq. of phosphonium salt 27 with benzene-1,3,5-tricarbaldehyde 74. The Prato reaction was however unsuccessful with reflux failing to produce any new product, while microwave irradiation produced uncharacterised baseline material (Scheme 3-21).

(i) Toluene, microwave.

Scheme 3-21. Unsuccessful synthesis of amphiphilic porphyrin-fullerene conjugate.
3.5 Conclusion and Future Directions

A series of precursor H$_2$O soluble porphyrin phosphonium salts (m-ester 27, p-silyl 36 and p-ester 51) were synthesised for use in construction of amphiphilic porphyrin molecules and arrays. The synthesis of phosphonium salts 51 and 36 needed to be modified from standard procedures due to problematic Vilmeier formylation (51) and the inability to remove copper from the porphyrin core (36).

Phosphonium salts 27 and 36 were used to create amphiphilic molecules, with porphyrin dyads synthesised using the step-by-step approach.$^{[78a]}$ 3-Benzoeic acid amphiphilic arrays were synthesised to form a series of arrays with controlled metal centers. The methodology allowed for formation of Zn-Zn, Zn-Fe and Zn-free-base porphyrin dyads. Future array synthesis for the benzoic acid containing porphyrins should now be directed towards arrays with 3 or more porphyrins. Linear arrays and arrays based from a central tetra formyl porphyrin should be the focus, with metals in the porphyrin cores introduced to achieve directional energy transfer.

A sulfonic acid amphiphilic porphyrin and porphyrin dyad were also synthesised, with conversion of the trimethyl silyl group to the sulfonic acid group giving the compound aqueous solubility. The sulfonic acid group improved dyad solubility, with the dyad showing improved solubility in acidic conditions in comparison to its benzoic acid counterpart.

The successful synthesis of amphiphilic porphyrin dyads will allow for maquette binding studies to be performed. This study is the focus of Mr Christopher Hobbs thesis.

Porphyrin styryl aldehydes were then used to produce porphyrin fullerene conjugates. The free-base and zinc porphyrin fullerene triads and a porphyrin fullerene dyads were able to be characterized were and sent to the Guldi group at Friedrich-Alexander University Erlangen-Nuremberg for photophysical characterisation. The successful synthesis of the porphyrin-fullerene conjugates will allow for future research to be begun to synthesise water soluble derivatives similar to the amphiphilic dyads.
Chapter 4
Simplified Synthesis of Vinyl β-Substituted Porphyrin Dyes and Dyads
4.1 Introduction

The need to generate a large and diverse range of amphiphilic porphyrin arrays resulted in various synthetic approaches being considered, that could be used to overcome some of the limitations of Wittig chemistry that was previously utilised to produce porphyrin dyads and arrays. Chapter 3 showed that synthetic ease and versatility is increased with the use of porphyrin building blocks. It was decided that due to β-pyrrolic formylporphyrins being readily available in our laboratory and our experience using Knoevenagel reactions for the generation of dyes for DSSCs (Scheme 4-1A), that Knoevenagel chemistry should be investigated for creation of amphiphilic porphyrin arrays (Scheme 4-1B). The proposed method would provide a simple scalable methodology, and would also allow for synthesis and characterisation of hydrophobic molecules to determine the versatility of the reaction methodology.

Scheme 4-1. A) Knoevenagel condensations used for attaching binding groups to porphyrins for DSSCs. B) Proposed use of Knoevenagel condensations for porphyrin dyad synthesis
4.1.1 Non-Wittig Synthetic Approaches Towards Amphiphilic Porphyrin Arrays

The successful synthesis of compounds in Chapter 3 by Wittig chemistry has provided a means to synthesise amphiphilic porphyrin dyads. The synthesis of these molecules was however coupled with problems that have also been previously reported with hydrophobic vinyl linked porphyrins and porphyrin arrays.\cite{106} The production of undesired and difficult to purify methyl porphyrin sideproducts and the formation of E/Z isomers require an additional isomerisation for porphyrin arrays synthesised by Wittig chemistry (Scheme 4-2). Both issues reduce the effectiveness of the Wittig synthesis as well as the purity of the resulting arrays.\cite{106}

\[ (i) \text{DBU, CHCl}_3. \]

Scheme 4-2. Problems associated with Wittig coupling between porphyrin phosphonium salts and substituted aldehydes.

E/Z isomers are considered a minor synthetic problem as the all E isomer can be produced with iodine treatment, while the presence of the methyl side product is more of an issue. Refinement
of the Wittig reaction by the use of DBU in degassed, dry solvent and under an inert atmosphere has lowered the amount of methyl side product. Small amounts of contamination are still problematic with diligent chromatography required to produce pure product.\cite{78a} This purification issue along with the 6 step porphyrin phosphonium salt synthesis resulted in a search to find a synthetic methodology to synthesise amphiphilic porphyrin arrays that could overcome these concerns.

To minimise steps in the synthesis of amphiphilic porphyrin arrays, meso-meso linked porphyrins were not considered due to their extended synthesis and purification requirements. Meso-meso linked porphyrins are commonly prepared with an early synthetic step being a low yielding, difficult to purify statistical porphyrin mixture. The meso-meso linked dyad of Zhang et al. produces two problematic purifications, with the mixed aldehyde porphyrin condensation and subsequent bromination yielding 19% and 55% respectively (Scheme 4-3).\cite{138} Therefore only the synthesis of β-linked arrays was considered.

\[(\text{i}) \text{TFA, DDQ. (ii) NBS. (iii) a) Phenylboronic acid, Pd(PPh}_{3})_{4}, \text{Cs}_{2}\text{CO}_{3}; \text{b) Zn(OAc)}_{2}.2\text{H}_{2}\text{O. (iv) (bis(trifluoroacetoxy)iodo)benzene. (v) KOH, EtOH (EtOH)/H}_{2}\text{O/THF.}}\)

\[\text{Scheme 4-3. Synthesis of JY07 by Zhang et al.}\]
Functionalisation of the β-pyrrolic position has resulted in porphyrins with groups suitable for binding to surfaces or porphyrin array formation. The extension of conjugation and resultant extension of the porphyrin π-system has the added bonus of increased performance in devices such as DSSCs.

Along with Wittig chemistry, Suzuki-Miyaura cross coupling and Mizoroki-Heck reactions are both used in the β-functionalisation of porphyrins. The use of cross coupling reactions is once again limited by the yield and purification of porphyrin starting materials. The synthesis of asymmetric porphyrins is dependent upon the mono functionalisation of the porphyrin core, which is difficult to control for borylation and bromination. Mono substitution is achievable for both; however di-substituted compounds are usually present and difficult to purify from the desired mono substituted material. Once the starting material is isolated, Suzuki-Miyaura and Mizoroki-Heck reactions produce high yielding functionalised asymmetric porphyrins and porphyrin arrays. The porphyrins and porphyrin arrays synthesised by Cai et al. show the versatility of Suzuki-Miyaura cross coupling however the borylated starting materials were continually contaminated with the unwanted mono or diborylated material (Figure 4-1).

Figure 4-1. Suzuki-Miyaura cross coupled porphyrin arrays by Cai et al.
β-Pyrrolic formylporphyrins have been prepared for a wide range of porphyrins with high yields of easy-to-purify material obtained. Our group has extensive knowledge of the preparation and use of β-pyrrolic formylporphyrins with their synthesis being required for the preparation of porphyrin phosphonium salts for use in Wittig chemistry (Chapter 3). As demonstrated by us and other researchers, the β-pyrrolic formylporphyrins provide an excellent substrate for coupling reactions. Moura et al. have used aldol condensation on formylporphyrins to generate an α,β-unsaturated ketone unit in the β-pyrrolic position for metal ion sensing (Scheme 4-4). Ke et al. have also shown that Knoevenagel condensation is capable of extending conjugation from the β-pyrrolic formyl group (Scheme 4-5). Work in our laboratory has indicated that Knoevenagel condensation is useful for adding functionality to extended β-pyrrolic conjugated systems (Figure 4-2A) and meso substituted porphyrins (Figure 4-2B).

Scheme 4-4. Aldol condensation of β-pyrrolic formylporphyrin by Moura et al.

Scheme 4-5. Knoevenagel condensation of β-pyrrolic formylporphyrin by Ke et al.
Therefore, the use of synthons such as phenylacetonitriles and 1,4-phenylenediacetonitrile in Knoevenagel condensations could provide a facile route to both vinyl-substituted porphyrins and porphyrin dyads (Scheme 4-6). The condensation of commercially available phenyl acetonitriles to β-pyrrolic formylporphyrins would provide a synthetic series similar to vinyl linked compounds (Wittig chemistry) and allow for a direct comparison between the two synthetic methodologies. Using 1,4-phenylenediacetonitrile in one or two steps, the proposed approach would provide a simplified method of producing both symmetric (Route C) and asymmetric (Route B) porphyrin arrays.
4.2 Synthesis

4.2.1 Synthesis of Substituted Porphyrin Monomers

In order to determine reaction versatility, electron rich and electron poor phenylacetonitriles were used to form a series of asymmetric porphyrins. Methyl 4-(cyanomethyl)benzoate 82 was reacted with formyl TPP 14 and formyl tetraxylylporphyrin (TXP) 17, at RT using DBU to form 88.

Scheme 4-6. Proposed Knoevenagel condensation routes for the synthesis of functionalised porphyrins and porphyrin dyads.
and 85 in 84% and 93% yields, respectively (Scheme 4-6 and Table 4-1). The more electron rich phenylacetonitrile 83 failed to react under the same conditions, with reflux in CHCl₃ also failing to give any desired products.

![Diagram](image)

(i) DBU, CH₂Cl₂, RT. (ii) DBU, DCE, microwave. (iii) KOTBu, DMF, microwave.

**Scheme 4-7.** Synthesis of functionalised porphyrins 85-90 and Zn85-Zn90.

**Table 4-1.** Reaction conditions and yields of porphyrins 85-90.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Reaction Conditions</th>
<th>Base</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>RT</td>
<td>DBU</td>
<td>93</td>
</tr>
<tr>
<td>88</td>
<td>RT</td>
<td>DBU</td>
<td>84</td>
</tr>
<tr>
<td>86</td>
<td>Microwave, 100°C</td>
<td>DBU</td>
<td>37</td>
</tr>
<tr>
<td>89</td>
<td>Microwave, 100°C</td>
<td>DBU</td>
<td>37</td>
</tr>
<tr>
<td>87</td>
<td>Microwave, 100°C</td>
<td>KOTBu</td>
<td>59</td>
</tr>
<tr>
<td>90</td>
<td>Microwave, 100°C</td>
<td>KOTBu</td>
<td>57</td>
</tr>
</tbody>
</table>

The reaction was then performed under microwave irradiation using DBU, with formyl TPP 14 and formyl TXP 17 forming 89 and 86 in similar yields (37%). The reaction went to completion with parameters set at 100°C and 250 watts for 50 min; at 80°C and shorter reaction times starting material was still present in both cases after irradiation. The presence of a strong
electron donating methoxy group in 84 suppressed the reaction and a stronger base had to be used. Microwave conditions of 100°C and 250 watts for 20 min with potassium tert-butoxide (KOtBu) produced 90 and 87 in 57% and 59% yield respectively (Scheme 4-7 and Table 4-1). The characterisation of these porphyrin products and those following is discussed later in this chapter (Section 4.3) given the similar nature of the materials.

The substitution pattern of the phenylacetonitriles affected the reactivity of the compound towards Knoevenagel condensation. While electron deficient phenylacetonitriles react under mild conditions, electron donating substituents tend to suppress the condensation requiring microwave irradiation or microwave irradiation and a stronger base. Microwave conditions however produced side products as shown by the increased level of uncharacterised baseline tar. This material, which was not observed in the formation of 85 and 88, resulted in a decreased yield for all microwave irradiated reactions (Table 4-1).

Since zinc porphyrins are typically used for light harvesting, all the resulting condensation products were converted to zinc porphyrins. Zinc insertions were performed using standard techniques to form compounds Zn85- Zn90.\(^{[146]}\)

The previous use of vinyl linked porphyrin 92 in a DSSC presented the opportunity for a direct comparison between the hydrolysed Knoevenagel product (Scheme 4-7) and 92 as one way to assess the effect of the added cyano group.\(^{[79]}\) This comparison of porphyrin performance in DSSCs will be discussed in Section 4.3.8. The required hydrolysis was performed by refluxing the porphyrin in THF, H₂O and MeOH in the presence of aqueous KOH for 22 h, followed by neutralisation with 2M aqueous H₃PO₄ (Scheme 4-8).\(^{[79]}\)

\[(i) \text{ KOH, THF, } H_2O, \text{ MeOH, reflux, } 22 \text{ h.} \]

**Scheme 4-8.** Hydrolysis of Zn85 to form 91 and structure of vinyl linked porphyrin 92.
4.2.2 Dyad Synthesis

Following the successful synthesis of vinyl linked porphyrin monomers using Knoevenagel condensation, the development of a Knoevenagel route to porphyrin dyads was undertaken.

To investigate the synthesis of acrylonitrile linked porphyrin arrays, it was decided to first look at hydrophobic porphyrin dyads since arrays synthesised by Wittig chemistry were typically simpler to make, purify and characterise when compared to amphiphilic arrays. The successful synthesis of hydrophobic symmetrical, unsymmetrical and mixed metal arrays could provide great scope for future applications of these porphyrins. The knowledge gained from these synthetic methods, would then be used to investigate amphiphilic porphyrin dyads for maquette binding studies.

4.2.3 Synthesis of Symmetrical Porphyrin Dyads

Initially it was decided to explore symmetrical porphyrin dyad formation that could be produced in one step. Two eq. of formylporphyrin 93 were reacted with 1 eq. of 1,4-phenylenediacetonitrile at RT with DBU in chloroform. After 4 h, no increase of the desired dyad 94 was evident by TLC, with monosubstituted product and starting aldehyde 93 also present. The reaction was therefore stopped and column chromatographed to isolate the dyad. The similar Rf values of the dyad 94 and monosubstituted material resulted in problematic purification, with the dyad only isolated in 12% yield (Scheme 4-9).
Scheme 4-9. Synthesis of porphyrin dyad Zn94.

The $^1$H NMR spectrum of the unpurified porphyrin mixture and subsequent deconvolution using topspin NMR software of the pyrrolic NH peaks showed that the dyad 94 was present in 29% (Figure 4-3). The overlapping nature of the porphyrin dyad 94 band and monosubstituted material during column chromatography meant only the leading edge of the dyad fraction could be collected, resulting in the poor collected yields.
Figure 4-3. Deconvolution of pyrrolic NH peaks. NMR spectrum obtained on the crude reaction material after the attempted synthesis of 94.

This synthesis was attempted under various conditions, however a difficult-to-purify mixture was consistently obtained in all cases. Yields were not improved by heating to reflux in CHCl₃, microwave irradiation or by increasing the ratio of formylporphyrin 93 to 1,4-phenylenediacetonitrile (4:1 and 10:1). To overcome the poor yields, an investigation of the dyad formation using the two-step synthesis was then undertaken as it also provided a means for the fabrication of the more synthetically variable dyads.

4.2.4 Synthesis of Porphyrin Dyad Precursors

The condensation of porphyrin aldehydes to produce monofunctionalised materials was originally attempted using an excess (4 eq.) of 1,4-phenylenediacetonitrile to ensure dyad formation was minimised. Reaction at reflux in CHCl₃ produced 96 in 58% yield. Purification was once again problematic with the reaction producing the symmetrical porphyrin dyad in 11% yield. To push the reaction to completion, microwave irradiation was used, which along with 10 eq. of 1,4-phenylenediacetonitrile and excess DBU gave 96 in 68% with no symmetrical dyad present. The conditions of microwave irradiation of 100°C and 250 Watts for 30 min. produced porphyrins 97 (78%), 98 (80%) and 99 (43%) (Scheme 4-9). A lower yield of ester-containing porphyrin 99 was associated with an increased amount of baseline material, which was likely to
be the hydrolysed porphyrin ester, although this was not characterised due to the difficulty in purifying it.

![Diagram](image)

**Scheme 4-10.** Synthesis of dyad precursors 96-99 and Fe98.

The successful synthesis of these porphyrin dyad precursors opened up the possibility of introducing metals into the precursor in order to create mixed metal arrays. In particular the introduction of iron is problematic in that iron(III) is paramagnetic and prevents characterisation of iron porphyrins by NMR spectroscopy. Therefore it is useful to leave the introduction of iron into a porphyrin to as late a step in a synthesis as possible. As in haem, iron porphyrins are useful for protein attachment due to their small molecule binding capability. Consequently, the insertion of iron(III) into precursor 98 was investigated.

Following work in Chapter 3, porphyrin 98 was refluxed with FeCl₂ followed by exposure to molecular O₂ to produce Fe(III) porphyrin Fe98 in 58% yield (Scheme 4-10). The characterisation of Fe98 by MALDI mass spectrometry is described in Section 4.3.
4.2.5 Synthesis of Unsymmetrical Porphyrin Dyads

The synthesis of cyanocompounds 96-99 provides precursors towards the synthesis of a series of differing porphyrin dyads. Given the successful use of microwave irradiation to achieve the synthesis of these precursors it was then used to form the desired dyads.

Initial attempts to synthesise dyad 101 were performed using equal eq. of porphyrin 96 and formylporphyrin 17. Purification of early reactions showed that reaction completion was not being achieved and separation of dyad 101 from starting material 96 was problematic. This resulted in the use of 2.5 eq. of formylporphyrin 17 as this material could be easily separated from the porphyrin dyad. The microwave conditions used for the syntheses of 96-99 (100°C, 250 W, 30 min) never afforded complete dyad conversion, while increases in reaction time to 60 min increased unwanted baseline material. Full conversion and best yields of 80% were achieved with microwave conditions of 120°C and 250 W for 30 min, with excess DBU (Scheme 4-11).

The establishment of a dyad synthesis procedure paved the way for the investigation into the mixed free-base-metal dyads. Adjustments to the established procedure were necessary for the formation of free-base-zinc(II) porphyrin dyad 102 due to the loss of zinc from the porphyrin core during the reaction.

In order to determine what this was due to, a number of control experiments were undertaken. Zinc TPP was heated under the microwave conditions in DCE, DCE and excess DBU, and DCE with excess H2O. The zinc ion was retained in the porphyrin core only in the case of the zinc TPP in DCE. It was postulated that due to the hydroscopic nature of DBU, H2O was causing the displacement of the zinc resulting in a mixture of inseparable free-base-zinc(II) and free-base-free-base dyads. Dry sodium methoxide was therefore used for the synthesis of 102 resulting in a yield of 70% after 60 min without any loss of zinc from the dyad (Scheme 4-11).

Synthesis of free-base-iron(III) porphyrin dyad 103 was achieved by the reaction of Fe98 and formylporphyrin 17. Highest yields of 45% were achieved with DBU under microwave irradiation at 120°C and 250 W (Scheme 4-11). It was observed during the reaction that baseline material was forming earlier than for dyad 101, suggesting that the reaction time needed to be decreased. To ensure complete conversion, the other microwave conditions were maintained with the reaction time decreased to 20 min. This ensured conversion of porphyrin Fe98 to dyad 103 was achieved in 45% yield but with the least amount of material degradation.
As is common for the formation of zinc porphyrins, the formation of the zinc dyads was easily carried out. Zinc insertion was achieved according to standard conditions to produce quantitative yields of 104 and 105 (Scheme 4-11).[^146]

(i) DBU, DCE, microwave. (ii) Sodium Methoxide, THF, microwave.

**Scheme 4-11. Synthesis of porphyrin dyads 101-105.**

The synthesis of an amphiphilic porphyrin dyad was then investigated. The reaction was first attempted by reacting tetraphenylporphyrin Knoevenagel precursor 98 with the corresponding carboxyphenyl formylporphyrin 18. The reaction was performed using DBU in DCE with
microwave conditions established for the production of hydrophobic dyads (120°C, 250 W for 30 min) however no dyad was observed. The reaction was then performed using Knoevenagel precursor 99 and formyl TPP 14 reversing the ester placement. The reaction was carried out for 15 min and 30 min using identical conditions a number of times (Scheme 4-12). Purification of the reaction mixtures by flash chromatography consistently gave unreacted formyl TPP 14 as the only observable porphyrin. The ester 99 was never observed, suggesting that hydrolysis of the ester groups may have occurred before the Knoevenagel condensation leading to intractable products. Consequently, this approach was unsuccessful for the preparation of amphiphilic porphyrin dyads.

**Scheme 4-12.** Unsuccessful synthesis of amphiphilic porphyrin dyad.
4.2.6 Synthesis of Porphyrin Trimer

Wittig chemistry has been used to synthesise a large variety of both linear and branched porphyrin arrays, with the largest array being a porphyrin nonamer.\[78a\] The reaction between porphyrin phosphonium salts and benzene-1,3,5-tricarbaldehyde has however never gone to completion. The addition of 2 porphyrins is possible, however deactivation of the third aldehyde has resulted in failed attempts in the production of the porphyrin trimer.\[110\] The successful syntheses of the porphyrin dyads by Knoevenagel condensation offered the opportunity to investigate the development of a porphyrin trimer.

Work by Aakeröy et al. has shown three Knoevenagel condensations are possible for small molecule reactions with 2,2',2''-(benzene-1,3,5-triyl)triacetonitrile 106.\[147\] Tricyano compound 106 was successfully prepared from 1,3,5-tris(bromomethyl)benzene. However formation of a porphyrin trimer using this reagent was unsuccessful.\[148\] Condensation of porphyrins in both single step or step-by-step syntheses and using differing microwave conditions always resulted in the formation of porphyrin 107 (Scheme 4-13). Formation of this monosubstituted porphyrin was easily observed by $^1$H NMR spectroscopy due to the presence of a single vinyl proton and 2:1 ratio of the acetonitrile-phenyl aromatic protons. All other characterisation data was consistent with this structure.
(i) NaCN, DMSO, 40°C, 16 h. (ii) DBU, DCE, microwave.

Scheme 4-13. Synthesis of 107, in an attempt to synthesise a porphyrin trimer.

4.3 Characterisation

4.3.1 NMR Spectroscopy

The principal characterisation technique for the Knoevenagel condensation porphyrin series was $^1$H NMR spectroscopy. 2D COSY spectra were often used to help with peak assignment. All spectra were recorded in CDCl$_3$ apart from 91, which was recorded in acetone-$d_6$.

4.3.2 NMR Analysis of Functionalised Porphyrin Monomers

$^1$H NMR spectroscopy shows a change in the electronics of the modified porphyrins. The $^1$H NMR spectra of the CN styryl porphyrins 85-90 all show similar chemical shifts characteristic of these
types of molecules as previously reported, with the key difference being the influence of the cyano group both electronically and through space on its neighbouring protons.\textsuperscript{[112]} Thus, compared to the previously reported styryl-substituted porphyrins, the introduction of the cyano group results in a downfield shift of β-pyrrolic proton H$_3$. For example, comparison of 4-methoxy styryl porphyrin 87 (Figure 4-4) and the non-cyano substituted derivative shows a shift of H$_3$ from 9.05 ppm to 9.48 ppm.\textsuperscript{[112]} Clearly, the neighbouring cyano group deshields this proton. The remaining 6 β-pyrrolic protons are observed approximately between 9.0 ppm to 8.7 ppm as previously reported. Commonly, spin-spin coupling of $^3$$J$ = 5.0 Hz is observed, however the overlap of signals complicates the coupling.

Tetraxylylporphyrin derivatives have ortho xylyl aromatic proton peaks between 7.9 and 7.7 ppm, with 86 and 87 having 4 slightly broad singlets and 85 having one distinct singlet with the other 3 overlapping. The para xylyl peaks are further upfield than the ortho signals and are found between 7.4 and 7.2 ppm. Due to the asymmetric nature of the porphyrin, the para xylyl signals show greater chemical shifts as 3 broad singlets (1:2:1). The unsymmetrical nature of the porphyrin also affects the methyl peaks of the xylyl groups with the signals observed as 4 singlets between 2.6 and 2.4 ppm, as shown for the spectra of 87 in Figure 4-4.
Figure 4-4. $^1$H NMR spectra of 87.
The phenyl substituted signals of TPP derivatives 88-90 are more complex than their tetraxylyl counterparts, with ortho aromatic signals observed as multiplets at 8.3 (2H) and 8.2 ppm (6H). Meta and para signals were recorded as multiplets between 7.8 ppm and 7.6 ppm.

As expected with the vinylic substitution by the cyano group, the vinyl signals (85-87 and 90) are singlets between 7.7 ppm and 7.5 ppm, although this singlet is buried in a multiplet for ester porphyrin 88. Surprisingly, in only one case, styryl porphyrin 89 is a small 4 bond coupling of $^4J=1.2$ Hz to $H_3$ observed.

The mono-substituted porphyrins 85, 87, 88 and 90 $H_{AR}$ peaks are doublets with assignment determined from both coupling constants and COSY spectra while the protons for 86 and 89 are observed as 2 multiplets in a ratio of 2:3 (ortho: meta/para protons). The slightly broad singlet at -2.6 ppm is assigned to the highly shielded pyrrolic NH groups at the centre of the porphyrin core (Figure 4-4). The addition of zinc to the porphyrin results in the disappearance of this signal.

The series of porphyrin monomers 96-99 also show the same $^1H$ NMR spectral characteristics. All the compounds show the presence of an $H_{benzyl}$ signal, a singlet at 3.8 ppm. A representative spectrum of porphyrin 96 shows a tightly grouped set of signals in the aromatic region. $H_o$ and $H_m$ are however determined from the COSY NMR spectrum, while the doublets of $H_{AR}$ are determined from the COSY spectrum and the spin-spin coupling of $^3J=8.0$ Hz (Figure 4-5).
Figure 4-5. $^1$H NMR spectra of 96.
4.3.3 NMR Analysis of Porphyrin Dyads

The addition of a second porphyrin to form a Knoevenagel porphyrin dyad shows similar $^1$H NMR spectra trends to the porphyrin monomers. The creation of unsymmetrical porphyrin dyads complicates the downfield region, with the differing phenyl groups overlapping and producing multiplets. The use of COSY spectra however helped resolve all peaks for assignment. For aromatic region simplicity, the symmetrical porphyrin dyad $^1$H NMR spectrum is shown (Figure 4-6). The aromatic region for 94 is similar to previously discussed spectra, with singlet of $H_3$ downfield from the other $\beta$-pyrrolic protons due to the deshielding effect from the porphyrin core and acrylonitrile group. The disappearance of the $H_{\text{benzylic}}$ peak indicates dimer formation, while the single broad pyrrolic NH peak indicates the presence of a single isomer.
Figure 4-6. $^1$H NMR spectra of 94.
4.3.4 Isomer Identification

Analysis of $^1$H NMR spectra of compounds synthesised by Wittig chemistry shows a complex downfield aromatic region and 2 pyrrolic NH peaks, due to the formation of E/Z isomers.$^{[106]}$ The simplicity of the $^1$H NMR signal indicated that Knoevenagel condensation was producing one isomer. To determine the orientation of the molecule, nuclear overhauser effect (NOE) and 2D nuclear overhauser effect spectroscopy (NOESY) spectra were collected for 87. Analysis of 3D structures created in Chemdraw 3D with MM2 energy minimisation, shows for the Z isomer $H_{\text{vinyl}}$ and $H_{\text{AR}}$ are in close proximity (Figure 4-7b). The $E$ isomer however has the nitrile group near $H_{\text{vinyl}}$ and therefore will not produce any thru space cross peaks between $H_{\text{vinyl}}$ and $H_{\text{AR}}$ (Figure 4-7a).

![Figure 4-7. Computer generated 3D structures of E/Z isomers of porphyrin 87, highlighting the through space correlation associated around the acrylonitrile group (green, purple).](image)

By selecting $H_{\text{vinyl}}$ the 1D NOE NMR spectrum shows positive signals for $H_3$, $H_{\text{D-Xyl}}$ and $H_{\text{AR}}$ indicating that the configuration is the Z isomer (Figure 4-8). NOESY was also performed with a cross peak observed between $H_{\text{vinyl}}$ and $H_{\text{AR}}$, confirming the bonds Z isomer configuration (Figure 4-9).
**Figure 4-8.** NOE spectra of 87 showing coupling from $H_{\text{vinyl}}$ to $H_3$, and $H_{\text{AR}}$.

**Figure 4-9.** NOESY spectra of 87, showing the cross peak between $H_{\text{vinyl}}$ and $H_{\text{AR}}$. 
4.3.5 Mass Spectrometry

Low resolution characterisation of synthesised porphyrins was performed by the author using MALDI mass spectrometry. MALDI mass spectrometry also aided TLC for reaction monitoring with the determination of reaction completion and identification of desired products. 1,8,9-Anthracenetriol was the matrix used for all porphyrins, which along with variation of laser power, gave consistent, good quality spectra for $M^+$, $MH^+$ and $M^+\cdot Cl^-$. MALDI mass spectra were used for the characterisation of molecules to support $^1$H NMR spectra. MALDI mass spectrometry however became the predominant characterisation technique, along with UV-vis spectroscopy of porphyrins that were unable to be characterized by $^1$H NMR spectra. Compounds Fe98, 103 and 105 were primarily characterised by MALDI mass spectra due to the paramagnetic nature of iron(III) porphyrins (Figure 4-10). Depending on the porphyrin and laser intensity, the chloride counter ion could be seen in very low intensity however $M^+\cdot Cl^-$ was dominant and more commonly observed.

Figure 4-10. MALDI mass spectrum of 105, using 1,8,9-anthracenetriol as the matrix.
4.3.6 UV-vis Absorption Spectroscopy

UV-vis absorption spectroscopy was carried out on all porphyrins for characterisation purposes. As solvent, CH$_2$Cl$_2$ was predominantly used, however DMF was required for the acid-containing porphyrin 91. The typical porphyrin absorption features are observed for all porphyrin compounds with free-base porphyrins exhibiting a strong Soret band at 420-435 nm and four Q bands as a result of $D_{2h}$ symmetry and the metallated compounds giving similar Soret bands but only two Q bands as a result of $D_{4h}$ symmetry.[128]

![UV-vis spectra of 89 and 108 in CH$_2$Cl$_2$.](image)

Figure 4-11. UV-vis spectra of 89 and 108 in CH$_2$Cl$_2$.

A comparison between cyanoporphyrin 89 and its vinyl linked counterpart 108 was made to determine the effect of the acrylonitrile group. The spectra show that the introduction of the electron-withdrawing group result in a red shift of the Soret peak by 7 nm from 422 nm to 429 nm (Figure 4-11). Other cyano containing porphyrins show a similar shift.

The Soret bands of the porphyrin cyanodyads are also redshifted in relation to their vinyl linked counter parts, with the Zn94 Soret peak centered at 437 nm (425 nm for and 422 nm). For example, the Soret band of vinyl linked ZnTPP-ZnT3EP dyad 59 was centered at 425 nm and that
of ZnTXP-ZnT3EP dyad 60 at 422 nm. As described in Section 3.3.8, the conjugation of the porphyrin cores had the potential to split the Soret peaks, however as with the vinyl linked dyads, the single broad Soret peak in the spectra of the porphyrin cyanodyads suggests limited electronic coupling. A shoulder is not observed for the cyano linked dyads, due to the cyano groups affecting compound planarity and therefore reducing electronic coupling.

4.3.7 Electrochemical Analysis

The effect that the newly introduced acrylonitrile group brings to the electronic nature of asymmetric porphyrins was probed by electrochemical analysis (Figure 4-12). The electrochemical data for porphyrins ester porphyrin Zn88, phenyl porphyrin Zn89, methoxy porphyrin Zn90 and vinyl linked porphyrin 109 was obtained and each shows the presence of four reversible processes, two oxidations and two reductions (Table 4-2). A comparison between porphyrin Zn89 and porphyrin 109 should show the direct influence of the acrylonitrile group. Comparison of ester porphyrin Zn88, phenyl porphyrin Zn89 and methoxy porphyrin Zn90 should show if the acrylonitrile or substituents on the phenyl ring are the dominant electronic feature.

Figure 4-12. Structure of vinyl linked porphyrin 109.
Table 4-2. E/V vs. Fc/Fc+· for Zn88, Zn89, Zn90 and 109 in CH₂Cl₂. TPP 2 included as reference.[114]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn88</td>
<td>0.33</td>
<td>0.62</td>
</tr>
<tr>
<td>Zn89</td>
<td>0.33</td>
<td>0.60</td>
</tr>
<tr>
<td>Zn90</td>
<td>0.31</td>
<td>0.59</td>
</tr>
<tr>
<td>109</td>
<td>0.29</td>
<td>0.55</td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Comparison between Zn89 and 109 shows that the major contribution of the nitrile group is observed in the reduction of the porphyrin. The introduction of the cyano electron withdrawing group shifts electron density off the porphyrin core, resulting in a shift of reduction potential by 0.14 and 0.15 V vs. ferrocene/ferrocenium (Fc/Fc+·) (Figure 4-13).[112]

Figure 4-13. Cyclic voltammogram of Zn89 in comparison to 109 in CH₂Cl₂.

Reduction of the porphyrin is also affected by the substituents on the benzene ring, while oxidation does not show any major changes (Table 4-2). Compared to Zn89, the introduction of the electron withdrawing ester group in Zn88 shifts both reduction potentials more positively by 0.7 and 0.8 V vs. Fc/Fc+· (Figure 4-14). The introduction of the electron donating methoxy group has less of an effect, however reduction potentials are -0.3 V higher.
The introduction of an electron withdrawing group (Zn88) and an electron donating group (Zn90) is able to affect the electron density of the porphyrin; however the introduction of the nitrile group by the Knoevenagel condensation is the dominant feature in the electrochemistry of this series of porphyrins.

4.3.8 Dye Sensitised Solar Cell Performance

The DSSC performance of porphyrin 91 and porphyrin 92 was performed by Dr Klaudia Wagner. The comparison was required to ensure that acrylonitrile linked porphyrins could not only be made in similar yields and fewer steps to compounds linked by Wittig chemistry, but also compete with them in application based performance.

The two porphyrins were used as sensitisers in sandwich configuration Gratzel cells with the results of 12 µm film cells summarised in Table 4-3.

Figure 4-14. Cyclic voltammogram of Zn85, Zn86 and Zn87 in CH₂Cl₂.
Table 4-3. DSSC performances of 91 and 92 in 12 µm film cells.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>( V_{oc} ) (mV)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>FF</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91</td>
<td>630</td>
<td>7.05</td>
<td>0.70</td>
<td>3.11</td>
</tr>
<tr>
<td>92</td>
<td>608</td>
<td>7.12</td>
<td>0.71</td>
<td>3.07</td>
</tr>
</tbody>
</table>

Photovoltage and photocurrent are comparable between 91 and 92 with the results within sample error while photovoltaic efficiency is the same between the two porphyrins. The complementary results indicate that Knoevenagel coupling is an adequate method for simplified dye synthesis for DSSCs.

4.4 Conclusions and Future Directions

Knoevenagel chemistry has been utilised to provide a series of functionalised porphyrins with moderate to excellent yields. The development of a new method towards porphyrin functionalisation had several benefits, including reduced synthetic steps and the formation of one isomer which was proven by 1D NOE and NOESY NMR spectroscopy.

Porphyrin dyads were also achieved by Knoevenagel chemistry, with dyads produced by both one and two-step methodologies. The one step method produced dyads in low difficult to purify yields and therefore dyad synthesis was more commonly performed in two steps. The two-step procedure allowed for control of both porphyrin substitution and metal centres, with free-base-free-base, free-base-Zn, Zn-Zn and Zn-Fe dyads made. The synthesis of amphiphilic dyads and a porphyrin trimer were however unsuccessful using Knoevenagel chemistry and should be investigated for future work. Benzoic acid containing porphyrins should be targeted due to the success of the dyads produced in Chapter 3. Arrays larger than 2 porphyrins should also be investigated, with linear and branched arrays believed to be achievable.

Electrochemical analysis of the functionalised porphyrin monomers (Zn88-Zn90) in relation to a Wittig linked counterpart (109) shows the incorporation of the electron withdrawing cyano group is able to shift electron density off the porphyrin core.\(^{[112]}\) Electrochemical analysis indicated that the cyano group is the dominating feature, however the substitution pattern off the benzene ring was able to affect the reduction of the porphyrin.

DSSC performance between porphyrin 91 and its Wittig linked counterpart 92 showed comparable performances for photovoltage, photocurrent and photovoltaic efficiency. The
performance indicates porphyrin 91 can be made in similar yields, with less steps in comparison to Wittig chemistry.
Chapter 5
Synthesis of a Covalently Linked Porphyrin Hydrogel
Chapter 5- Synthesis of a Covalently Linked Porphyrin Hydrogel

5.1 Introduction

The use of a wide variety of solid supports for biological applications, typically in an aqueous environment, is currently a major focus of research for the Intelligent Polymer Research Institute (IPRI). The development in this thesis of a wide variety of amphiphilic porphyrins and arrays presented a unique opportunity to explore the functionalisation of biocompatible solid supports such as hydrogels. Therefore, this chapter explores the new functionalisation of one particular type of hydrogel commonly used for actuation purposes.

5.1.1 Porphyrin Hydrogels

Hydrogels are cross-linked swollen 3D polymer networks that can accommodate large volumes of water and can be made from various synthetic and natural products. Depending on polymer network and crosslinking technique, the hydrogels characteristics can be altered in regard to strength, flexibility and swelling behaviour. Recently hydrogels have shown promise as various biological tissue mimics, however their properties also compliment various porphyrin-based applications. The development of porphyrin applications has resulted in a series of non-covalent and covalent approaches to construct porphyrin-hydrogel matrices.

5.1.2 Non-Covalent Porphyrin Hydrogels

Once a cross-linked polymer network is established, doping of a hydrogel can be performed to impart added functionality to the structure by either surface modification or physical encapsulation. Porphyrin-hydrogel constructs have been prepared in this manner, by firstly achieving a fully formed gel network followed by soaking of the gel in a porphyrin solution. The non-covalent attachment of porphyrins can result in compound leeching, however such materials are stable enough for use in in vivo imaging, metal sensing, singlet O₂ generation and modelling of photosynthetic systems.

Ng et al. and Mandal et al. incorporated a manganese tetraphenol porphyrin and chlorophyll-a respectively into dehydrated hydrogels. 5-Hydroxy-N-pentyl maleimide and N-vinyl-2-pyrrolidone (Ng et al.) and chitosan (Mandal et al.) gels were cast, evaporated and immersed in solutions of the respective tetrapyrrrole to form the desired swollen gel.
Charged polymer systems have also been employed by Brady et al. to incorporate oppositely charged porphyrins into the cast gels. Anionic (2-hydroxyethyl methacrylate and 2-methacrylic acid) and cationic (2-hydroxyethyl methacrylate and 2-(diethylamino)ethyl methacrylate) copolymers were prepared and once gelation was achieved were immersed in corresponding, oppositely charged porphyrin solution. Repetitive soakings of the gels in tetra(4-sulfophenyl)porphyrin (TPPS) and tetramethylpyridiniumporphyrin (TMPyP) solutions achieved control of doping level in the final material, with ionic bonding ensuring high levels of doping and stability (Figure 5-1).\textsuperscript{[156]}

![Figure 5-1. Passive incorporation of charged porphyrins into oppositely charged gel networks.\textsuperscript{[156]}]

5.1.3 Sol Gel Porphyrin Hydrogel

Thermosensitive hydrogels are gels that undergo a phase transition (sol-gel transition) at specific temperatures to form a solid material.\textsuperscript{[157]} The gel is able to form a reversible non-flowing solid structure from a flowing solution with the only external stimuli being changes in temperature.\textsuperscript{[158]} PEG polymer blends have been shown to undergo sol-gel transformations with PEG-poly(lactic-co-glycolic acid)-PEG copolymers transitioning from solution at RT to a gel at body temperature. Various factors are believed to drive the sol-gel transition, however the PEG blends are believed to gel due to an increase in polymer-polymer attraction and increase in
micelle growth.\textsuperscript{[159]} Using this chemistry, porphyrin-based thermosensitive gels are able to be synthesised by linking PEG to tetra(4-carboxyphenyl)porphyrin 110, followed by ring opening polymerisation of ε-caprolactone (Figure 5-2). The porphyrin-PEG-polycaprolactone copolymer undergoes two sol-gel transformations with the material forming a solid gel between 30°C and 40°C.\textsuperscript{[160]}

![Figure 5-2. A porphyrin-PEG-Polycaprolactone based sol-gel.\textsuperscript{[159]}](image)

5.1.4 Covalent Porphyrin Hydrogels

To increase the long term stability of synthesised porphyrin hydrogel constructs, the porphyrin had to be incorporated into the hydrogel backbone. By using a porphyrin as a cross linking unit, the leaching of porphyrins that is characteristic of passively incorporated porphyrin hydrogels could be limited. By covalently anchoring the porphyrin into the gel structure, dye loading would also be increased.

Amide coupling has been used to form tetra(4-carboxyphenyl)porphyrin 110 and polyetheramine (Jeffamine) based hydrogels, with complete gelation occurring for high molecular weight PEG-diamines above 3000 Da. Fluorescence imaging indicated improved gel
stability after 7 days with a significantly higher porphyrin concentration in comparison to passively incorporated porphyrin hydrogel (Figure 5-3).\textsuperscript{[161]}

![Figure 5-3](image.png)

**Figure 5-3.** PEG based hydrogel with a covalently attached porphyrin incorporated into the polymer backbone.\textsuperscript{[161]}

### 5.1.5 Epoxy Amine Hydrogels

From the vast field of hydrogel synthesis available, one facile route for formation of a complete polymer network is epoxy-amine chemistry.\textsuperscript{[162]} The nucleophilic addition of a primary or secondary amine to an epoxide group produces a hemiaminal, which when combined with appropriate polymers can produce hydrogels. Calvert *et al.* and Stevens *et al.* have shown that epoxy-amine chemistry can use Jeffamine and poly(ethylene glycol) diglycidyl ether (PEGDGE) to achieve reproducible structures (Figure 5-4).\textsuperscript{[150, 163]}

![Scheme 5-1](image.png)

**Scheme 5-1.** PEGDGE and Jeffamine and the corresponding polymerisation reaction to form an epoxy amine linked hydrogel.\textsuperscript{[163]}
The ease of hydrogel formation using epoxy-amine chemistry meant the methodology could potentially be used to synthesise porphyrin hydrogels. By developing a new method for porphyrin hydrogel creation, it was hoped that the more available lower molecular weight Jeffamines (<3000 Da, Section 5.1.4) could be used.\cite{16}
The ability to produce a porphyrin hydrogel in a simple and cheap manner would mean the easily available gels could be used for various applications such as biological imaging and aqueous based sensors.

### 5.2 Epoxy Amine Based Porphyrin Hydrogel

#### 5.2.1 Synthesis of Porphyrin-Jeffamine

As previously stated (Section 5.1.4), porphyrin hydrogels have been synthesied using a one step approach by linking tetra(4-carboxyphenyl)porphyrin \textbf{110} and high molecular weight Jeffamines.\cite{16}
This approach was therefore attempted using porphyrin \textbf{110} and the low molecular weight Jeffamine T403. All attempts resulted in no complete gel formation indicating the extra step is necessary was all low molecular weight Jeffamines (Figure 5-4).

![Failed gel formation using Jeffamine T403 and porphyrin 110.](image)

**Figure 5-4.** Failed gel formation using Jeffamine T403 and porphyrin \textbf{110}.

A two step approach (Route B, Scheme 5-2) was therefore adopted for the synthesis of the epoxy amine based porphyrin hydrogel. It was proposed that linking the porphyrin to a Jeffamine initially, followed by gel formation would allow gel formation and better material characterisation than attempting to characterise the formed porphyrin hydrogel itself.
To generate the porphyrin-jeffamine intermediate 111 the reaction had to attempt to eliminate the potential of a porphyrin arrays or a porphyrin-jeffamine network forming. To increase the potential for each carboxylic acid group reacting with an individual Jeffamine molecule, excess Jeffamine T403 was added to tetra(4-carboxyphenyl)porphyrin 110. As polymers are usually difficult to handle during organic reactions, this excess was only slight to ensure purification of porphyrin-jeffamine 111 was achievable.

Tetracarboxy porphyrin 110 was used, due to the ability to do an amide coupling with the amine groups of Jeffamine. Carbonyldiimidazole was originally used to perform the amide coupling reaction, however once Jeffamine T403 was added to the reaction mixture (porphyrin 110 and carbonyldiimidazole in either DMF or THF) the porphyrin instantly precipitated out of solution. Isolation and characterisation of the precipitate by both infrared spectroscopy (IR) and gel permeation chromatography (GPC) indicated that no coupling had occurred.

Amide coupling was successful using the Schotten-Baumann reaction, in which an acid chloride is generated in situ. Porphyrin 110 was dissolved in excess thionyl chloride and stirred overnight. The excess thionyl chloride was then removed and the resulting acid chloride treated with Jeffamine and triethylamine. The reaction instantly turned from green to red and was stirred for a further 24 h and the desired porphyrin-jeffamine porphyrin 111 was isolated (Scheme 5-3). The purple product at RT was a sticky gel that was difficult to handle, however cooling it with liquid N₂ allowed it to be satisfactorily handled.
i) Thionyl chloride, RT. ii) Triethylamine, RT


Porphyrin 111 characterisation was performed by both $^1$H NMR spectroscopy and IR spectroscopy. No product mass peaks could be detected by MALDI mass spectrometry and the compound was out of ES mass spectrometry's mass range. MALDI mass spectrometry could, however, support the conversion of porphyrin 110 to jeffamine-porphyrin 111. A mixture of porphyrin 107 and jeffamine typically shows the presence of a peak at 791 m/z that is the mass of tetracarboxyporphyrin 110, however after amide coupling this peak is no longer present.

The $^1$H NMR spectrum was not well defined, with multiplets replacing sharp peaks after the attachment of the 4 polymer chains to the porphyrin. The spectrum was dominated by Jeffamine T403 signals that are present as 2 large multiplets between 3.8-2.8 ppm and 1.8-0.7 ppm.
Comparison between Jeffamine and porphyrin-Jeffamine 111 showed these peaks were identical. The presence of the porphyrin was evident from downfield peaks corresponding to β-pyrrolic (8.9-8.8 ppm) and the ortho and meta aromatic signals (8.3-8.1 ppm) were also present as broad multiplets. The pyrrolic NH signals are also present as a broad singlet at -2.8 ppm.

IR spectroscopy was used to support 1H NMR spectroscopy and ensure amide coupling was successful, through the presence of the characteristic amide I, II and III stretches. Experiments were performed on both a control (Jeffamine and acid porphyrin mixture) and the failed carbonyldiimidazole reaction, which were compared to porphyrin-Jeffamine 111. All samples showed the presence a primary amine peak at 1550 cm\(^{-1}\) and an ether peak at 1100 cm\(^{-1}\) from the jeffamine polymer.

Successful amide coupling will be shown by the presence of secondary amide bands and the disappearance of carbonyl bands. Analysis of the IR spectra shows the presence of the amide I band at 1650 cm\(^{-1}\) that is indicative of the amide C=O stretch. A small carbonyl C=O stretch band is present at 1700 cm\(^{-1}\) that is also observed as a much more intense band in the control spectra. The presence of this band indicates that some residual carbonyl is present after the amide coupling reaction, however the disappearance of the carbonyl C-O-H bend at 1375 cm\(^{-1}\) indicates that, although we cannot quantify the amount of free benzoic acid groups the majority of the acid has been converted. Amide II N-H bend at 1550 cm\(^{-1}\) is shadowed by the presence of the amine N-H bend, due to the high free amine content in the sample while the amide III band is present in the spectra at 1300 cm\(^{-1}\). The high amount of hydrogen bonding in both samples is shown by the large band centered 2900 cm\(^{-1}\) that also shadows the presence of the characteristic N-H stretch (Figure 5-5).
5.2.2 Synthesis of Epoxy Amine Porphyrin Gel

The successful synthesis of the porphyrin-Jeffamine conjugate allowed for investigation into gel formation. Gel formation using epoxy-amine chemistry is commonly performed in aqueous media, however due to the lack of water solubility of porphyrin-Jeffamine 111, the porphyrin-based gel was prepared in DMF.\textsuperscript{164} The gels could then be swollen in H\textsubscript{2}O with DMF being removed from the structure by diffusion.\textsuperscript{162}

Functional group stoichiometry was used for gel formation with the ratio of amine groups to epoxide groups equal. This theory was originally used hoping each amine undergoes one reaction to form a hemiaminal, with low expectations for both amine hydrogens undergoing the reaction. Porphyrin-Jeffamine 111 and 4 mol equivalents of PEGDGE were dissolved in 10 mL, 5 mL, 2 mL, and 1 mL of DMF, poured into molds and placed in a temperature and humidity cabinet at 40 °C for 5 days. A humidity cabinet was used in order to prevent condensation forming from the reaction contents. Heating and sonication were required to dissolve porphyrin-Jeffamine 111 in the 2 mL and 1 mL samples. Gel formation was however only successful for the 1 mL
sample (Figure 5-6), with the 2 mL forming a sticky viscous paste and the 5 mL and 10 mL samples remaining as liquids.

Figure 5-6. Image of swollen porphyrin-PEGDGE hydrogel 112.

The synthesised gels were placed in individual beakers and swollen in excess milli-Q H$_2$O. The solvent was replaced daily to ensure DMF diffusion out of the sample, with the gels weighed daily until a constant weight was achieved. The swelling experiments were performed at RT (23 ± 2°C). It is important to note that there was no evidence of leaching of the porphyrin from the hydrogel, further evidence for its covalent attachment to the gels. The degree of swelling and equilibrium H$_2$O content of the gel was determined from the following equations:\[165]\n
\[
\text{Swelling Ratio} = \frac{\text{Swollen weight of gel}}{\text{Dry weight of gel}}
\]

\[
\text{Equilibrium Water Content} = \frac{\text{Weight of water in gel}}{\text{Swollen weight of gel}} \times 100
\]
Five identical samples were prepared so as to accurately determine the swelling ratio. The swelling ratio of the synthesised gel was 2.89 ± 0.04 and the percentage equilibrium H₂O content was 65.3 ± 0.5%. These values are similar to standard epoxy amine gels, however it was believed that the gel would not have the desired permeability if used for heavy metal detection. Nonetheless, this study has shown that porphyrins can be incorporated into the gel's polymer backbone.

In order to produce a gel more suitable for heavy metal detection, a more permeable gel structure is required that would result from a higher swelling ratio and greater H₂O content. This would lead to a gel with both poor mechanical strength and increased permeability. As a sensor is not designed for mechanical purposes, the poor strength can be tolerated.

Swelling of hydrogels increases with decrease of polymer concentration. As gel formation was unsuccessful with decreased concentrations of porphyrin-Jeffamine 111 and PEGDGE, the study turned to using porphyrin-Jeffamine 111 as a smaller fraction of the amine content by using further Jeffamine T403 in the gel formation.

The gels were once again synthesised using stoichiometric amounts of the amine functional groups to the epoxide groups. Jeffamine content could have been increased to any level, however to ensure swelling was achieved with a high porphyrin content experiments were performed using 1/8th of amine content coming from porphyrin-jeffamine 111 and 7/8th from Jeffamine T403. Porphyrin-jeffamine 111, Jeffamine T403 and PEGDGE were dissolved in 7 mL, 10 mL and 15 mL of DMF and were placed in a temperature and humidity cabinet at 40°C. The samples were left for 7 days with only the 7 mL sample forming a gel (Figure 5-7).

![Image of swollen porphyrin-Jeffamine-PEGDGE hydrogel 113.](image-url)
Five samples of the gel were once again immersed in milli-Q H$_2$O at RT (23 ± 2°C) with daily solvent changes and weighing of material. The resulting swelling ratio of gel 113 was increased to 13.09 ± 1.43, while H$_2$O content increased to 92.29 ± 0.85%. The drastic increase of these gel characteristics indicated that the permeability of the gel, for ion transport and subsequent metal detection would be significantly improved.

5.2.3 Rheology

To ensure the higher dilution porphyrin hydrogel 113 was capable of forming a complete network and not a sample of high molecular weight polymers, hydrogel 113 was examined by rheological testing. Rheological testing was performed with a controlled strain rheometer (Anton Paar Physica MCR 301, parallel plate, 21°C), with 4 samples tested under a strain amplitude sweep (frequency 10 rad/s) between 0.01% and 100% strain. The technique enables the solid and liquid components of the gel also known as the elastic or storage (G’) and viscous or loss (G″) modulus to be separated.\textsuperscript{[168]} These components are represented as individual plateaus, with the region between the two plateaus commonly known as the linear viscoelastic (LVE) region. The end of the LVE region is shown by a deflection from the plateau and is due to the irreversible deformation of the hydrogel.\textsuperscript{[169]}
Strain amplitude sweep shows a plateau for both storage ($G'$) and loss ($G''$) at $8.40 \pm 2.62$ kPa and $0.26 \pm 0.03$ kPa, respectively (Figure 5-8). Bakarich et al. state that a high $G'/G''$ value indicates the successful formation of a cross-linked polymer network, with high values of 11 supporting the successful formation. The high $G'/G''$ value of 32 obtained for porphyrin hydrogel 113 therefore proves the gel is a complete network.

5.2.4 Binding of Heavy Metals

Sensors based on the modification of fluorescence have been used in analytical chemistry for purposes such as medicinal and environmental sciences. Shifts of molecular fluorescence or creation of fluorescence can be induced in a system by the binding of an analyte to a target site. A porphyrin core is an ideal site for binding metallic analytes, with the distortion of the core able to alter the physical properties of the porphyrin.
Porphyrrins are able to bind a wide range of metals from metal salts in organic solvents. The formation of the highly permeable gel opened the way to investigate the binding of heavy metals such as mercury or cadmium with a view to developing a sensing system for these metals. Since mercury and cadmium porphyrins show a reasonable fluorescence, the fluorescence change of the gel was studied after metal binding.\textsuperscript{172}

The porphyrin gels were placed in 0.1 M solutions of mercury (II) chloride and cadmium (II) acetate, with a control was also placed in milli-Q H\textsubscript{2}O. The samples were left for 7 days, with distinct colour changes observed for each gel exposed to heavy metal ions. The control remained the standard purple colour, while the mercury and cadmium changed the gels to green and brown respectively (Figure 5-9).

![Figure 5-9. Colour change associated with mercury (A) and cadmium (B) porphyrin binding using porphyrin-Jeffamine-PEGDGE hydrogel 113.](image-url)

The colour changes were supported by the fluorescence changes of the gels. Measurements were performed on the solid samples, with excitation at 420 nm and fluorescence spectra recorded between 600 nm and 760 nm. The porphyrin gel control showed 2 peaks at 660 nm and 725 nm, which is typical of a free-base porphyrin. Mercury sensing studies using self assembled porphyrin multilayers indicates that the peak present at 660 nm for free-base porphyrins will shift and decrease in intensity, while the 760 nm peak will dramatically decrease after metal binding.\textsuperscript{173} This was evident in the fluorescence spectra of the mercury and cadmium bound hydrogels with the mercury gel showing a characteristic fluorescence at 655
nm, with a shoulder also present off the peak at 710 nm. The cadmium sample had a single peak at 670 nm with a slight shoulder also present around 710 nm (Figure 5-10). The changes in fluorescence spectra support the formation of metalloporphyrins indicating the possibility of using the porphyrin hydrogel as a heavy metal ion sensor. Unfortunately new workplace safety guidelines at IPRI prevented further studies on the detection limit of the gel for mercury and cadmium.

\[ \text{Figure 5-10. Normalised fluorescence spectra of free-base, mercury and cadmium containing gels.} \]

### 5.3 Conclusions and Future Directions

The successful synthesis of a porphyrin-jeffamine conjugate 111 allowed for investigation into an epoxy amine chemistry, porphyrin hydrogel. The generation of functionalised porphyrin 111 incorporated a low molecular weight Jeffamine (<3000 Da), which in previous studies failed to form porphyrin hydrogels.\textsuperscript{[16]} The characterisation of porphyrin-jeffamine 111 was problematic as it was unable to determine if 100% of the available benzoic acid groups had reacted to form an amide. Future research into this would involve the use of higher equivalents of jeffamine to ensure a higher certainty around amide coupling. The porphyrin was however highly functionalised with jeffamine polymer and therefore allowed for investigation into an adaptable porphyrin hydrogel methodology that can incorporate a variety of available Jeffamine polymers.
The use of porphyrin 111 and PEGDGE was successful in forming a hydrogel, with a porphyrin in the polymer backbone. Hydrogels with porphyrins incorporated into the polymer backbone have shown increased stability and increased dye loading in comparison to passively incorporated porphyrin hydrogels.\(^{163}\) Hydrogel 112 used equivalent reactive group stoichiometry to form the gel, with the formed network having poor a poor swelling ratio and H\(_2\)O content.

The future goals of utilising this hydrogel for heavy metal detection indicated that the swelling ratio needed to be increased to ensure a highly permeable structure. A combination of porphyrin 111, Jeffamine T403 and PEGDGE was capable of increasing H\(_2\)O content from 65\% to 92\%. The newly formed gel was characterised by rheology and indicated the high H\(_2\)O content gel was capable of forming a complete cross-linked polymer network. Detection of both mercury and cadmium was successful with fluorescence used to detect the heavy metals.

The successful formation of a highly permeable porphyrin hydrogel opens the door for the material to be incorporated into a heavy metal sensor. Although detection of metals was achieved in this thesis, the formation of a highly selective sensor still needs a lot of development. One method for increasing the sensitivity and selectivity of the porphyrin hydrogel would be to either print or electrospray the the material, with binding of metals analysed by electrochemistry.
Chapter 6
Experimental
6.1 General Experimental

6.1.1 Physical Measurements

$^1$H NMR spectra were obtained at 400 MHz using a Bruker Ultrashield 400 Plus spectrometer. $^1$H NMR data is expressed in ppm, with all peaks shifted in reference to tetramethylsilane as the internal standard. Peaks are reported as position (δH), multiplicity (s= singlet, br s= broad singlet, d= doublet, m= multiplet), relative integral, coupling constant (J, Hz) and assignment.

Electronic absorption spectra were obtained using a Shimadzu, UV Spectrophotometer, UV-180. AR grade solvents were used for experiments, apart from experiments conducted with milli-Q H$_2$O.

MALDI-TOF mass spectrometry was performed using Shimadzu Biotech Axima Confidence mass spectrometer. Samples were prepared by firstly placing dissolved matrix on the MALDI plate and allowing it to dry. The porphyrin was then applied to the target plate and allowed to dry.

Electrospray MS (ES-MS) was performed using Shimadzu LCMS-2020 Liquid Chromatogram mass spectrometer. HPLC grade solvent was used for all samples. High resolution ES-MS was performed by Dr David Harman at Western Sydney University, Sydney, Australia.

Gas Chromatography MS was performed using an Agilent Technologies 7890A GC system with a 5975C Inert MSD with Triple-Axis detector. HPLC grade solvent was used for all samples.

High performance liquid chromatography was performed using a Shimadzu UFLC LC-20AT Prominence Liquid Chromatograph with RID-10A Refractive Index detector and Sedere Sedex60LT detector. HPLC grade solvent was used for all samples.

All flow chemistry experiments were performed on a Uniqsis FlowSyn flow chemistry apparatus, with both a chip and coil reactor connected. All experiments used AR grade solvents, with isopropanol used to clean the tubing between experiments.

Fourier transform IR was performed on a Shimadzu (IRPrestige-21) FT-IR spectrometer. Experiments were performed when combined with KBr and analysed by KBr specular reflectance.

Fluorescence spectra were recorded on a JY Fluorolog 22. All samples were recorded as solids.
Electrochemical experiments were performed in a three-electrode cell with a glassy carbon working electrode, a platinum mesh as the counter electrode and Ag|AgCl (leakless) as the reference electrode. All potentials are reported versus the apparent formal potential of the ferrocene/ferrocenium couple. The Cyclic Voltammograms (CVs) of compounds were performed at 1 mM in degassed CH$_2$Cl$_2$ with 100 mM of tetrabutylammonium perchlorate present. CV measurements were performed using a CHI 76D electrochemical analyser (CH instruments, CHI650D). All electrochemical experiments were performed at RT (23 ± 2°C) in air.

Rheology measurements were obtained using Anton Paar Physica MCR 301, with parallel plates at 21°C and a frequency of 10 rad/s.

### 6.1.2 Reagents

Solvents and reagents were obtained from a variety of different suppliers. Dry solvents were usually AR grade and obtained from a LC Technology Solutions solvent dispenser. To achieve degassed dry solvents the solvent was bubbled with argon gas and sonicated. Solvents used for chromatography were laboratory grade. DCE and acetonitrile were both HPLC grade for use in experimentation. All solvents used for GC-MS, ES-MS and GPC experimentation were HPLC grade.

Methyl 3-formylbenzoate was prepared by a 3 step reaction from m-toluic acid (Aldrich, 99%). The three step reaction consisted of experiments similar to the esterification (Rahim et al.), bromination (Wang et al.) and Sommelet (Shahrisa et al.) reactions referenced.$^{[174]}$

### 6.1.3 Experimental Procedures

TLC was performed using precoated aluminium silica TLC plates (Merck TLC silica gel 60). Column chromatography was performed using silica gel (Merck silica gel 60 (0.040-0.063 mm)). Gradient elution is implied for all dual solvent system, with the major band collected unless stated otherwise. All fractions collected that contained a single TLC spot were combined, filtered through filter paper and the solvent removed in vacuo. In vacuo implies rotary evaporation followed by high vacuum oven or high vacuum connected to a desiccator.

All solid precipitates were either collected by gravity or vacuum filtration through a sintered glass filter, then washed with ice cold precipitating solvent and dried under high vacuum (high vacuum oven or high vacuum connected to a desiccator). All porphyrin experiments were carried out in dry, degassed solvent and under an argon atmosphere.
6.2 Synthesis and Functionalisation of Porphyrins by Flow Chemistry

General Procedure

All flow chemistry porphyrin syntheses were performed using a generalised procedure. The generalised procedure was adapted from the Adler-Longo porphyrin synthesis method. Pyrrole and arylaldehyde were prepared in propionic acid to 0.2M in separate schott bottles. The reagents were connected to pumps A and B of Uniqsis FlowSyn flow chemistry apparatus, with mixing occurring in the chip reactor and heating (141°C) occurring on the 2mL coil reactor. The crude product was deposited in a collection vial, for either UV-vis analysis or purification. Yields were obtained between 4.5-29.0%.

**T4MeOP, 1.**

5,10,15,20-tetra(4-methoxyphenyl)porphyrin

![Chemical structure](image)

Chemical Formula: C_{40}H_{36}N_{4}O_{4}

Exact Mass: 734.29

Molecular Weight: 734.86

Pyrrole and 4-methoxybenzaldehyde were prepared via the generalised procedure and reacted at 0.08 mL min\(^{-1}\) to produce compound 1 at 9.6%. \(^{1}\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.86 (s, 8H, H\(_{\beta\text{-pyrrolic}}\)), 8.14 (d, 8H, \(J=8.5\) Hz, H\(_{o\text{-Ar}}\)), 7.28 (d, 8H, \(J=8.5\) Hz, H\(_{m\text{-Ar}}\)), 4.10 (s, 12H, H\(_{\text{OMe}}\)), -2.74 (br s, 2H, NH). Spectral data in agreement with literature. \(^{[175]}\)
TPP, 2.

5,10,15,20-tetraphenylporphyrin

\[
\begin{align*}
\text{Chemical Formula: } & C_{44}H_{50}N_4 \\
\text{Exact Mass: } & 614.25 \\
\text{Molecular Weight: } & 614.75
\end{align*}
\]

Pyrrole and benzaldehyde were prepared via the generalised procedure and reacted at 0.08 mL min\(^{-1}\) to produce compound 2 at 29.0%. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.87 (s, 8H, H\(_{\beta}\)-pyrrolic), 8.25 (m, 8H, H\(_o\)-Ar), 7.78 (m, 8H, H\(_o\)-Ar), 2.73 (br s, 2H, NH). Spectral data in agreement with literature. \([10, 175]\)

T4BrP, 3.

5,10,15,20-tetra(4-bromophenyl)porphyrin

\[
\begin{align*}
\text{Chemical Formula: } & C_{44}H_{26}Br_4N_4 \\
\text{Exact Mass: } & 925.89 \\
\text{Molecular Weight: } & 930.34
\end{align*}
\]

Pyrrole and 4-bromobenzaldehyde were prepared via the generalised procedure and reacted at 0.08 mL min\(^{-1}\) to produce compound 3 at 19.5%. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.83 (s, 8H, H\(_{\beta}\)-pyrrolic), 8.05 (d, 8H, J= 8.5 Hz, H\(_o\)-Ar), 7.88 (d, 8H, J= 8.5 Hz, H\(_m\)-Ar), 2.73 (br s, 2H, NH). Spectral data in agreement with literature. \([176]\)
T4EP, 4.

5,10,15,20-tetra(4-ethylphenyl)porphyrin

Pyrrole and 4-ethylbenzaldehyde were prepared via the generalised procedure and reacted at 0.06 mL min\(^{-1}\) to produce compound 4 at 7.4%. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.85 (s, 8H, \(H_{\beta}\)-pyrrolic), 8.12 (d, 8H, \(J=8.1\) Hz, \(H_{o-Ar}\)), 7.56 (d, 8H, \(J=8.1\) Hz, \(H_{m-Ar}\)), 3.0 (q, 8H, \(J=7.5\) Hz, \(CH_2CH_3\)), 1.52 (t, 12H, \(J=7.4\) Hz, \(CH_2CH_3\)), -2.74 (br s, 2H, NH). Spectral data in agreement with literature. \(^{[93a]}\)

T3,5tertBP, 5.

5,10,15,20-tetra(3,5-di-tert-butylphenyl)porphyrin

Pyrrole and 3,5-di-tert-butylbenzaldehyde were prepared via the generalised procedure and reacted at 0.08 mL min\(^{-1}\) to produce compound 5 at 4.5%. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.88 (s, 8H, \(H_{\beta}\)-pyrrolic), 8.08 (d, 8H, \(J=1.9\) Hz, \(H_{o-Ar}\)), 7.78 (t, 4H, \(J=1.9\) Hz, \(H_{p-Ar}\)), 1.52 (s, 72H, \(H_{\text{tert-butoxide}}\)), -2.67 (br s, 2H, NH). Spectral data in agreement with literature. \(^{[177]}\)
T4EP, 6.

5,10,15,20-tetra(4-methoxycarbonylphenyl)porphyrin

\[
\text{Chemical Formula: C}_{52}\text{H}_{66}\text{N}_{4}\text{O}_{3}
\]

\[
\text{Exact Mass: 846.27}
\]

\[
\text{Molecular Weight: 846.90}
\]

Pyrrole and methyl 4-formylbenzoate were prepared via the generalised procedure and reacted at 0.08 mL min\(^{-1}\) to produce compound 6 at 12.5%. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.81 (s, 8H, H\(\beta\)-pyrrolic), 8.44 (d, 8H, \(^3\)J = 8.0 Hz, H\(\delta\)-Ar), 8.29 (d, 8H, \(^3\)J = 8.0 Hz, H\(m\)-Ar), 4.11 (s, 12H, CO\(_2\)CH\(_3\)), -2.74 (br s, 2H, NH). Spectral data in agreement with literature. \(^{178}\)

T2,5MP, 7.

5,10,15,20-tetra(2,5-dimethoxyphenyl)porphyrin

\[
\text{Chemical Formula: C}_{52}\text{H}_{66}\text{N}_{4}\text{O}_{3}
\]

\[
\text{Exact Mass: 854.33}
\]

\[
\text{Molecular Weight: 854.96}
\]

Pyrrole and methyl 2,5-dimethoxybenzaldehyde were prepared via the generalised procedure and reacted at 0.06 mL min\(^{-1}\) to produce compound 7 at 14.5%. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.77 (m, 8H, H\(\beta\)-pyrrolic), 7.60 (m, 4H, H\(\delta\)-Ar), 7.27 (m, 8H, H\(m,p\)-Ar), 3.90 (m, 12H, H\(\delta\)-Ar), 3.50 (m, 12H, H\(\text{OMe}\)), -2.65 (br s, 2H, NH). Spectral data in agreement with literature. \(^{94c}\)
CuTPP, 9.

5,10,15,20-tetraphenylporphyrinato copper(II)

TPP 2 dissolved in CHCl₃ (0.001 M) and copper acetate in MeOH (0.001 M) were connected to pumps A and B of Uniqsis FlowSyn flow chemistry apparatus. Complete conversion was achieved with an overall flow rate of 4 mL min⁻¹. Ratios of porphyrin to copper acetate were 1:1.4 with mixing performed at the chip reactor and heating (50°C) on the 2 mL coil reactor. The product was deposited in a collection vial with spectral data in agreement with literature.[179]

CuTPP-CHO, 11.

2-formyl-5,10,15,20-tetraphenylporphyrinato copper(II)

Cu-TPP 9 dissolved in DCE (0.004 M) and Vilsmeier complex in DCE (0.40 M) were connected to pumps A and B of Uniqsis FlowSyn flow chemistry apparatus. Best results were achieved with flow rates of 0.2 mL min⁻¹ (CuTPP) and 0.4 mL min⁻¹ (Vilsmeier complex). Mixing was performed at the chip reactor and heating (120°C) on the 20 mL coil reactor. The product was deposited in a collection vial, followed by neutralisation with aq. sat. NaHCO₃. The product was then taken to HPLC analysis or purified by column chromatography. Spectral data in agreement with literature.[180]
TPP-CHO, 14.

2-formyl-5,10,15,20-tetraphenylporphyrin

Cu-TPP 9 dissolved in DCE (0.004 M) and Vilsmeier complex in DCE (0.40 M) were connected to pumps A and B of Uniqsis FlowSyn flow chemistry apparatus. Flow rates of 0.2 mL min$^{-1}$ (CuTPP) and 0.4 mL min$^{-1}$ (Vilsmeier complex) were used with mixing performed at the chip reactor and heating (120°C) on the 20 mL coil reactor. Product was deposited in a collection vial and stirred with conc. H$_2$SO$_4$ (5 mL) for 20 min. The mixture was then hydrolysed with H$_2$O (20 mL), neutralised with aq. sat. NaHCO$_3$ (2x 25 mL) and extracted with CH$_2$Cl$_2$ (25 mL). The organic layer was then dried with MgSO$_4$, dried in vacuo and purified by column chromatography (CH$_2$Cl$_2$:Hexane (4:1)) to give 14 (0.14 g) as a purple solid. Spectral data in agreement with literature.$^{[181]}$
6.3 Synthesis of Vinyl Linked Amphiphilic Porphyrin Molecules

General Phosphonium Salt Synthesis

Phosphonium salt synthesis (25, 26 and 27) were performed following literature precedents.\cite{79, 98}
2-(4-bromophenyl)-5,5-dimethyl-1,3-dioxane, 28.

\[
\begin{align*}
\text{Chemical Formula: } & \text{C}_{12}\text{H}_{15}\text{BrO}_2 \\
\text{Exact Mass: } & 270.03 \\
\text{Molecular Weight: } & 271.15
\end{align*}
\]

4-bromobenzaldehyde (10.85 g, 59 mmol), 2,2-dimethyl-1,3-propanediol (12.29 g, 118 mmol) and \( p \)-toluenesulfonic acid (36 mg, 0.2 mmol) were dissolved in toluene (70 mL) in a round bottom flask with Deans-Stark apparatus attached. The reaction was heated to 140°C and stirred for 14 h. The reaction mixture was concentrated \textit{in vacuo} and the residue was purified by flash chromatography (silica, CH\(_2\)Cl\(_2\)). Concentration \textit{in vacuo} resulted in the crystallisation of the desired product \textbf{28} (14.45 g, 90\%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.47 (d, 2H, \( ^3J= 8.7 \text{ Hz, H}_{\text{AR}} \)), 7.35 (d, 2H, \( ^3J= 8.7 \text{ Hz, H}_{\text{AR}} \)), 5.29 (s, 1H, H\(_1\)), 3.72 (d, 2H, \( ^3J= 11.0 \text{ Hz, H}_{2} \)), 3.58 (d, 2H, \( ^3J= 11.0 \text{ Hz, H}_{2} \)), 1.24 (s, 3H, H\(_3\)), 0.75 (s, 3H, H\(_3\)). Spectral data in agreement with literature.\(^{[182]}\)

(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)trimethylsilane, 29.

\[
\begin{align*}
\text{Chemical Formula: } & \text{C}_{12}\text{H}_{24}\text{O}_2\text{Si} \\
\text{Exact Mass: } & 264.15 \\
\text{Molecular Weight: } & 264.44
\end{align*}
\]

\textbf{28} (14.45 g, 53 mmol) was dissolved in THF (100 mL) and was taken to -90°C (acetone, liquid N\(_2\)). 2 M \( n \)-butyllithium (55.7 mL, 111 mmol) was added in a continual stream and the reaction was then warmed to RT. Once the reaction mixture had turned from yellow to green, the reaction was again cooled to 90°C and trimethylsilyl chloride (13.5 mL, 106 mmol) added. The reaction was warmed to RT and stirred for 90 min then quenched by pouring into ice cold H\(_2\)O (250 mL). The aq. layer was then extracted with Et\(_2\)O, dried over MgSO\(_4\) and concentrated \textit{in vacuo}. The
reaction residue was then purified by flash chromatography (silica, CH₂Cl₂: hexane (1:1)). Concentration in vacuo gave 29 (9.85 g, 70%) as a yellow oil. ¹H-NMR (400 MHz, CDCl₃): δ 7.53 (d, 2H, δJ = 8.1 Hz, H₉₈), 7.48 (d, 2H, δJ = 8.1 Hz, H₉₉), 5.38 (s, 1H, H₁), 3.76 (d, 2H, δJ = 11.1 Hz, H₂), 3.64 (d, 2H, δJ = 11.1 Hz, H₂), 1.29 (s, 3H, H₃), 0.79 (s, 3H, H₃), 0.31 (s, 9, H₉₉). 

4-(Trimethylsilyl)benzaldehyde, 30.

Chemical Formula: C₇H₄O₅Si
Exact Mass: 178.08
Molecular Weight: 178.30

29 (9.85 g, 37 mmol) and TFA (30 mL) were dissolved in CH₂Cl₂ (30 mL) and H₂O (10 mL) and were stirred at RT for 90 min. GCMS analysis indicated reaction completion and was therefore poured into ice cold H₂O (250 mL). The aq. layer was then extracted with CH₂Cl₂, washed with sat. aq. NaHCO₃ and dried over MgSO₄. Concentration in vacuo gave 30 (6.37 g, 96%) as a yellow oil. ¹H-NMR (400 MHz, CDCl₃): δ 10.02 (s, 1H, CHO), 7.84 (d, 2H, δJ = 8.1 Hz, H₉₈), 7.69 (d, 2H, δJ = 8.1 Hz, H₉₉), 0.31 (s, 9, H₉₉). LR-GCMS: m/z = 178.1 (M+). Spectral data in agreement with literature.[183]

T4SiP, 31.

5,10,15,20-Tetra(4-(trimethylsilyl)phenyl)porphyrin.

Chemical Formula: C₅₅H₃2N₄Si₄
Exact Mass: 902.41
Molecular Weight: 903.46

4-(Trimethylsilyl)benzaldehyde 30 (2.018 g, 11 mmol) and pyrrole (0.758 g, 11 mmol) were added to refluxing propionic acid (40 mL). The reaction was refluxed for 30 min and once cooled to RT
was filtered thru a sintered funnel and washed with MeOH. The remaining powder was subsequently dried to give 31 (0.386 g, 15%) as a purple powder. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.86 (s, 8H, H$_{\beta\text{pyrrolic}}$), 8.20 (d, 8H, $^3$J=8.05 Hz, H$_{\alpha\text{-Ar}}$), 7.89 (d, 8H, $^3$J=8.05 Hz, H$_{m\text{-Ar}}$), 0.51 (s, 36H, Si(CH$_3$)$_3$), -2.76 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 420 (5.37), 516 (3.92), 552 (3.66), 592 (3.43), 648 (3.43) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$ = 903.3 (M$^+$). HRMS, $m/z$: calcd for MH$^+$ (C$_{56}$H$_{63}$N$_4$Si$_4$): 903.4130, found: 903.4116.

CuT4SiP, 32.

5,10,15,20-Tetra(4-(trimethylsilyl)phenyl)porphyrinato copper(II).

To a refluxing solution of porphyrin 31 (0.386 g, 0.4 mmol) in CHCl$_3$ (100 mL) was added Cu(OAc)$_2$·H$_2$O (0.10 g, 0.5 mmol) in MeOH (5 mL). After 30 min the reaction was adjudged complete by MALDI mass spectrometry analysis. On cooling to RT, the reaction mixture was concentrated in vacuo. Crystallisation in CH$_2$Cl$_2$/MeOH gave 32 (0.371 g, 96%) as a purple powder. UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 416 (5.33), 539 (3.94) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$ = 964.4 (M$^+$). HRMS, $m/z$: calcd for M$^+$ (C$_{56}$H$_{60}$CuN$_4$Si$_4$): 963.3191, found: 963.3234.
CuT4SiP-CHO, 33.

2-Formyl-5,10,15,20-tetra(4-(trimethylsilyl)phenyl)porphyrinato copper(II).

![Chemical Structure Image]

**Chemical Formula**: C$_{57}$H$_{60}$CuN$_4$Si$_4$

**Exact Mass**: 991.31

**Molecular Weight**: 993.00

Vilsmeier complex was prepared by the slow addition of POCl$_3$ (7 mL) to dry DMF (10 mL) under argon at 0°C. After 20 min of stirring the vicious solution was added to a RT solution of porphyrin 32 (0.50 g, 0.52 mmol) in 50 mL DCE. After 30 min stirring, the reaction was heated to reflux for 16 h. Once cooled to RT the reaction mixture was added to H$_2$O (100 mL), extracted and the organic layer washed with sat. aq. NaHCO$_3$ (2 x 25 mL) and dried over MgSO$_4$. The solvent was removed in vacuo and column chromatographed (silica, CH$_2$Cl$_2$). The major band was collected, crystallised in CH$_2$Cl$_2$/MeOH and dried to give 33 (0.369 g, 72%) as a purple powder. UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 430 (5.22), 553 (3.93), 593 (3.80) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$ = 994.5 (M$^+$). HRMS, $m/z$: calcd for MH$^+$ (C$_{57}$H$_{62}$CuN$_4$OSi$_4$): 992.3219, found: 992.3229.

CuT4SiP-CH$_2$OH, 34.

2-Hydroxymethyl-5,10,15,20-tetra(4-(trimethylsilyl)phenyl)porphyrinato copper(II).

![Chemical Structure Image]

**Chemical Formula**: C$_{57}$H$_{62}$CuN$_4$OSi$_4$

**Exact Mass**: 993.33

**Molecular Weight**: 995.02

Porphyrin 33 (0.200 g, 0.20 mmol), NaBH$_4$ (0.196 g, 5.18 mmol) in THF (20 mL) and H$_2$O (340 µL) was stirred for 40 min at RT. TLC analysis indicated consumption of starting material, with
presence of new red band. H₂O (200 mL) was added to the reaction and the organic layer extracted with CH₂Cl₂. The organic layer was washed with sat. aq. NaHCO₃ (2 x 25 mL), H₂O (2 x 25 mL) and then dried over MgSO₄. The reaction was dried in vacuo and crystallised in CH₂Cl₂/MeOH to give 34 (190 mg, 95%) as a purple powder. UV-vis (CH₂Cl₂) λ_max (log ε) 416 (5.32), 539 (3.94) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 996.6 (M⁺). HRMS, m/z: calcd for MH⁺ (C₅₇H₆₃CuN₄OSi₄): 994.3375, found: 994.3394.

CuT4SiPps, 36.

(5,10,15,20-Tetra(4-(trimethylsilyl)phenyl)porphyrinato copper(II)cyl)methyltriphenylphosphonium chloride.

SOCl₂ (70 µL, 0.97 mmol) was added to a 0°C solution of porphyrin 34 (190 mg, 0.191 mmol) and dry pyridine (0.18 mL, 2.2 mmol) in dry CH₂Cl₂ (30 mL) under argon. After stirring for 15 min, the reaction was warmed to RT and stirred for a further 85 min. Chloroform (100 mL) was added to the reaction and stirred for 15 min. The solution was then washed with H₂O (2 x 25 mL), sat. aq. NaHCO₃ (2 x 25 mL), dried over MgSO₄ and the organic layer dried in vacuo. Due to compound instability, the dried product was taken directly to phosphonium salt synthesis. The solution of 35 in chloroform (20 mL) was heated to reflux and PPh₃ (2.00 g, 7.6 mmol) added. The reaction was stirred for 16 h and upon cooling to RT was directly purified by column chromatography (silica, CH₂Cl₂: MeOH (1:0, 1:9:1)). The major band was crystallised in CH₂Cl₂/MeOH to give 36 (132 mg, 54%) as a purple powder. UV-vis (CH₂Cl₂) λ_max (log ε) 422 (5.33), 545 (3.97), 580 (3.48) nm. HRMS, m/z: calcd for M⁺-Cl (C₇₅H₇₆CuN₄PSi₄): 1238.4181, found: 1238.4152.
CuT4SiP=Ph, 37.

\((E)\)-2-(2-phenylethenyl)-5,10,15,20-tetra(4-(trimethylsilyl)phenyl)porphyrinato copper(II).

\[
\text{Chemical Formula: } C_{34}H_{60}CuN_4Si_4 \\
\text{Exact Mass: } 1065.37 \\
\text{Molecular Weight: } 1067.12
\]

A solution of porphyrin phosphonium salt 36 (30 mg, 24 µmol) and benzaldehyde (8 mg, 72 µmol) were stirred in degassed CHCl\(_3\) (3 mL) under argon at reflux. DBU (11 µL, 72 µmol) in degassed CHCl\(_3\) (1 mL) was added over 10 min and the reaction was stirred for a further 15 min. On cooling to RT the reaction mixture was then concentrated \textit{in vacuo} and purified by flash chromatography (silica, CH\(_2\)Cl\(_2\)). The major band was collected and concentrated \textit{in vacuo}. Crystallisation from CH\(_2\)Cl\(_2\)/MeOH gave the desired product 37 (21 mg, 81%) as a purple powder. UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\epsilon\)) 424 (4.88), 484 (3.40), 582 (3.40) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \(m/z\) = 1068.8 (M\(^+\)). HRMS, \(m/z\): calcd for M\(^+\) (C\(_{64}\)H\(_{66}\)CuN\(_4\)Si\(_4\)): 1065.3661, found: 1065.3650.

T4SiP=Ph, 38.

\((E)\)-2-(2-phenylethenyl)-5,10,15,20-tetra(4-(trimethylsilyl)phenyl)porphyrin.

\[
\text{Chemical Formula: } C_{34}H_{68}N_4Si_4 \\
\text{Exact Mass: } 1004.45 \\
\text{Molecular Weight: } 1005.59
\]

Methane sulfonic acid (49 µL, 0.76 mmol) was added to a solution of porphyrin 37 (20 mg, 19 µmol) in CH\(_2\)Cl\(_2\)(2 mL) and stirred for 2 min. TLC analysis indicated copper was fully removed.
CH₂Cl₂ (10 mL) was added, followed by 1 M NaOH (10 mL). The organic layer was then separated, washed with sat. aq. NaHCO₃ (2 x 25 mL) and dried over MgSO₄. Solvent was removed in vacuo and crystallisation from CH₂Cl₂/MeOH gave the desired product 38 (18 mg, 95%) as a purple powder. ¹H-NMR (400 MHz, CDCl₃): δ 9.01 (s, 1H, Hβ-pyrrolic), 8.85-8.75 (m, 5H, Hβ-pyrrolic), 8.68 (d, 1H, 3J= 4.6 Hz, β-pyrrolic), 8.25-8.14 (m, 8H, H₀-Ar), 7.94-7.86 (m, 8H, Hₘ-Ar), 7.33-7.20 (m, 6H, HAR and Hvinyl), 7.04 (d, 1H, 3J= 16.1 Hz, Hvinyl), 0.54-0.48 (m, 36H, HMe-Si), -2.57 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax (log ε) 425 (4.96), 524 (3.87), 561 (3.67), 599 (3.48), 653 (3.30) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1006.8 (M⁺). HRMS, m/z: calcd for MH⁺ (C₆₄H₆₈N₄Si₄): 1005.4599, found: 1005.4608.

TPP=-PhCHO, 39.

4-{(E-2-(5,10,15,20-tetraphenylporphyrin-2-yl)ethen-1-yl)benzaldehyde.

A solution of porphyrin phosphonium salt 25 (95 mg, 0.10 mmol) and terephthaldehyde (67 mg, 0.5 mmol) were stirred in degassed CHCl₃ (8 mL) under argon at reflux. DBU (46 µL, 0.3 mmol) in degassed CHCl₃ (1 mL) was added over 10 min and the reaction was stirred for a further 10 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH₂Cl₂). The major band was collected and concentrated in vacuo. Crystallisation from CH₂Cl₂/MeOH gave the desired product 39 (61 mg, 82%) as a purple powder. ¹H-NMR (400 MHz, CDCl₃): δ 9.99 (s, 1H, CHO), 9.01 (s, 1H, Hβ-pyrrolic), 9.01 (s, 1H, Hβ-pyrrolic), 8.83-8.76 (m, 5H, Hβ-pyrrolic), 8.72 (d, 1H, 3J= 5.0 Hz, Hβ-pyrrolic), 8.26-8.16 (m, 8H, H₀-Ar), 7.95-7.69 (m, 14H, Hₘ,p-Ar and HAR), 7.34 (d, 2H, 3J= 8.0, Hvinyl), 7.29 and 7.13 (d, 2H, 3J= 16.4 Hz, Hvinyl), -2.57 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax (log ε) 429 (4.76), 525 (3.74), 566 (3.54), 600 (3.35), 656 (2.91) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 745.9 (M⁺). HRMS, m/z: calcd for MH⁺ (C₅₃H₃₇N₄O): 745.2967, found: 745.2990.
ZnTPP-\textsuperscript{-}-PhCHO, Zn39.

4-\(E\)-2-(5,10,15,20-tetraphenylporphyrinato zinc(II)yl)ethen-1-yl)benzaldehyde.

Porphyrin 39 (25 mg, 34 \(\mu\)mol) was dissolved in CHCl\(_3\) (5 mL) and stirred at RT. A solution of Zn(OAc)\(_2\)-2H\(_2\)O (10 mg, 44 \(\mu\)mol) in MeOH (0.5 mL) was added and stirred for 30 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture concentrated \textit{in vacuo}. Crystallisation in CH\(_2\)Cl\(_2\)/MeOH gave the desired product Zn39 (24 mg, 89\%) as a purple powder. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.97 (s, 1H, CHO), 9.13 (s, 1H, H\textsubscript{\(\beta\)-pyrrolic}), 8.95-8.88 (m, 5H, H\textsubscript{\(\beta\)-pyrrolic}), 8.81 (d, 1H, \(^3\)J= 4.8 Hz, H\textsubscript{\(\beta\)-pyrrolic}), 8.26-8.16 (m, 8H, H\textsubscript{o-Ar}), 7.85-7.71 (m, 14H, H\textsubscript{p,m-Ar} and H\textsubscript{AR}), 7.36 (d, 2H, \(^3\)J=8.1 Hz, H\textsubscript{vinyl}), 7.27 and 7.19 (d, 2H, \(^3\)J= 15.8 Hz, H\textsubscript{vinyl}). \textit{Assignment aided by COSY spectra}. UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda\text{max} \text{ (log \(\varepsilon\))} 434 (5.10), 557 (4.10), 594 (3.81) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \(m/z\) = 808.9 (M\textsuperscript{+}). HRMS, \(m/z\): calcd for MH\textsuperscript{+} (C\(_{53}\)H\(_{35}\)N\(_4\)OZn): 807.2102, found: 807.2134.

FeTPP-\textsuperscript{-}-PhCHO, Fe39.

4-\(E\)-2-(5,10,15,20-tetraphenylporphyrinato iron(III)yl)ethen-1-yl)benzaldehyde.

Acetonitrile (10 mL) was refluxed under argon for 2 h to remove any dissolved oxygen. The reaction’s temperature was then lowered to 70\(^\circ\)C and iron(II) chloride (180 mg, 0.91 mmol)
added. A solution of porphyrin aldehyde 39 (50 mg, 0.067 mmol) in 5 mL of degassed CHCl₃ was then added to the reaction over 5 min. The reaction was then heated back up to reflux, stirred for 3 h and then left exposed to air overnight at RT. The reaction mixture was then concentrated *in vacuo*, redissolved in CH₂Cl₂ and washed with 0.1M HCl (3 x 25 mL). The reaction was purified by column chromatography (silica, 100% CH₂Cl₂ - 98% CH₂Cl₂: 2% MeOH) and filtered through filter paper to give the desired compound Fe₃⁹ as a brown powder (49 mg, 82%). UV-vis (CH₂Cl₂) \( \lambda_{\text{max}} \) (log ε) 429 (4.38), 513 (3.65), 659 (3.10) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \( m/z = \) 798.6 (M⁺- Cl⁻). HRMS, \( m/z \): calcd for MH⁺-Cl (C₅₃H₃₅N₄O): 798.2082, found: 798.2083.

**TPP-CuT4SiP dyad, 40.**

1-(E-2-(5,10,15,20-tetraphenylporphyrin-2-yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetra(4-trimethylsilyl)phenyl)porphyrinato copper(II)yl)ethen-1-yl)benzene.

A solution of porphyrin aldehyde 39 (24 mg, 32 µmol) and porphyrin phosphonium salt 36 (50 mg, 41 µmol) were stirred in degassed CHCl₃ (4 mL) under argon at reflux. DBU (19 µL, 123 µmol) in degassed CHCl₃ (0.5 mL) was added over 10 min and the reaction was stirred for a further 40 min. On cooling to RT the reaction mixture was then concentrated *in vacuo* and purified by flash chromatography (silica, CH₂Cl₂: Hexane (4:1). The major band was collected and concentrated *in vacuo*. The isomeric mixture and I₂ (10 mg, 39 µmol) were then dissolved in CH₂Cl₂ and stirred for 16 h. Sat. aq. Na₂S₂O₃ (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with H₂O (2 x 25 mL). Crystallisation from CH₂Cl₂/MeOH
gave the desired product 40 (28 mg, 52%) as a purple powder. UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\epsilon$) 425 (5.34), 554 (4.36), 591 (4.31) nm. HRMS, $m/z$: calcd for MH$^+$ (C$_{110}$H$_{96}$CuN$_8$Si$_4$): 1704.6209, found: 1704.6228.

**TPP-T4SiP dyad, 41.**

1-(E-2-(5,10,15,20-tetraphenylporphyrin-2-yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetra(4-(trimethylsilyl)phenyl)porphyrin-2-yl)ethen-1-yl)benzene.

Methane sulfonic acid (45 µL, 0.70 mmol) was added to a solution of 40 (20 mg, 12 µmol) in CH$_2$Cl$_2$ (2 mL) and stirred for 5 min. TLC analysis indicated copper was fully removed. CH$_2$Cl$_2$ (10 mL) was added, followed by 1 M NaOH (10 mL). The organic layer was then separated, washed with sat. aq. NaHCO$_3$ (2 x 25 mL) and dried over MgSO$_4$. Solvent was removed in vacuo and crystallisation from CH$_2$Cl$_2$/MeOH gave the desired product 41 (19 mg, 95%) as a purple powder. $^1$H-NMR (400 MHz, CDCl$_3$): δ 9.05 (s, 1H, H$_{\beta\text{-pyrrolic}}$), 9.03 (s, 1H, H$_{\beta\text{-pyrrolic}}$), 8.86-8.70 (m, 12H, H$_{\beta\text{-pyrrolic}}$), 8.30-8.19 (m, 16H, H$_{\text{-Silyl}}$ and H$_{\text{-Ar}}$), 7.98-7.72 (m, 20H, H$_{\text{m-Silyl}}$ and H$_{\text{m,p-Ar}}$), 7.34 and 7.05 (d, 2H, $^3$J= 16.2 Hz, H$_{\text{vinyl}}$), 7.29 and 7.01 (d, 2H, $^3$J= 16.1 Hz, H$_{\text{vinyl}}$), 7.20 (s, 4H, H$_{\text{Ar}}$), 0.53-0.50 (m, 36H, H$_{\text{Me-Si}}$), -2.54 (br s, 4H, NH). Assignment aided by COSY spectra. UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\epsilon$) 425 (5.09), 523 (4.29), 572 (4.13), 598 (3.97), 653 (3.46) nm. HRMS, $m/z$: calcd for MH$^+$ (C$_{110}$H$_{98}$N$_8$Si$_4$): 1643.7070, found: 1643.7113.
T4SP-\(\text{-}\text{Ph, 42.}\)

\(^{(E)}\)2-(2-phenylethenyl)-5,10,15,20-tetra(4-benzenesulfonic acid) porphyrin.

![](image)

Porphyrrin 38 (18 mg, 18 µmol) was dissolved in \(\text{CCl}_4\) (5 mL) and heated to reflux under argon. Trimethylsilyl chlorosulfonate (35 µL, 220 µmol) was added and the reaction was stirred for 4 h. Upon cooling to RT 1 M NaOH solution (10 mL) was added to the reaction and stirred for a further 30 min. The aq. layer was then separated and washed with \(\text{CH}_2\text{Cl}_2\) (2 x 20 mL) and purified through dialysis tubing (12000-14000 Da) for 7 days. Solvent was removed \textit{in vacuo} to give the desired product 42 (18 mg, 92%) as a brown solid. \(^1\text{H-NMR (400 MHz, DMSO-\text{d}_6): \delta 9.19-8.66 (m, 7H, H}_\beta\text{-pyrrolic), 8.32-7.22 (m, 23H), -2.66 (br s, 2H, NH). UV-vis (DMF) }\lambda_{\text{max}} \text{ (log } \varepsilon) \text{ 428 (4.98), 524 (3.82), 564 (3.77), 604 (3.59), 655 (3.31) nm. HRMS, } m/z : \text{ calcd for MH}^+\text{-Na}^+ \text{ (C}_{53}\text{H}_{37}\text{N}_4\text{O): 1037.1291, found: 1037.1311.}\)
TPP-T4SP dyad, 43.

1-\(\text{E}-2-(5,10,15,20\text{-tetraphenylporphyrin-2-yl})\text{ethen-1-yl})\)-4-\(\text{E}-2-(5,10,15,20\text{-tetra(4-benzenesulfonic acid)porphyrin-2-yl})\text{ethen-1-yl})\)benzene.

Porphyrrin 41 (10 mg, 6 µmol) was dissolved in CCl\(_4\) (5 mL) and heated to reflux under argon. Trimethylsilyl chlorosulfonate (35 µL, 220 µmol) was added and the reaction was stirred for 5 h. Upon cooling to RT 1 M NaOH solution (10 mL) was added to the reaction and stirred for a further 30 min. The aq. layer was then separated and washed with CH\(_2\)Cl\(_2\) (2 x 20 mL) and purified through dialysis tubing (12000-14000 Da) for 7 days. Solvent was removed in vacuo to give the desired product 43 (10 mg, 91%) as a brown solid. \(^1\)H-NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 8.93-7.65 (m, 58H), -2.66 (br s, 4H, NH). UV-vis (DMF) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 424 (4.31), 522 (3.42), 558 (3.27), 601 (2.97), 644 (2.70) nm. HRMS, \(m/z\): calcd for MH\(^+\)-Na\(^+\) \(\text{C}_{98}\text{H}_{67}\text{Na}_4\text{O}_{12}\text{S}_4\): 1675.3761, found: 1675.3778.
TPyP, 44.

5,10,15,20-Tetra(4-pyridinyl)porphyrin.

![Chemical Structure]

Chemical Formula: $\text{C}_{42}\text{H}_{26}\text{N}_8$

Exact Mass: 618.23

Molecular Weight: 518.70

4-pyridine carboxaldehyde (4.01 g, 37 mmol) and pyrrole (2.48 g, 37 mmol) were added to refluxing propionic acid (80 mL). The reaction was refluxed for 45 min and once cooled to RT was filtered thru a sintered funnel and washed with MeOH. The remaining powder was subsequently dried to give 44 (0.511 g, 9%) as a purple powder. $^1\text{H}$-NMR (400 MHz, CDCl$_3$): $\delta$ 9.07 (d, 8H, $^{3}J = 5.8$ Hz, H$_{\text{pyridinyl}}$), 8.87 (s, 8H, H$_{\beta}$-pyrrolic), 8.16 (d, 8H, $^{3}J = 5.8$ Hz, H$_{\text{pyridinyl}}$), -2.92 (br s, 2H, NH). MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$ = 620.5 (M$^+$). Spectral data in agreement with literature.$^{[184]}$

CuT4EP, 47.

5,10,15,20-Tetra(4-methoxycarbonylphenyl)porphyrinato copper(II)

![Chemical Structure]

Chemical Formula: $\text{C}_{52}\text{H}_{36}\text{CuN}_4\text{O}_8$

Exact Mass: 907.18

Molecular Weight: 908.41

To a refluxing solution of 6 (0.500 g, 0.59 mmol) in CHCl$_3$ (200 mL) was added Cu(OAc)$_2$·H$_2$O (0.16 g, 0.8 mmol) in MeOH (10 mL). After 30 min the reaction was adjudged complete by MALDI mass spectrometry analysis. On cooling to RT, the reaction mixture was concentrated in vacuo. Crystallisation in CH$_2$Cl$_2$/MeOH gave 47 (0.520 g, 97%) as a purple powder. UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$
(log ε) 416 (5.33), 540 (3.98), 576 (3.10) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 908.3 (M⁺). HRMS, m/z: calcd for M⁺ (C₅₀H₃₆CuN₄O₈): 907.1829, found: 907.1854.

**T4EP-CHO, 48.**

2-Formyl-5,10,15,20-tetra(4-methoxycarbonylphenyl)porphin

Vilsmeier complex was prepared by the addition of POCl₃ (1 mL) over 5 min, to dry DMF (2 mL) at 0°C under argon. After 20 min stirring, the Vilsmeier complex (1.5 mL) was added to a solution of porphyrin 47 (0.100 g, 0.11 mmol) in o-dichlorobenzene (5 mL) in a small microwave vessel. The reaction was heated to 100°C, 160 Watts for 30 min in a microwave reactor. Vilsmeier complex (1.5 mL) was again added to the microwave vessel and the reaction subjected to the same microwave reaction conditions. The reaction mixture was then added to a dry round bottom flask and the mixture stirred vigorously. Conc. H₂SO₄ (4.0 mL) was added and after 20 min the reaction mixture was quenched with H₂O (25 mL) and extracted with CHCl₃ (10 mL). The organic layer was washed with sat. aq. NaHCO₃ (2 x 25 mL) and the solvent removed in vacuo.

The residue was column chromatographed (silica, CH₂Cl₂: Et₂O), first eluting with CH₂Cl₂ to remove o-dichlorobenzene, CH₂Cl₂: Et₂O (49:1) to give 6 (35 mg, 38%) and then CH₂Cl₂: Et₂O (19:1) to give desired compound 48 (36 mg, 38%, recrystallised from CH₂Cl₂: MeOH) as a purple powder. ¹H-NMR (400 MHz, CDCl₃): δ 9.33 (s, 1H, H₁-pyrrolic), 9.30 (s, 1H, CHO), 8.87-8.80 (m, 4H, H₁-pyrrolic), 8.76-8.72 (m, 2H, H₃-pyrrolic), 8.47-8.41 (m, 8H, H₀-Est), 8.30-8.23 (m, 8H, H₀-Est), 4.14-4.08 (m, 12H, CO₂CH₃), -2.58 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λₘₚₐₓ (log ε) 430 (5.30), 525 (3.99), 558 (3.71), 599 (3.57), 661 (3.54) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 876.4 (M⁺). HRMS unable to be obtained.
T4EP-CH$_2$OH, 49.

2-Hydroxymethyl-5,10,15,20-tetra(4-methoxycarbonylphenyl)porphyrin

Porphyrrin aldehyde 48 (64 mg, 73 µmol) and NaBH$_4$ (63 mg, 1.67 mmol) in THF (5 mL), CH$_2$Cl$_2$ (5 mL) and H$_2$O (109 µL) were stirred at RT. TLC indicated that after 1 h, starting material was consumed with the appearance of a new more polar red band. H$_2$O (100 mL) was added and the aq. layer extracted with CH$_2$Cl$_2$ (100 mL). The organic layer was washed with sat. aq. NaHCO$_3$ (2 x 25 mL), separated, dried over MgSO$_4$ and concentrated in vacuo. The residue was column chromatographed (silica, CH$_2$Cl$_2$:Et$_2$O (23:2)). Recrystallisation from CH$_2$Cl$_2$:MeOH gave 49 (56 mg, 86%) as purple powder. $^1$H-NMR (400 MHz, CDCl$_3$): δ 8.90 (s, 1H, H$_β$-pyrrolic), 8.83-8.70 (m, 5H, H$_β$-pyrrolic), 8.53 (d, 1H, $^3$J=4.5 Hz, H$_β$-pyrrolic), 8.45-8.37 (m, 8H, H$_o$-Est), 8.27-8.09 (m, 8H, H$_m$-Est), 4.83 (s, 2H, CH$_2$OH), 4.10 (s, 12H, CO$_2$CH$_3$), 1.60 (s, 1H, CH$_2$OH), -2.58 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log ε) 419 (5.35), 515 (3.95), 544 (3.68), 589 (3.42), 645 (3.14) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 877.8 (M$^+$). HRMS, m/z: calcd for MH$^+$ (C$_{53}$H$_{40}$N$_4$O$_9$): 877.2874, found: 877.2894.

(5,10,15,20-Tetra(4-methoxycarbonylphenyl)porphyrin-2-yl)methyltriphenylphosphonium chloride

\[
\text{SOCl}_2 \text{ (20 µL, 0.28 mmol) was added to a 0°C solution of porphyrin 49 (55 mg, 63 µmol) and dry pyridine (48 µL, 54 µmol) in dry CH}_2\text{Cl}_2 \text{ (10 mL) under argon. After stirring for 15 min, the reaction was warmed to RT and stirred for a further 45 min. Chloroform (25 mL) was added to the reaction and stirred for 15 min. The solution was then washed with H}_2\text{O (2 x 25 mL), sat. aq. NaHCO}_3 \text{ (2 x 25 mL), dried over MgSO}_4 \text{ and the organic layer dried in vacuo. Due to compound instability, the dried product was taken directly to phosphonium salt synthesis. The solution of 50 in chloroform (5 mL) was heated to reflux and PPh}_3 \text{ (0.32 g, 1.22 mmol) added. The reaction was stirred for 16 h and upon cooling to RT was directly purified by column chromatography (silica, CH}_2\text{Cl}_2: \text{MeOH (1:0, 19:1)). The major band was crystallised in CH}_2\text{Cl}_2/\text{MeOH to give 51 (64 mg, 88%) as a purple powder.}}
\]

\[
\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\text{): }\delta \text{ 8.23 (m, 6H), 8.47-8.23 (m, 16H), 7.94-7.90 (m, 2H), 7.66-7.52 (m, 7H), 7.32-7.27 (m, 7H), 4.20-4.08 (m, 12H, CO}_2\text{Me), 4.03 (br s, 2H, CH}_2\text{), -2.80 (bs s, 2H, NH). UV-vis (CH}_2\text{Cl}_2 \text{)} \lambda_{\text{max}} \text{ (log } \varepsilon \text{) 424 (5.19), 520 (3.79), 544 (3.50), 594 (3.26), 651 (3.18) nm. HRMS, } \text{m/z: calcd for M}^+\text{-Cl (C}_71\text{H}_54\text{N}_4\text{O}_8\text{P): 1121.3679, found: 1121.3657.}}
\]
T3EP−=−Ph, 53.

(Z)-2-(2-phenylethenyl)-5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin.

A solution of porphyrin phosphonium salt 27 (25 mg, 22 µmol) and benzaldehyde (14 mg, 132 µmol) were stirred in degassed CHCl₃ (3 mL) under argon at reflux. DBU (10 µL, 66 µmol) in degassed CHCl₃ (1 mL) was added over 10 min and the reaction was stirred for a further 10 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH₂Cl₂). The major band was collected and concentrated in vacuo. Crystallisation from CH₂Cl₂/MeOH gave the desired product 53 (18 mg, 86%) as a purple powder.

1H-NMR (400 MHz, CDCl₃): δ 8.92-8.85 (m, 5H, Hβ-pyrrolic), 8.80-8.65 (m, 6H, Hβ-pyrrolic and Hο-Est), 8.54- 8.34 (m, 8H, Hο,p-Est), 7.91-7.81 (m, 4H, Hm-Est), 7.36-7.18 (m, 6H, HAR and Hvinyl), 6.89 (d, 1H, 3J= 15.9 Hz, Hvinyl), 4.02-3.96 (m, 12H, CO₂CH₃), -2.61 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax (log ε) 424 (4.64), 523 (3.57), 561 (3.26), 598 (3.13), 663 (2.53) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 950.4 (M⁺). HRMS, m/z: calcd for MH⁺ (C₆₀H₄₅N₄O₈): 949.3237, found: 949.3271.
T3CP-=-Ph, 54.

\((E)-2-(2\text{-phenylethenyl})-5,10,15,20\text{-tetra}(3\text{-carboxyphenyl})\text{porphyrin.} \)

\[
\text{Chemical Formula } C_{56}H_{37}N_4O_8
\]
\[\text{Exact Mass: 892.25 } \]
\[\text{Molecular Weight: 892.91} \]

A solution of porphyrin 53 (20 mg, 21 µmol) in THF (6 mL) was heated to reflux and stirred. KOH (50 mg, 0.89 mmol) in MeOH:H\text{2}O (10:1, 6 mL) was added and stirred for 16 h. On cooling to RT the reaction mixture was concentrated \textit{in vacuo}. The reaction mixture was then redissolved in H\text{2}O (5 mL) and 2M H\text{3}PO\text{4} (455 µL, 0.91 mmol) added. The green precipitate was then filtered and washed with ice cold H\text{2}O (3 x 20 mL) and dried \textit{in vacuo} to give 54 (17 mg, 89%) as a purple powder. 1H-NMR (400 MHz, DMSO-d\text{6}, 80°C): δ 8.99 (s, 1H, H\text{β-pyrrolic}), 8.86-8.78 (m, 10H, H\text{β-pyrrolic} and H\text{o-Acid}), 8.54-8.39 (m, 8H, H\text{o,p-Acid}), 8.02-7.93 (m, 4H, H\text{m-Acid}), 7.42-7.22 (m, 6H, H\text{AR} and H\text{vinyl}), 6.89 (d, 1H, 3\text{J}= 16.5 Hz, H\text{vinyl}), -2.57 (br s, 2H, NH). \textit{Assignment aided by COSY spectra. UV-vis (DMSO) }\lambda_{\text{max}} (\text{log } \varepsilon) 423 (5.14), 522 (4.36), 559 (4.24), 597 (4.10), 650 (4.00) \text{ nm. HRMS, } m/z: \text{ calcd for MH}^+ (C_{56}H_{37}N_4O_8): 893.2611, \text{ found: 893.2612.} \]

TXP-=-PhCHO, 55.

4-\(E\)-2-(5,10,15,20-tetrakis(3,5-dimethylphenylporphyrin-2-yl)ethen-1-yl)benzaldehyde.

\[
\text{Chemical Formula } C_{51}H_{53}N_4O
\]
\[\text{Exact Mass: 856.41 } \]
\[\text{Molecular Weight: 857.09} \]
A solution of porphyrin phosphonium salt 26 (150 mg, 0.10 mmol) and terephthaldehyde (113 mg, 0.84 mmol) were stirred in degassed CHCl₃ (10 mL) under argon at reflux. DBU (65 µL, 0.42 mmol) in degassed CHCl₃ (1 mL) was added over 10 min and the reaction was stirred for a further 15 min. On cooling to RT the reaction mixture was then concentrated *in vacuo* and purified by flash chromatography (silica, CH₂Cl₂). The major band was collected and concentrated *in vacuo*. Crystallisation from CH₂Cl₂/MeOH gave the desired product 55 (109 mg, 91%) as a purple powder. 

\[ ^1H-NMR \quad (400 \text{ MHz, CDCl}_3): \delta \text{ 10.03 (s, 1H, CHO), 9.03 (s, 1H, H}_{\beta\text{-pyrrolic}}, 8.83-8.78 (m, 6H, H}_{\beta\text{-pyrrolic}}, 7.88-7.80 (m, 10H, H}_{\text{o-Xyl and H}_{\text{AR}}}, 7.46-7.38 (m, 6H, H}_{\text{p-Xyl and H}_{\text{AR}}}, 7.32 \text{ and 7.20 (d, } 2H, \text{ J} = 16.2 \text{ Hz, } H_{\text{vinyl}}, 2.63 (s, 6H, H}_{\text{Me-Xyl}}, 2.60 (s, 6H, H}_{\text{Me-Xyl}}, 2.52 (s, 6H, H}_{\text{Me-Xyl}}, -2.59 \text{ (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH}_2\text{Cl}_2) \lambda_{\text{max}} (\log \varepsilon) 428 (4.87), 526 (3.82), 568 (3.60), 602 (3.41), 656 (3.15) \text{ nm. MALDI-TOF MS (1,8,9-anthracenetriol): } m/z = 858.0 \text{ (M}^+)\text{. HRMS, } m/z: \text{ calcd for MH}^+ (C_{61}H_{51}N_4O): 857.4219, \text{ found: 857.4211.}\]

**FeTXP-=-PhCHO, Fe55.**

4-(E-2-((5,10,15,20-tetrakis(3,5-dimethyphenyl)porphyrinato iron(III))ethyl)benzaldehyde.

Acetonitrile (20 mL) was refluxed under argon for 2 h to remove any dissolved oxygen. The reaction’s temperature was then lowered to 70°C and iron(II) chloride (350 mg, 1.76 mmol) added. A solution of porphyrin aldehyde 55 (100 mg, 0.117 mmol) in 10 mL of degassed CHCl₃ was then added to the reaction over 10 min. The reaction was then heated back up to reflux, stirred for 3 h and then left exposed to air overnight at RT. The reaction mixture was then concentrated *in vacuo*, redissolved in CH₂Cl₂ and washed with 0.1M HCl (3 x 25 mL). The reaction mixture was then purified by column chromatography (silica, 100% CH₂Cl₂ - 98% CH₂Cl₂: 2% MeOH) and filtered through filter paper to give the desired compound Fe55 as a brown powder (97 mg, 87%). UV-vis (CH₂Cl₂) \( \lambda_{\text{max}} (\log \varepsilon) \) 432 (4.34), 507 (3.70), 672 (3.11) nm. MALDI-TOF MS (1,8,9-
anthracenetriol): \(m/z = 910.9\) (M\(^+\)- Cl\(^-\)). HRMS, \(m/z\): calcd for MH\(^+\)-Cl (C\(_{61}\)H\(_{51}\)FeN\(_4\)O): 910.3334, found: 910.3323.

**T3EP=-PhCHO, 56.**

4-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin-2-yl)ethen-1-yl)benzaldehyde.

A solution of porphyrin phosphonium salt 27 (136 mg, 0.12 mmol) and terephthaldehyde (86 mg, 0.64 mmol) were stirred in degassed CHCl\(_3\) (8 mL) under argon at reflux. DBU (70 µL, 0.46 mmol) in degassed CHCl\(_3\) (1 mL) was added over 10 min and the reaction was stirred for a further 10 min. On cooling to RT the reaction mixture was then concentrated \textit{in vacuo} and purified by flash chromatography (silica, CH\(_2\)Cl\(_2\):diethyl ether (19:1)). The major band was collected and concentrated \textit{in vacuo}. Crystallisation from CH\(_2\)Cl\(_2\)/MeOH gave the desired product 56 (80 mg, 66%) as a purple powder. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.02 (s, 1H, CHO), 8.93-8.85 (m, 5H, H\(_{\beta\text{-pyrrolic}}\) and H\(_{\text{o-Est}}\)), 8.81-8.64 (m, 6H, H\(_{\beta\text{-pyrrolic}}\)), 8.56-8.33 (m, 8H, H\(_{\text{o,p-Est}}\)) 7.92-7.81 (m, 6H, H\(_{\text{m-Est}}\) and H\(_{\text{AR}}\)), 7.33-6.97 (m, 4H, H\(_{\text{AR}}\) and H\(_{\text{vinyl}}\)), 4.01-3.98 (m, 9H, CO\(_2\)CH\(_3\)), 3.90 (s, 3H, CO\(_2\)CH\(_3\)), -2.60 (br s, 2H, NH). Assignment aided by COSY spectra. Spectral data in agreement with literature.\(^{[79]}\)
ZnT3EP-=PhCHO, Zn56.

4-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrinato zinc(II)yl)ethen-1-yl)benzaldehyde.

Porphyrin 56 (25 mg, 26 µmol) was dissolved in CHCl₃ (5 mL) and stirred at RT. A solution of Zn(OAc)₂·2H₂O (7 mg, 34 µmol) in MeOH (0.5 mL) was added and stirred for 30 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product Zn56 (20 mg, 74%) as a purple powder. 

¹H-NMR (400 MHz, CDCl₃): δ 9.95 (s, 1H, CHO), 8.98 (s, 1H, Hβ-pyrrolic), 8.89-8.74 (m, 10H, Hβ-pyrrolic and Hα-Est), 8.49-8.32 (m, 8H, Hα,β-Est) 7.90-7.74 (m, 6H, Hm-Est and HαR), 7.31-6.98 (m, 4H, HαR and Hvinyl), 3.95-3.82 (m, 12H, CO₂CH₃). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax (log ε) 432 (5.23), 557 (4.21), 595 (3.86) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1039.0 (M⁺). HRMS, m/z: calcd for MH₂⁺ (C₆₂H₄₀N₄O₈Zn): 1038.2607, found: 1038.2258.
TPP-T3EP dyad, 57.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin-2-yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetraphenylporphyrin-2-yl)ethen-1-yl)benzene.

A solution of porphyrin aldehyde 39 (20 mg, 27 µmol) and porphyrin phosphonium salt 27 (40 mg, 35 µmol) were stirred in degassed CHCl₃ (5 mL) under argon at reflux. DBU (21 µL, 138 µmol) in degassed CHCl₃ (1 mL) was added over 20 min and the reaction was stirred for a further 20 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH₂Cl₂: Et₂O (1:0, 19:1)). The major band was collected and concentrated in vacuo. The isomeric mixture and I₂ (10 mg, 39 µmol) were then dissolved in CH₂Cl₂ and stirred for 16 h. Sat. aq. Na₂S₂O₃ (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with H₂O (2 x 25 mL). Crystallisation from CH₂Cl₂/MeOH gave the desired product 57 (24 mg, 62%) as a purple powder. ¹H-NMR (400 MHz, CDCl₃): δ 9.04 (s, 1H, Hβ-pyrrolic), 8.97-8.65 (m, 13H, Hβ-pyrrolic), 8.58-8.39 (m, 8H, H-o-Est), 8.29-8.19 (m, 8H, H-o-Ar), 8.04-7.72 (m, 20H, H-m,p-Est and H-m,p-Ar), 7.23 and 7.17 (ABq, 4H, 3J= 8.0 Hz, H₆Ar), 7.33 and 7.06 (d, 2H, 3J= 16.5 Hz, H_vinyl), 7.30 and 6.95 (d, 2H, 3J= 16.5 Hz, H_vinyl), 4.04-3.99 (m, 12H, CO₂CH₃), -2.54 (br s, 2H, NH), -2.56 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λ_max (log ε) 425 (5.44) (shoulder at 494), 522 (4.60), 572 (4.43), 601 (4.29), 657 (3.70) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1590.1 (M⁺). HRMS, m/z: calcd for MH⁺ (C₁₀₆H₇₄N₈O₈): 1586.5630, found: 1586.7230.
TXP-T3EP dyad, 58.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin-2-yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin-2-yl)ethen-1-yl)benzene.

A solution of porphyrin aldehyde 55 (18 mg, 21 µmol) and porphyrin phosphonium salt 27 (32 mg, 27 µmol) were stirred in degassed CHCl₃ (5 mL) under argon at reflux. DBU (12 µL, 81 µmol) in degassed CHCl₃ (1 mL) was added over 20 min and the reaction was stirred for a further 30 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH₂Cl₂: Et₂O (1:0, 19:1)). The major band was collected and concentrated in vacuo. The isomeric mixture and I₂ (10 mg, 39 µmol) were then dissolved in CH₂Cl₂ and stirred for 16 h. Sat. aq. Na₂S₂O₃ (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with H₂O (2 x 25 mL). Crystallisation from CH₂Cl₂/MeOH gave the desired product 58 (23 mg, 64%) as a purple powder. ¹H-NMR (400 MHz, CDCl₃): δ 9.05 (s, 1H, Hβ-pyrrolic), 8.96-8.89 (m, 8H, Hα-Est), 8.86-8.38 (m, 21H, Hβ-pyrrolic and Hα,p-Est), 7.98-7.82 (m, 12H, Hm-Est and Hα-Xyl), 7.64 (s, 1H, Hp-xyl), 7.48 (s, 1H, Hp-xyl), 7.40 (s, 2H, Hp-xyl), 7.34 and 7.08 (d, 2H, ³J= 16.2 Hz, Hvinyl), 7.32 and 6.96 (d, 2H, ³J= 16.1 Hz, Hvinyl), 7.29 and 7.20 (ABq, 4H, ³J= 8.4 Hz, Hα-tet), 4.05-3.97 (m, 12H, CO₂CH₃), 2.69-2.58 (m, 24H, HMe-Xyl), -2.56 (br s, 4H, NH). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax (log ε) 421 (5.37) (shoulder at 493), 521 (4.48), 572 (4.28), 600 (4.16), 655 (3.62) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1702.5 (M⁺). HRMS, m/z: calcd for MH⁺ (C₁₁₄H₉₁N₈O₈): 1700.7038, found: 1700.7076.
ZnTPP-ZnT3EP dyad, 59.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrinato zinc(II)yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetraphenylporphyrinato zinc(II)yl)ethen-1-yl)benzene.

Porphyrin dyad 57 (25 mg, 16 µmol) was dissolved in CHCl₃ (6 mL) and stirred at RT. A solution of Zn(OAc)₂·2H₂O (9 mg, 40 µmol) in MeOH (0.5 mL) was added and stirred for 40 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product 59 (24 mg, 89%) as a purple powder. ³¹H-NMR (400 MHz, CDCl₃): δ 9.13 (m, 1H, Hβ-pyrrolic), 9.01 (s, 1H, Hβ-pyrrolic), 8.95-8.78 (m, 12H, Hβ-pyrrolic), 8.63-8.18 (m, 16H, Hβ-Est and Hβ-Ar), 8.02-7.71 (m, 20H, Hm,p-Est and Hm,p-Ar), 7.31-6.89 (m, 8H, HAr and Hvinyl), 3.99-3.86 (m, 12H, CO₂CH₃). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax (log ε) 426 (5.47) (shoulder at 494), 559 (4.55), 600 (4.41) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1715.6 (M⁺). HRMS, m/z: calcd for M⁺ (C₁₀₆H₇₀N₈O₈Zn₂): 1710.3900, found: 1710.3911.
ZnTXP-ZnT3EP dyad, 60.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrinato zinc(II))yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II))yl)ethen-1-yl)benzene.

Porphyrin dyad 58 (34 mg, 16 µmol) was dissolved in CHCl₃ (10 mL) and stirred at RT. A solution of Zn(OAc)₂·2H₂O (11 mg, 48 µmol) in MeOH (1.0 mL) was added and stirred for 60 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture was concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product 60 (30 mg, 82%) as a purple powder.¹H-NMR (400 MHz, CDCl₃): δ 9.16 (s, 1H, H₇-pyrrolic or H₀-Est), 9.03 (s, 1H, H₇-pyrrolic or H₀-Est), 8.99-8.78 (m, 16H, H₇-pyrrolic and H₀-Est), 8.63 (br d, 1H, J= 7.7 Hz, H₀-Est or H₀-Est), 8.50-8.38 (m, 7H, H₀,p-Est), 8.00-7.80 (m, 12H, H₇-Est and H₀-Xyl), 7.62 (s, 1H, H₇-Xyl), 7.47 (s, 1H, H₇-p-Xyl), 7.40 (s, 2H, H₇-p-Xyl), 7.33 and 7.24 (m, 4H, Hvinyl and HAr), 7.18 (d, 2H, J= 8.1 Hz, HAr), 7.10 (d, 1H, J= 16.5 Hz, Hvinyl), 6.97 (d, 1H, J= 15.8 Hz, Hvinyl), 3.98-3.88 (m, 12H, CO₂CH₃), 2.69-2.58 (m, 24H, HMe-Xyl).

Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax(log ε) 422 (5.51) (shoulder at 490), 558 (4.52), 600 (4.33) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1828.42 (M⁺). HRMS, m/z: calcd for MH⁺ (C₁₁₄H₇₈N₈O₈Zn₂): 1823.5230, found: 1823.5291.
ZnTPP-ZnT3CP dyad, 61.

1-(E-2-(5,10,15,20-tetra(3-carboxyphenyl)porphyrinato zinc(II)yl)ethen-1-yl)-4-(E-2-(5,10,15,20-
tetraphenylporphyrinato zinc(II)yl)ethen-1-yl)benzene.

KOH (50 mg, 0.89 mmol) dissolved in MeOH:H$_2$O (10:1, 6 mL) was added to porphyrin dyad 59
(20 mg, 12 µmol) dissolved in THF (6 mL). The reaction was stirred at reflux under argon for 16
h. On cooling to RT the reaction mixture was concentrated in vacuo. The reaction mixture was
then redissolved in H$_2$O (10 mL) and 2M H$_3$PO$_4$ (455 µL, 0.91 mmol) added. The green precipitate
was then filtered and washed with ice cold H$_2$O (3 x 20 mL) and dried in vacuo to give 61 (10 mg,
50%) as a purple powder. $^1$H-NMR (400 MHz, acetone-d$_6$): δ 9.15 (s, 2H, H$_\beta$-pyrrolic), 8.96-8.79 (m,
12H, H$_\beta$-pyrrolic), 8.61-8.46 (m, 8H, H$_o$-Acid), 8.32-8.18 (m, 8H, H$_o$-Ar), 8.13 (m, 1H, H$_m$-Acid), 8.04- 7.74
(m, 19H, H$_m$,-Acid and H$_m$,-Ar), 7.45-7.08 (m, 8H, H$_AR$ and H$_vinyl$), 3.99-3.86 (m, 12H, CO$_2$CH$_3$).

Assignment aided by COSY spectra. UV-vis (DMF) $\lambda_{max}$ (log ε) 434 (5.64) (shoulder at 499), 571
(4.72), 611 (4.56) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1659.5 (M$^+$). HRMS, m/z:
calcd for M$^+$ (C$_{102}$H$_{62}$N$_8$O$_8$Zn$_2$): 1654.3274, found: 1654.3295.
ZnTXP-ZnT3CP dyad, 62.

1-\((E-2-(5,10,15,20\text{-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II)})\text{ethen-1-yl})-4-\((E-2-(5,10,15,20\text{-tetra(3-carboxyphenyl)porphyrinato zinc(II)})\text{ethen-1-yl})\text{benzene.}

KOH (72 mg, 1.28 mmol) dissolved in MeOH:H\text{2}O (10:1, 6 mL) was added to porphyrin dyad 60 (30 mg, 16 µmol) dissolved in THF (5 mL). The reaction was stirred at reflux under argon for 16 h. On cooling to RT the reaction mixture was concentrated \textit{in vacuo}. The reaction mixture was then redissolved in H\text{2}O (10 mL) and 2M H\text{3}PO\text{4} (650 µL, 1.30 mmol) added. The green precipitate was then filtered and washed with ice cold H\text{2}O (3 x 20 mL) and dried \textit{in vacuo} to give 62 (21 mg, 75%) as a purple powder.

\textsuperscript{1}H-NMR (400 MHz, acetone-d\text{6}): \(\delta\) 9.17 (s, 2H, H\text{β-pyrrolic} or H\text{o-Acid}), 8.96-8.78 (m, 17H, H\text{β-pyrrolic} and H\text{o,p-Acid}), 8.60-8.44 (m, 7H, H\text{m-Acid}), 8.17-8.10 (m, 1H, H\text{m-Acid}), 8.06-7.80 (m, 12H, H\text{p-Xyl}, H\text{vinyl} and H\text{AR}), 7.57-6.91(m, 12H, H\text{p-xyl}, H\text{vinyl} and H\text{AR}), 2.73 (s, 3H, H\text{Me-Xyl}), 2.69 (s, 3H, H\text{Me-Xyl}), 2.66 (s, 6H, H\text{Me-Xyl}), 2.64-2.59 (s, 12H, H\text{Me-Xyl}). \textit{Assignment aided by COSY spectra.}

UV-vis (DMF) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 428 (5.00) (shoulder at 498), 568 (3.99), 610 (3.80) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \textit{m/z} = 1771.7 (M\text{+}). HRMS, \textit{m/z}: calcd for MH\text{+} (C\text{110}H\text{79}N\text{8}O\text{8}Zn\text{2}): 1767.4604, found: 1767.4569.
FeTPP-T3EP dyad, 64.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin-2-yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetraphenylporphyrinato iron(III)yl)ethen-1-yl)benzene.

A solution of porphyrin aldehyde Fe39 (30 mg, 36 µmol) and porphyrin phosphonium salt 27 (50 mg, 44 µmol) were stirred in degassed CHCl₃ (6 mL) under argon at reflux. DBU (28 µL, 190 µmol) in degassed CHCl₃ (1 mL) was added over 20 min and the reaction was stirred for a further 40 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH₂Cl₂: MeOH (1:0, 97:3)). The major band was collected and concentrated in vacuo. The isomeric mixture and I₂ (15 mg, 59 µmol) were then dissolved in CH₂Cl₂ and stirred for 19 h. Sat. aq. Na₂S₂O₃ (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with 0.1 M HCl (2 x 25 mL). Crystallisation from CH₂Cl₂/MeOH gave desired product 64 (34 mg, 57%) as a purple powder. UV-vis (CH₂Cl₂) λ_max (log ε) 424 (5.33) (shoulder at 493), 520 (4.45), 567 (4.17), 600 (4.05), 656 (3.64) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1644.4 (M⁺-Cl). HRMS, m/z: calcd for M⁺-Cl⁻ (C₁₀₆H₇₆FeN₈O₈): 1640.4823, found: 1640.4792.
FeTXP-T3EP dyad, 65.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin-2-yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato iron(III)yl)ethen-1-yl)benzene.

A solution of porphyrin aldehyde Fe55 (32 mg, 34 µmol) and porphyrin phosphonium salt 27 (50 mg, 44 µmol) were stirred in degassed CHCl₃ (6 mL) under argon at reflux. DBU (28 µL, 190 µmol) in degassed CHCl₃ (1 mL) was added over 15 min and the reaction was stirred for a further 50 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH₂Cl₂: MeOH (1:0, 97:3)). The major band was collected and concentrated in vacuo. The isomeric mixture and I₂ (15 mg, 59 µmol) were then dissolved in CH₂Cl₂ and stirred for 30 h. Sat. aq. Na₂S₂O₃ (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with 0.1 M (2 x 25 mL). Crystallisation from CH₂Cl₂/MeOH gave desired product 65 (37 mg, 61%) as a purple powder. UV-vis (CH₂Cl₂) \( \lambda_{\text{max}} \) (log ε) 420 (5.41) (shoulder at 494), 518 (4.49), 566 (4.20), 594 (4.15), 656 (4.01) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \( m/z = 1756.4 \) (M⁺-Cl). HRMS, \( m/z \): calcd for M⁺ (C₁₁₄H₈₈ClFeN₈O₈): 1787.5763, found: 1787.5791.
FeTPP-ZnT3EP dyad, 66.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrinato zinc(II)yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetraphenylporphyrinato iron(III)yl)ethen-1-yl)benzene.

Porphyrin dyad 64 (21 mg, 13 µmol) was dissolved in CHCl₃ (10 mL) and stirred at RT. A solution of Zn(OAc)₂·2H₂O (4 mg, 17 µmol) in MeOH (1.0 mL) was added and stirred for 30 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture was concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product 66 (21 mg, 91%) as a purple powder. UV-vis (CH₂Cl₂) λmax (log ε) 427 (5.12) (shoulder at 494), 558 (4.12), 597 (3.93) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1707.7 (M⁺- Cl). HRMS, m/z: calcd for MH⁺-Cl (C₁₀₆H₇₀FeN₈O₈Zn): 1705.4060, found: 1707.3148.
FeTXP-ZnT3EP dyad, 67.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrinato zinc(II)yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato iron(III)yl)ethen-1-yl)benzene.

Porphyrin dyad 65 (37 mg, 21 µmol) was dissolved in CHCl₃ (10 mL) and stirred at RT. A solution of Zn(OAc)₂·2H₂O (6 mg, 27 µmol) in MeOH (1.0 mL) was added and stirred for 30 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture was concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product 67 (38 mg, 95%) as a purple powder. UV-vis (CH₂Cl₂) λₘₐₓ (log ε) 421 (5.55) (shoulder at 494), 554 (4.45), 597 (4.21) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1819.2 (M⁺- Cl). HRMS, m/z: calcd for M⁺ (C₁₁₄H₈₆ClFeN₉O₈Zn): 1849.4898, found: 1849.4985.
FeTPP-ZnT3CP dyad, 68.

1-(E-2-(5,10,15,20-tetra(3-carboxyphenyl)porphyrinato zinc(II))ethen-1-yl)-4-(E-2-(5,10,15,20-tetraphenylporphyrinato iron(III))ethen-1-yl)benzene.

A solution of porphyrin dyad 66 (26 mg, 15 µmol) in THF (6 mL) was heated to reflux and stirred. KOH (50 mg, 0.89 mmol) in MeOH:H₂O (10:1, 6 mL) was added and stirred for 16 h. On cooling to RT the reaction mixture was concentrated in vacuo. The reaction mixture was then redissolved in H₂O (10 mL) and 2M H₃PO₄ (455 µL, 0.91 mmol) added. The green precipitate was then filtered and washed with ice cold H₂O (3 x 20 mL) and dried in vacuo to give 68 (22 mg, 88%) as a purple powder. UV-vis (DMF) λ max (log ε) 430 (5.14) (shoulder at 500), 570 (4.13), 610 (3.94) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1651.3 (M⁺-Cl⁻). HRMS, m/z: calcld for M⁺-Cl⁻ (C₁₀₂H₆₂FeN₈O₈Zn): 1646.3331, found: 1646.3374.
FeTXP-ZnT3CP dyad, 69.

1-(E-2-(5,10,15,20-tetra(3-carboxyphenyl)porphyrinato zinc(II)yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato iron(III)yl)ethen-1-yl)benzene.

KOH (55 mg, 0.98 mmol) dissolved in MeOH:H$_2$O (10:1, 6 mL) was added to porphyrin dyad 67 (38 mg, 21 µmol) dissolved in THF (6 mL). The reaction was stirred at reflux under argon for 17 h. On cooling to RT the reaction mixture was concentrated in vacuo. The reaction mixture was then redissolved in H$_2$O (10 mL) and 2M H$_3$PO$_4$ (500 µL, 1.00 mmol) added. The green precipitate was then filtered and washed with ice cold H$_2$O (3 x 20 mL) and dried in vacuo to give 69 (26 mg, 70%) as a purple powder. UV-vis (DMF) $\lambda_{max}$ (log $\varepsilon$) 427 (5.42) (shoulder at 500), 563 (4.26), 607 (4.00) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$= 1763.7 (M$^+$.H$_2$PO$_4^-$). HRMS, $m/z$: calcd for M$^+$ (C$_{110}$H$_{80}$FeN$_8$O$_{12}$PZn): 1793.4272, found: 1793.4288.
TPP-ZnT3EP dyad, 70.

1-\((E-2-(5,10,15,20\text{-tetra}(3\text{-methoxycarbonylphenyl})\text{porphyrinato zinc(II)yl})\text{ethen-1-yl})-4-(E-2-(5,10,15,20\text{-tetraphenylporphyrin-2-yl})\text{ethen-1-yl})\text{benzene.}

A solution of porphyrin aldehyde Zn56 (16 mg, 15 µmol) and porphyrin phosphonium salt 25 (19 mg, 20 µmol) were stirred in degassed CHCl₃ (3 mL) under argon at reflux. DBU (7 µL, 47 µmol) in degassed CHCl₃ (0.5 mL) was added over 10 min and the reaction was stirred for a further 35 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH₂Cl₂: Et₂O (1:0, 19:1)). The major band was collected and concentrated in vacuo. The isomeric mixture and I₂ (10 mg, 39 µmol) were then dissolved in CH₂Cl₂ and stirred for 16 h. Sat. aq. Na₂S₂O₃ (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with H₂O (2 x 25 mL). Crystallisation from CH₂Cl₂/MeOH gave the desired product 70 (13 mg, 52%) as a purple powder. ¹H-NMR (400 MHz, CDCl₃): δ 9.04 (s, 1H, Hβ-pyrrolic), 9.01 (s, 1H, Hβ-pyrrolic), 8.94-8.74 (m, 16H, Hβ-pyrrolic and Ho-Est), 8.64 (br d, 1H, 3J= 8.1 Hz, Ho-Est or Hp-Est), 8.53 (br d, 1H, 3J= 8.1 Hz, Ho-Est or Hp-Est), 8.49- 8.21 (m, 14H, Ho,p-Est and Hm,p-Ar), 8.04-7.73 (m, 16H, Hm-Est and Hm,p-Ar), 7.35-7.14 (m, 6H, HAr and Hvinyl), 7.05 and 6.96 (d, 2H, 3J= 16.4 Hz, Hvinyl), 4.01-3.94 (m, 12H, CO₂CH₃), -2.53 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CH₂Cl₂) λmax (log ε) 426 (5.34) (shoulder at 490), 561 (4.39), 599 (4.29) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1652.9 (M⁺). HRMS, m/z: calcd for MH⁺ (C₁₀⁶H₇₂N₆O₈Zn): 1649.4843, found: 1649.4877.
ZnTPP-T3EP dyad, 71.

1-(E-2-(5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin-2-yl)ethen-1-yl)-4-(E-2-
(5,10,15,20-tetraphenylporphyrinato zinc(II)yl)ethen-1-yl)benzene.

A solution of porphyrin aldehyde Zn39 (24 mg, 27 µmol) and porphyrin phosphonium salt 27 (52
mg, 45 µmol) were stirred in degassed CHCl₃ (3 mL) under argon at reflux. DBU (9 µL, 61 µmol)
in degassed CHCl₃ (0.5 mL) was added over 10 min and the reaction was stirred for a further 35
min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash
chromatography (silica, CH₂Cl₂: Et₂O (1:0, 19:1)). The major band was collected and
concentrated in vacuo. The isomeric mixture and I₂ (10 mg, 39 µmol) were then dissolved in
CH₂Cl₂ and stirred for 16 h. Sat. aq. Na₂S₂O₃ (25 ml) was then added and continued to stir for 30
min. The organic layer was then separated and washed with H₂O (2 x 25 mL). Crystallisation from
CH₂Cl₂/MeOH gave the desired product 71 (16 mg, 36%) as a purple powder. ¹H-NMR (400 MHz,
CDCl₃): δ 9.07 (s, 1H, Hβ-pyrrolic), 8.90- 8.57 (m, 17H, Hβ-pyrrolic and H₀-Est), 8.49- 8.11 (m, 16H, H₀,p-Est
and H₀-Ar), 7.95-7.62 (m, 16H, Hₘ-Est and Hₘ,p-Ar), 7.26-7.07 (m, 6H, H₀-Ar and Hₗ-vinyl), 7.01 and 6.86
(d, 2H, ³J= 16.2 Hz, Hₗ-vinyl), 3.96-3.87 (m, 12H, CO₂CH₃), -2.64 (br s, 2H, NH). Assignment aided by
COSY spectra. UV-vis (CH₂Cl₂) λₘₑₓ (log ε) 424 (5.35) (shoulder at 492), 562 (4.34), 598 (4.19) nm.
MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1653.1 (M⁺). HRMS, m/z: calcd for MH⁺
(C₁₀₆H₇₂N₈O₈Zn): 1649.4843, found: 1649.4873.
TPP-ZnT3CP dyad, 72.

1-(E-2-(5,10,15,20-tetra(3-carboxyphenyl)porphyrinato zinc(II)yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetraphenylporphyrin-2-yl)ethen-1-yl)benzene.

KOH (34 mg, 0.64 mmol) dissolved in MeOH:H₂O (10:1, 6 mL) was added to porphyrin dyad 70 (13 mg, 8 µmol) dissolved in THF (4 mL). The reaction was stirred at reflux under argon for 16 h. On cooling to RT the reaction mixture was concentrated *in vacuo*. The reaction mixture was then redissolved in H₂O (5 mL) and 2M H₃PO₄ (350 µL, 0.7 mmol) added. The green precipitate was then filtered and washed with ice cold H₂O (3 x 20 mL) and dried *in vacuo* to give 72 (13 mg, 100%) as a purple powder. 

**1H-NMR (400 MHz, acetone-d₆):** δ 9.17-9.14 (m, 2H, Hβ-pyrrolic), 8.96-8.75 (m, 16H, Hβ-pyrrolic and Hα-Acid), 8.58-8.20 (m, 16H, Hα,p-Acid and Hα-Ar), 8.05-7.76 (m, 16H, Hm-Acid and Hm,p-Ar), 7.44-7.02 (m, 8H, Hα and Hvinyl), -2.49 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (DMF) λ_max (log ε) 431 (5.01) (shoulder at 501), 527 (4.10), 610 (3.97) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1597.3 (M⁺). HRMS, m/z: calcd for MH⁺ (C₁₀₂H₆₄N₈O₈Zn): 1593.4217, found: 1593.4247.
ZnTPP-T3CP dyad, 73.

1-(E-2-(5,10,15,20-tetra(3-carboxyphenyl)porphyrin-2-yl)ethen-1-yl)-4-(E-2-(5,10,15,20-tetraphenylporphyrinato zinc(II)yl)ethen-1-yl)benzene.

KOH (45 mg, 0.80 mmol) dissolved in MeOH:H₂O (10:1, 5 mL) was added to porphyrin dyad 71 (16 mg, 10 µmol) dissolved in THF (6 mL). The reaction was stirred at reflux under argon for 16 h. On cooling to RT the reaction mixture was concentrated in vacuo. The reaction mixture was then redissolved in H₂O (5 mL) and 2M H₃PO₄ (425 µL, 0.85 mmol) added. The green precipitate was then filtered and washed with ice cold H₂O (3 x 20 mL) and dried in vacuo to give 73 (14 mg, 88%) as a purple powder. ¹H-NMR (400 MHz, acetone-d₆): δ 9.15 (s, 1H, H β-pyrrolic), 8.98-8.78 (m, 17H, H β-pyrrolic and H o-Acid), 8.62-8.17 (m, 16H, H o,p-Acid and H o-Ar), 8.07-7.76 (m, 16H, H m-Acid and H m,p-Ar), 7.40-6.99 (m, 8H, H AR and H vinyl), -2.48 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (DMF) λmax (log ε) 429 (5.00) (shoulder at 499), 573 (4.08), 608 (3.97) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1596.1 (M⁺). HRMS, m/z: calcd for MH⁺ (C₁₀₂H₆₄N₈O₈Zn): 1593.4217, found: 1593.4208.
Benzene-1,3,5-tricarbaldehyde, 74.

Mesitylene (5.6 mL, 40 mmol) was dissolved in CHCl₃ (60 mL) and stirred under infrared and mercury lamp exposure. N-Bromosuccinimide (30 g, 170 mmol, 1.4 eq. per methyl) was added over 35 min and then stirred for a further 16 h. Upon cooling to RT, the solution was filtered and the filtrate concentrated in vacuo. GCMS analysis indicated bromination had was completed with several brominated products present. The crude product was therefore taken directly to the Sommelet reaction. The crude brominated material, hexamethylenetetramine (50 g, 357 mmol), H₂O (30 mL) and glacial acetic acid (30 mL) were heated to 110°C for 3 h. Upon cooling to RT, conc. HCl (3 mL) was added, stirred for 15 min and extracted with CH₂Cl₂ (50 mL). The organic layer was washed with sat. aq. NaHCO₃ (50 mL), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash chromatography (silica, CH₂Cl₂: Hexane (7:3, 9:1)) and concentrated in vacuo to give benzene-1,3,5-tricarbaldehyde 74 (245 mg, 3.8%) as a white powder.¹H-NMR (400 MHz, CDCl₃): δ 10.21 (s, 3H, CHO), 8.64 (s, 3H, H_AR). LR-GCMS: m/z = 162.0 (M⁺). Spectral data in agreement with literature.[135]
(TXP_{-})_{2}\text{PhCHO}, 75.

3,5-Bis(E-2-(5,10,15,20-tetrakis(3-methoxycarbonylphenyl)-porphyrin-2-yl)ethen-1-yl)benzaldehyde.

A solution of porphyrin phosphonium salt 26 (200 mg, 190 µmol) and benzene-1,3,5-tricarbaldehyde 74 (9 mg, 54 µmol) were stirred in degassed CHCl$_3$ (5 mL) under argon at reflux. DBU (29 µL, 190 µmol) in degassed CHCl$_3$ (1 mL) was added over 10 min and the reaction was stirred for a further 45 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH$_2$Cl$_2$:Hexane (4:1)). The major brown band was collected, concentrated in vacuo. The isomeric mixture and I$_2$ (10 mg, 39 µmol) were then dissolved in CH$_2$Cl$_2$ and stirred for 16 h. Sat. aq. Na$_2$S$_2$O$_3$ (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with H$_2$O (2 x 25 mL). Crystallisation from CH$_2$Cl$_2$/MeOH gave the desired product 75 (64 mg, 74%) as a brown powder.

$^1$H-NMR (400 MHz, CDCl$_3$): δ 10.21 (s, 1H, CHO), 9.18 (s, 2H, H$_\beta$-pyrrolic), 8.87-8.82 (m, 12H, H$_\beta$-pyrrolic), 7.94 (s, 4H, H$_o$-Xyl), 7.89 (s, 4H, H$_o$-Xyl), 7.84 (s, 8H, H$_o$-Xyl), 7.70 (s, 2H, H$_A$R), 7.53-7.39 (m, 11H, H$_p$-Xyl, H$_A$R and H$_{vinyl}$), 7.24 (d, 2H, $^3$J=16.1 Hz, H$_{vinyl}$), 2.69-2.54 (m, 48H, H$_{Me}$-Xyl), -2.54 (br s, 4H, NH). Assignment aided by COSY spectra. UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log ε) 427 (4.06), 525 (3.04), 563 (2.81), 599 (2.65), 652 (2.42) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 1610.2 (M$^+$). HRMS, m/z: calcd for MH$^+$ (C$_{115}$H$_{99}$N$_8$O): 1607.7942, found: 1607.7933.
(TXP-=-)2Ph-Fullerene, 76.

1,5-dihydro-1-methyl-2-(3,5-bis(E-2-(5,10,15,20-tetrakis(3-methoxycarbonylphenyl)-porphyrin-2-yl)ethen-1-yl)benzene)- 2'H-[5,6]Fullereno-C60-f0-[1,9-c]pyrrole.

Chemical Formula: C_{177}H_{373}N_{6}
Exact Mass: 2353.83
Molecular Weight: 2355.83

A solution of 75 (25 mg, 16 μmol), fullerene (223 mg, 0.31 mmol), sarcosine (42 mg, 0.47 mmol) in toluene (3 mL) was heated to 150°C, 250 W for 60 min in a microwave reactor. Once cooled to RT the reaction was column chromatographed (silica, toluene, CH₂Cl₂: hexane), first eluting with toluene to remove fullerene then CH₂Cl₂: Hexane (7:3) to collect the major brown band. Recrystallisation from CH₂Cl₂: hexane gave 76 (30 mg, 79%) as a purple/brown powder. ¹H-NMR (400 MHz, CDCl₃:CS₂ (1:1)): δ 8.79-8.68 (m, 14H, Hβ-pyrrolic), 7.92-7.71 (m, 18H, Hο-Xyl and HΑR), 7.46-7.26 (m, 13H, Hp-Xyl, HΑR and Hvinyl), 4.97 (s, 1H, Hpyrrolidine), 4.39 (d, 2H, J= 10.5 Hz, Hpyrrolidine), 2.94 (s, 3H, HMe-pyrrolidine), 2.70-2.47 (m, 48H, HMe-Xyl), -2.69 (br s, 4H, NH). Assignment aided by COSY spectra. UV-vis (CS₂) λₘₐₓ (log ε) 427 (5.05), 525 (4.01), 563 (3.85), 598 (3.70), 650 (3.46) nm. HRMS, m/z: calcd for M⁺ (C_{53}H_{37}N_{4}O): found: 2353.9246.
**Zn(TXP-=-)\textsubscript{2}Ph-Fullerene, 77.**

1,5-dihydro-1-methyl-2-(3,5-bis(E-2-(5,10,15,20-tetrakis(3-methoxycarbonylphenyl)-porphyrinato zinc(II)yl)ethen-1-yl)benzene)-2'H-[5,6]Fullereno-C\textsubscript{60}-I\textsubscript{h}-[1,9-c]pyrrole.

Compound 76 (40 mg, 17 µmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (15 mL) and stirred at RT. A solution of Zn(OAc)**·**2H\textsubscript{2}O (11 mg, 48 µmol) in MeOH (1.0 mL) was added and stirred for 40 min. MALDI mass spectrometry indicated reaction completion. The reaction mixture was concentrated in vacuo and purified by flash chromatography (silica, CH\textsubscript{2}Cl\textsubscript{2}). Crystallisation in CH\textsubscript{2}Cl\textsubscript{2}: hexane gave the desired product 77 (31 mg, 74%) as a purple/brown powder. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}:CS\textsubscript{2} (1:1)): δ 8.90-8.78 (m, 14H, H\textsubscript{β}-pyrrolic), 7.89-7.70 (m, 18H, H\textsubscript{o-Xyl} and H\textsubscript{AR}), 7.45-7.25 (m, 13H, H\textsubscript{p-Xyl}, H\textsubscript{AR} and H\textsubscript{vinyl}), 4.95 (s, 1H, H\textsubscript{pyrrolidine}), 4.34 (d, 2H, \textsuperscript{3}J= 10.5 Hz, H\textsubscript{pyrrolidine}), 2.94 (s, 3H, H\textsubscript{Me-pyrrolidine}), 2.69-2.46 (m, 48H, H\textsubscript{Me-Xyl}). Assignment aided by COSY spectra. UV-vis (CS\textsubscript{2}) λ\textsubscript{max} (log ε) 440 (5.02), 561 (4.15), 599 (3.91) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 2487.7 (M\textsuperscript{+}). HRMS, m/z: calcd for MH\textsuperscript{+} (C\textsubscript{177}H\textsubscript{99}N\textsubscript{9}Zn\textsubscript{2}): 2477.6606, found: 2477.6709.
TXP=Ph3CHO, 78.

3-(E-2-(5,10,15,20-tetrakis(3,5-dimethylphenylporphyrin-2-yl)ethen-1-yl)benzaldehyde.

A solution of porphyrin phosphonium salt 26 (100 mg, 0.10 mmol) and terephthaldehyde (67 mg, 0.5 mmol) were stirred in degassed CHCl3 (10 mL) under argon at reflux. DBU (46 µL, 0.3 mmol) in degassed CHCl3 (1 mL) was added over 10 min and the reaction was stirred for a further 10 min. On cooling to RT the reaction mixture was then concentrated in vacuo and purified by flash chromatography (silica, CH2Cl2). The major band was collected and concentrated in vacuo. Crystallisation from CH2Cl2/MeOH gave the desired product 78 (77 mg, 90%) as a purple powder. 1H-NMR (400 MHz, CDCl3): δ 10.10 (s, 1H, CHO), 9.02 (s, 1H, Hβ-pyrrolic), 8.86-8.78 (m, 6H, Hβ-pyrrolic), 8.01 (s, 1H, Hαα), 7.87-7.73 (m, 9H, Hβ-Xyl and Hαα), 7.59-7.40 (m, 6H, Hp-Xyl), 7.32 and 7.12 (d, 2H, J= 16.1 Hz, Hvinyl), 2.63 (s, 6H, HMe-Xyl), 2.59 (s, 12H, HMe-Xyl), 2.52 (s, 6H, HMe-Xyl), -2.60 (br s, 2H, NH). UV-vis (CH2Cl2) λmax (log ε) 426 (5.23), 523 (4.11), 562 (3.80), 599 (3.64), 656 (3.41) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z 858.44 (M+). HRMS, m/z: calcd for M+ (C61H52N4O): 856.4141, found: 856.4149.
ZnTXP-\(\phi\)-Ph-Fullerene, 79.

1,5-dihydro-1-methyl-2-(3-(\(E\)-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin-2-yl)ethen-1-yl)benzene)-2'\(H\)-[5,6]Fullereno-C\(_{60}\)-I\(_h\)-[1,9]pyrrole.

A solution of 78 (25 mg, 29 \(\mu\)mol), fullerene (167 mg, 0.23 mmol), sarcosine (31 mg, 0.35 mmol) in toluene (3 mL) was heated to 150\(^\circ\)C, 250 W for 60 min in a microwave reactor. Once cooled to RT the reaction was column chromatographed (silica, toluene, CH\(_2\)Cl\(_2\): hexane), first eluting with toluene to remove fullerene then CH\(_2\)Cl\(_2\): Hexane (7:3) to collect the major brown band. Recrystallisation from CH\(_2\)Cl\(_2\): hexane gave 79 (25 mg, 53%) as a purple/brown powder. \(^1\)H-NMR (400 MHz, CDCl\(_3\):CS\(_2\) (1:1)): \(\delta\) 8.78-8.63 (m, 7H, \(H_\beta\)-pyrrolic), 7.79-7.68 (m, 12H, \(H_\alpha\)-Xyl and \(H_\alpha\)-Ar), 7.37-7.13 (m, 6H, \(H_p\)-Xyl and \(H_{\text{vinyl}}\)), 4.29 (s, 1H, \(H_{\text{pyrrolidine}}\)), 4.29 (d, 2H, \(J\) = 10.0 Hz, \(H_{\text{pyrrolidine}}\)), 2.86 (s, 3H, \(H_{\text{Me-pyrrolidine}}\)), 2.63-2.53 (m, 24H, \(H_{\text{Me-Xyl}}\)), -2.75 (br s, 2H, NH). Assignment aided by COSY spectra. UV-vis (CS\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 438 (4.62), 528 (3.65), 567 (3.38), 604 (3.29), 664 (2.81) nm. HRMS, \(m/z\): calcd for M\(^+\) (C\(_{123}\)H\(_{57}\)N\(_5\)): 1603.4614, found: 1603.4602.
ZnTP-X-Ph-Fullerene, 80.

1,5-dihydro-1-methyl-2-(3-\(\mathcal{E}\)-2-(5,10,15,20-tetrakis(3,5-dimethylphenylporphyrinato zinc(II))ethen-1-yl)benzene)- 2'\(H\)-[5,6]Fullereno-\(C_{60}\)-[1,9-c]pyrrole.

\[
\text{Chemical Formula: } C_{123}H_{56}N_5Zn \\
\text{Exact Mass: } 1665.37 \\
\text{Molecular Weight: } 1668.17
\]

Compound 79 (20 mg, 12 µmol) was dissolved in CH\(_2\)Cl\(_2\) (10 mL) and stirred at RT. A solution of Zn(OAc)\(_2\)-2H\(_2\)O (10 mg, 44 µmol) in MeOH (1.0 mL) was added and stirred for 40 min. MALDI mass spectrometry indicated reaction completion. The reaction mixture was concentrated in vacuo and purified by flash chromatography (silica, CH\(_2\)Cl\(_2\)). Crystallisation in CH\(_2\)Cl\(_2\): hexane gave the desired product 88 (15 mg, 75%) as a purple/brown powder. \(^1\)H-NMR (400 MHz, CDCl\(_3\):CS\(_2\) (1:1)): \(\delta\) 8.85-8.34 (m, 7H, H\(_\beta\)-pyrrolic), 7.89-7.23 (m, 18H), 5.16 (m, 1H, H\(_\text{pyrrolidine}\)), 4.24 (m, H\(_\text{pyrrolidine}\)), 2.80 (s, 3H, H\(_\text{Me-pyrrolidine}\)), 2.64-2.50 (m, 24H, H\(_\text{Me-Xyl}\)). UV-vis (CS\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 438 (4.71), 557 (3.81), 628 (3.33) nm. HRMS, \(m/z\) calcd for MH\(^+\) (C\(_{123}\)H\(_{56}\)N\(_5\)Zn): 1666.3827, found: 1666.3901.
3,5-Bis(\(E\)-2-(5,10,15,20-tetra(3,5-dimethylphenyl)-porphyrin-2-yl)ethen-1-yl)benzaldehyde.

A solution of porphyrin phosphonium salt 27 (140 mg, 120 \(\mu\)mol) and benzene-1,3,5-tricarbaldehyde 74 (6.5 mg, 40 \(\mu\)mol) were stirred in degassed CHCl\(_3\) (5 mL) under argon at reflux. DBU (18 \(\mu\)L, 120 \(\mu\)mol) in degassed CHCl\(_3\) (1 mL) was added over 10 min and the reaction was stirred for a further 35 min. On cooling to RT the reaction mixture was then concentrated \textit{in vacuo} and purified by flash chromatography (silica, CH\(_2\)Cl\(_2\):EtO\(_2\) (1:0, 9:1)). Two bands were collected and concentrated \textit{in vacuo}, which were shown by MALDI mass spectrometry to be the mono-substituted and di-substituted products. The isomeric di-substituted compound and I\(_2\) (10 mg, 39 \(\mu\)mol) were then dissolved in CH\(_2\)Cl\(_2\) and stirred for 16 h. Sat. aq. Na\(_2\)S\(_2\)O\(_3\) (25 ml) was then added and continued to stir for 30 min. The organic layer was then separated and washed with H\(_2\)O (2 x 25 mL). Crystallisation from CH\(_2\)Cl\(_2\)/MeOH gave the desired product 81 (35 mg, 47\%) as a brown powder. The isomeric mono-substituted compound was not investigated, however was collected (7 mg, 18\%) as a brown powder. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.13 (s, 1H, CHO), 9.12 (s, 1H, \(H_{\beta}\)-pyrrolic), 9.09 (s, 1H, \(H_{\beta}\)-pyrrolic), 9.01 (s, 2H, \(H_{o-Est}\)), 8.96 (s, 2H, \(H_{o-Est}\)), 8.91 (s, 4H, \(H_{o-Est}\)), 8.82-8.72 (m, 12H, \(H_{\beta}\)-pyrrolic), 8.61-8.38 (m, 16H, \(H_{o,m-Est}\)), 8.00-7.83 (m, 9H, \(H_{p-Est}\) and \(H_{AR}\)), 7.56 (s, 2H, \(H_{AR}\)), 7.38 (d, 2H, \(3^J=16.1\) Hz, \(H_{vinyl}\)), 7.03 (d, 2H, \(3^J=16.1\) Hz, \(H_{vinyl}\)), 4.04-3.97 (m, 24H, CO\(_2\)CH\(_3\)), -2.55 (br s, 4H, NH). \textit{Assignment aided by COSY spectra}. UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{max}\) (log \(\varepsilon\)) 427 (5.44), 524 (4.50), 564 (4.26), 601 (4.13), 662 (3.81) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \(m/z\)= 1850.16 (M\(^+\)). HRMS, \(m/z\): calcd for M\(^+\) (C\(_{115}\)H\(_{82}\)N\(_8\)O\(_{17}\)): 1846.5712, found: 1846.5734.
6.4 Simplified Synthesis of Vinyl β-Substituted Porphyrin Dyes and Dyads

**Porphyrin Monomer Series**

**TXP-CN=−PhCO\textsubscript{3}Me, 85.**

(Z)-2-(2-cyano-2-(4-methoxycarbonylphenyl)ethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin.

A solution of 2-formyl-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin 17 (200 mg, 0.265 mmol) and methyl 4-(cyanomethyl)benzoate 82 (140 mg, 0.799 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (15 mL) was stirred at RT under argon. Excess DBU (1.6 mL) was added and stirred for 60 min. The reaction mixture was directly purified by flash chromatography (silica, CH\textsubscript{2}Cl\textsubscript{2}) and concentrated *in vacuo*. Crystallisation in CH\textsubscript{2}Cl\textsubscript{2}/MeOH gave the desired product 85 (224 mg, 93%) as a purple solid. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 9.48 (s, 1\text{ H}, H_{\beta\text{-pyrrolic}}), 8.93 (d, 1\text{ H}, J= 5.0 \text{ Hz}, H_{\beta\text{-pyrrolic}}), 8.83 (d, 1\text{ H}, J= 5.0 \text{ Hz}, H_{\beta\text{-pyrrolic}}), 8.79 (d, 1\text{ H}, J= 5.0 \text{ Hz}, H_{\beta\text{-pyrrolic}}), 8.76-8.70 (m, 3\text{ H}, H_{\beta\text{-pyrrolic}}), 7.99 (s, 2\text{ H}, H_{\text{Ar}}), 7.86 (s, 2\text{ H}, H_{\text{o-Xyl}}), 7.77-7.73 (m, 6\text{ H}, H_{\text{o-Xyl}}), 7.66 (s, 1\text{ H}, H_{\text{vinyl}}), 7.42 (d, 2\text{ H}, J= 9.0 \text{ Hz}, H_{\text{Ar}}), 7.36 (s, 1\text{ H}, H_{\text{p-Xyl}}), 7.33 (s, 2\text{ H}, H_{\text{p-Xyl}}), 7.20 (s, 1\text{ H}, H_{\text{p-Xyl}}), 3.92 (s, 3\text{ H}, CO\textsubscript{2}CH\textsubscript{3}), 2.57 (s, 6\text{ H}, H_{\text{Me-Xyl}}), 2.53 (s, 6\text{ H}, H_{\text{Me-Xyl}}), 2.52 (s, 6\text{ H}, H_{\text{Me-Xyl}}), 2.40 (s, 6\text{ H}, H_{\text{Me-Xyl}}), -2.66 (br s, 2\text{ H}, NH). UV-vis (CH\textsubscript{2}Cl\textsubscript{2}) \(\lambda_{\text{max}} (\log \varepsilon) 436 (4.97), 527 (4.01), 569 (3.63), 604 (3.59), 663 (3.42) \text{ nm}. \) MALDI-TOF MS (1,8,9-anthracenetriol): \(m/z= 914.3 (M^+)\). HRMS, \(m/z\): calcd for MH\textsuperscript{+} (C\textsubscript{63}H\textsubscript{54}N\textsubscript{5}O\textsubscript{2}): 912.4278, found: 912.4244.
TXP-CN=-Ph, 86.

(Z)-2-(2-cyano-2-phenylethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin.

\[
\text{Chemical Formula: } C_{31}H_{51}N_{5} \\
\text{Exact Mass: } 853.41 \\
\text{Molecular Weight: } 854.11
\]

In a 10 mL microwave reaction vial, a solution of 2-formyl-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin 17 (60 mg, 79 μmol), phenylacetonitrile 83 (93 mg, 0.79 mmol), DBU (1.5 mL) in DCE (2.1 mL). The reaction was heated at 100°C, power 250 W for 50 min under microwave irradiation. The cooled reaction was then purified by flash chromatography (silica, 4:1 CH\textsubscript{2}Cl\textsubscript{2}/hexane) and crystallisation from CH\textsubscript{2}Cl\textsubscript{2}/MeOH, to give the desired product 86 (25 mg, 37%) as a purple-brown solid. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ 9.51 (s, 1H, H\textsubscript{β-pyrrolic}), 9.00 (d, 1H, \textsuperscript{3}J= 5.0, H\textsubscript{β-pyrrolic}), 8.90 (d, 1H, \textsuperscript{3}J= 5.0, H\textsubscript{β-pyrrolic}), 8.85 (d, 1H, \textsuperscript{3}J= 5.0, H\textsubscript{β-pyrrolic}), 8.83-8.78 (m, 3H, H\textsubscript{β-pyrrolic}), 7.94 (s, 2H, H\textsubscript{o-Xyl}), 7.83 (s, 2H, H\textsubscript{o-Xyl}), 7.82 (s, 2H, H\textsubscript{o-Xyl}), 7.80 (s, 2H, H\textsubscript{o-Xyl}), 7.62 (s, 1H, H\textsubscript{vinyl}), 7.45-7.37 (m, 8H, H\textsubscript{p-Xyl} + H\textsubscript{AR}), 7.24 (s, 1H, H\textsubscript{p-Xyl}), 7.26 (s, 6H, H\textsubscript{Me-Xyl}), 7.21 (s, 1H, H\textsubscript{p-Xyl}), 7.21 (s, 6H, H\textsubscript{Me-Xyl}), 7.21 (s, 6H, H\textsubscript{Me-Xyl}), 7.21 (s, 6H, H\textsubscript{Me-Xyl}), -2.61 (br s, 2H, NH). UV-vis (CH\textsubscript{2}Cl\textsubscript{2}) \textit{λ}\textsubscript{max} (log ε) 433 (5.29), 526.5 (4.21), 567 (3.85), 604 (3.79), 664 (3.83) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 855.6 (M\textsuperscript{+}). HRMS, m/z: calcd for MH\textsuperscript{+} (C\textsubscript{61}H\textsubscript{52}N\textsubscript{5}): 854.4223, found: 854.4418.

TXP-CN=-PhOMe, 87.

(Z)-2-(2-cyano-2-(4-methoxyphenyl)ethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin.

\[
\text{Chemical Formula: } C_{32}H_{52}N_{5}O \\
\text{Exact Mass: } 883.43 \\
\text{Molecular Weight: } 884.14
\]
A solution of 2-formyl-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin 17 (60 mg, 79 μmol), 4-methoxyphenylacetonitrile 84 (231 mg, 1.6 mmol), KOTBu (100 mg) in DMF (2.1 mL) was heated to 100°C, 250 W for 20 min in a microwave reactor. The cooled reaction was then purified by flash chromatography (silica, CH₂Cl₂) and crystallisation from CH₂Cl₂/MeOH, to give the desired product 87 (41 mg, 59%) as a purple-brown solid.

1H-NMR (400 MHz, CDCl₃): δ 9.48 (s, 1H, Hβ-pyrrolic), 8.98 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.89 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.84 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.82-8.78 (m, 3H, Hβ-pyrrolic), 7.93 (s, 2H,Hₐ-Xyl), 7.83 (s, 2H,Hₐ-Xyl), 7.82 (s, 2H,Hₐ-Xyl), 7.80 (s, 2H,Hₐ-Xyl), 7.48 (s, 1H, Hvinyl), 7.44-7.39 (m, 3H, Hₚ-Xyl), 7.36 (d, 2H, J= 9.5Hz, HAr), 7.27 (s, 1H, Hₚ-Xyl), 6.93 (d, 2H, J= 9.5Hz, HAr), 3.91 (s, 3H, CO₂CH₃), 2.64 (s, 6H, HMe-Xyl), 2.61 (s, 6H, HMe-Xyl), 2.60 (s, 6H, HMe-Xyl), 2.47 (s, 6H, HMe-Xyl), -2.61 (br s, 2H, NH). UV-vis (CH₂Cl₂) λmax (log ε) 431 (5.54), 525 (4.45), 567 (4.19), 603 (4.14), 664.5 (4.15) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 885.6 (M⁺). HRMS, m/z: calcd for MH⁺ (C₆₂H₄₅N₅O): 884.4328, found: 884.4579.

TPP-CN=PhCO₂Me, 88.

(Z)-2-(2-cyano-2-(4-methoxycarbonylphenyl)ethenyl)-5,10,15,20-tetraphenylporphyrin.

A solution of 2-formyl-5,10,15,20-tetrakis(phenyl)porphyrin 14 (30 mg, 47 μmol) and methyl 4-(cyanomethyl)benzoate 82 (49 mg, 0.28 mmol) in CH₂Cl₂ (8 mL) was stirred at RT under argon. Excess DBU (0.5 mL) was added and stirred for 30 min. The reaction mixture was directly purified by flash chromatography (silica, CH₂Cl₂) and concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product 88 (33 mg, 84%) as a purple solid. 1H-NMR (400 MHz, CDCl₃): δ 9.51 (s, 1H, Hβ-pyrrolic), 8.95 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.88 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.82 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.78 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.76 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.72 (d, 1H, J= 5.0Hz, Hβ-pyrrolic), 8.31-8.27 (m, 2H, Hₐ-Xyl), 8.22-8.13 (m, 6H, Hₐ-Xyl), 8.02 (d, 2H, J=9.0Hz, HA), 7.82-7.63 (m, 13H, Hₐ,Xyl+Hvinyl), 7.38 (d, 2H, J=9.0Hz, HA), 3.97 (s, 3H, CO₂CH₃), -2.57 (br s, 2H, NH). UV-vis (CH₂Cl₂) λmax (log ε) 432 (5.29), 525 (4.35), 570 (3.96), 603 (3.92), 663
(3.89) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 801.3 (M⁺). HRMS, m/z: calcd for MH⁺ (C₅₆H₈₂N₅O₂): 800.3026, found: 800.3148.

**TPP-CN=-Ph, 89.**

(Z)-2-(2-cyano-2-phenylethenyl)-5,10,15,20-tetraphenylporphyrin.

In a 10 mL microwave reaction vial, a solution of 2-formyl-5,10,15,20-tetraarylporphyrin 14 (30 mg, 47 μmol), phenylacetonitrile 83 (30 mg, 0.27 mmol), DBU (0.7 mL) in DCE (1.0 mL). The reaction was heated at 110°C, power 250 W for 50 min under microwave irradiation. The cooled reaction was then purified by flash chromatography (silica, CH₂Cl₂) and crystallisation from CH₂Cl₂/MeOH, to give the desired product 89 (13 mg, 37%) as a purple-brown solid. ¹H-NMR (400 MHz, CDCl₃): δ 9.49 (s, 1H, Hβ-pyrrolic), 8.94 (d, 1H, ₃J= 5.0 Hz, Hβ-pyrrolic), 8.87 (d, 1H, ₃J= 5.0 Hz, Hβ-pyrrolic), 8.83-8.76 (m, 3H, Hβ-pyrrolic), 8.72 (d, 1H, ₃J= 5.0 Hz, Hβ-pyrrolic), 8.32-8.27 (m, 2H, Hο-Ar), 8.24-8.17 (m, 6H, Hο-Ar), 7.84-7.66 (m, 12H, Hm,p-Ar), 7.61 (d, 1H, ₄J= 1.2 Hz, Hvinyl), 7.40-7.35 (m, 5H, HαAr), -2.59 (br s, 2H, NH). UV-vis (CH₂Cl₂) λₘₐₓ (log ε) 428 (5.26), 523 (4.22), 561 (3.85), 599 (3.78), 658 (3.57) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 740.6 (M⁺). HRMS, m/z: calcd for MH⁺ (C₅₃H₃₀N₅): 742.2971, found: 742.3005.
TPP-CN=PhOMe, 90.

(Z)-2-(2-cyano-2-(4-methoxyphenyl)ethenyl)-5,10,15,20-tetraphenylporphyrin.

A solution of 2-formyl-5,10,15,20-tetrakisphenylporphyrin 14 (60 mg, 93 μmol), 4-methoxyphenylacetonitrile 84 (82 mg, 0.56 mmol), KOTBu (100 mg) in DMF (2.1 mL) was heated to 100°C, 250 W for 20 min in a microwave reactor. The cooled reaction was then purified by flash chromatography (silica, CH$_2$Cl$_2$) and crystallisation from CH$_2$Cl$_2$/MeOH, to give the desired product 90 (41 mg, 57%) as a purple-brown solid.

General Procedure- Zinc Insertion of Monomer Series

Porphyrin monomers were converted to zinc(II) porphyrins according to the general procedure. The cyano linked porphyrin was dissolved in CH$_2$Cl$_2$ and stirred at RT. Zn(OAc)$_2$·2H$_2$O (1.3 eq.) in MeOH was added and continued to stir for 30 min. MALDI mass spectrometry indicated the reaction was complete and flash chromatography (silica, CH$_2$Cl$_2$) and concentration in vacuo gave the desired products.
ZnTXP-CN=PhCO$_2$Me, Zn85.

(Z)-2-(2-cyano-2-(4-methoxycarbonylphenyl)ethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II).

Porphyrrin 85 (40 mg, 44 µmol) was reacted with Zn(OAc)$_2$$\cdot$2H$_2$O. Zn85 was collected as a purple solid (40 mg, 93%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 9.63 (d, 1H, $^3$J= 1.0 Hz, H$_{\beta$-pyrrolic}), 8.99 (d, 1H, $^3$J= 5.0 Hz, H$_{\beta$-pyrrolic}), 8.89 (d, 1H, $^3$J= 5.0 Hz, H$_{\beta$-pyrrolic}), 8.87-8.84 (m, 3H, H$_{\beta$-pyrrolic}), 8.79 (d, 1H, $^3$J= 5.0 Hz, H$_{\beta$-pyrrolic}), 7.99 (d, 2H, $^3$J= 9.0 Hz, H$_{AR}$), 7.86 (s, 2H, H$_{o$-xyl} and H$_{vinyl}$), 7.45 (d, 2H, $^3$J= 9.0 Hz, H$_{AR}$), 7.36 (s, 1H, H$_{p$-xyl}), 7.33 (s, 2H, H$_{p$-xyl}), 7.20 (s, 1H, H$_{p$-xyl}), 3.91 (s, 3H, CO$_2$CH$_3$), 2.57 (s, 6H, H$_{Me$-xyl}), 2.53 (s, 6H, H$_{Me$-xyl}), 2.52 (s, 6H, H$_{Me$-xyl}), 2.39 (s, 6H, H$_{Me$-xyl}). UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$) 444 (5.11), 561 (4.12), 604 (3.98) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$ = 976.8 (M$^+$). HRMS, $m/z$: calcd for MH$^+$ (C$_{63}$H$_{52}$N$_5$O$_2$Zn): 974.3412, found: 974.3650.

ZnTXP-CN=-Ph, Zn86.

(Z)-2-(2-cyano-2-phenylethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II).

Porphyrrin 86 (42 mg, 49 µmol) was reacted with Zn(OAc)$_2$$\cdot$2H$_2$O. Zn86 was collected as a purple solid (40 mg, 89%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 9.65 (s, 1H, H$_{\beta$-pyrrolic}), 9.07 (d, 1H, $^3$J=4.5 Hz, H$_{\beta$-pyrrolic}), 8.97 (d, 1H, $^3$J=4.5 Hz, H$_{\beta$-pyrrolic}), 8.95-8.91 (m, 3H, H$_{\beta$-pyrrolic}), 8.87 (d, 1H, $^3$J=4.5 Hz, H$_{\beta$-pyrrolic}), 7.94 (s, 2H, H$_{o$-xyl}), 7.84 (s, 2H, H$_{o$-xyl}), 7.83 (s, 2H, H$_{o$-xyl}), 7.79 (s, 2H, H$_{o$-xyl}), 7.70 (s, 1H,
H\text{vinyl}) 7.46-7.36 (m, 8H, H\text{p-Xyl} + H\text{sar}), 7.23 (S, 1H, H\text{p-Xyl}), 2.64 (s, 6H, H\text{Me-Xyl}), 2.60 (s, 6H, H\text{Me-Xyl}), 2.59 (s, 6H, H\text{Me-Xyl}), 2.44 (s, 6H, H\text{Me-Xyl}). UV-vis (CH\text{2Cl}2) λ\text{max} (log ε) 437.5 (5.45), 559 (4.40), 600.5 (4.12) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 918.2 (M\text{+}). HRMS, m/z: calcd for MH\text{+} (C\text{61}H\text{50}N\text{5}Zn): 916.3358, found: 916.3765.

ZnTXP-CN=PhOMe, Zn87.

(Z)-2-(2-cyano-2-(4-methoxyphenyl)ethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II).

Porphyin 87 (42 mg, 48 µmol) was reacted with Zn(OAc)\text{2}·2H\text{2}O. Zn87 was collected as a purple solid (44 mg, 98%). 1H-NMR (400 MHz, CDCl\text{3}): δ 9.54 (s, 1H, Hβ-pyrrolic), 8.99 (d, 1H, ³J= 4.5, Hβ-pyrrolic), 8.90 (d, 1H, ³J= 4.5, Hβ-pyrrolic), 8.87-8.83 (m, 3H, Hβ-pyrrolic), 8.79 (d, 1H, ³J= 4.5, Hβ-pyrrolic), 7.79 (s, 2H,H\text{o-Xyl}), 7.76 (s, 2H,H\text{o-Xyl}), 7.75 (s, 2H,H\text{o-Xyl}), 7.70 (s, 2H,H\text{o-Xyl}), 7.48 (s, 1H, H\text{vinyl}), 7.36-7.32 (m, 3H, H\text{p-Xyl}), 7.30 (d, 2H, ³J= 9.0, H\text{sar}), 7.18 (s, 1H, H\text{p-Xyl}), 6.82 (d, 2H, ³J= 9.5, H\text{sar}), 3.78 (S,3H, H\text{Ome}), 2.57 (s, 6H, H\text{Me-Xyl}), 2.53 (s, 6H, H\text{Me-Xyl}), 2.52 (s, 6H, H\text{Me-Xyl}), 2.38 (s, 6H, H\text{Me-Xyl}). UV-vis (CH\text{2Cl}2) λ\text{max} (log ε) 436 (5.34), 559 (4.55), 599.5 (4.27) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 948.7 (M\text{+}). HRMS, m/z: calcd for MH\text{+} (C\text{62}H\text{52}N\text{5}O\text{2}Zn): 946.3463, found: 946.3771.
**ZnTPP-CN-PhCO\textsubscript{Me}, Zn88.**

(Z)-2-(2-cyano-2-(4-methoxycarbonylphenyl)ethenyl)-5,10,15,20-tetraphenylporphyrinato zinc(II).

![Chemical structure of Zn88](image1)

**Porphyrin 88** (40 mg, 44 µmol) was reacted with Zn(OAc)\textsubscript{2} \cdot 2H\textsubscript{2}O. **Zn88** was collected as a purple solid (28 mg, 93%). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ 9.62 (d, 1H, \textit{J}= 1.0 Hz, H\textsubscript{β-pyrrolic}), 9.00 (d, 1H, \textit{J}= 5.0 Hz, H\textsubscript{β-pyrrolic}), 8.95-8.87 (m, 4H, H\textsubscript{β-pyrrolic}), 8.75 (d, 1H, \textit{J}= 5.0 Hz, H\textsubscript{β-pyrrolic}), 8.29-8.14 (m, 8H, H\textsubscript{o-Ar}), 7.98 (d, 2H, \textit{J}= 9.0 Hz, H\textsubscript{Ar}), 7.81-7.65 (m, 13H, H\textsubscript{m,p-Ar} + H\textsubscript{vinyl}), 7.39 (d, 2H, \textit{J}= 9.0 Hz, H\textsubscript{Ar}), 3.92 (s, 3H, CO\textsubscript{2}CH\textsubscript{3}). UV-vis (CH\textsubscript{2}Cl\textsubscript{2}) \textit{λ}\textsubscript{max} (log \varepsilon) 439 (4.65), 559 (3.68), 603 (3.51) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \textit{m/z} = 861.4 (M\textsuperscript{+}). HRMS, \textit{m/z}: calcd for M\textsuperscript{+} (C\textsubscript{56}H\textsubscript{35}N\textsubscript{5}O\textsubscript{2}Zn): 861.2082, found: 861.2116.

**ZnTPP-CN=Ph, Zn89.**

(Z)-2-(2-cyano-2-phenylethenyl)-5,10,15,20-tetraphenylporphyrinato zinc(II).

![Chemical structure of Zn89](image2)

**Porphyrin 89** (12 mg, 17 µmol) was reacted with Zn(OAc)\textsubscript{2} \cdot 2H\textsubscript{2}O. **Zn89** was collected as a purple solid (10 mg, 71%). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ 9.59 (s, 1H, H\textsubscript{β-pyrrolic}), 9.00 (d, 1H, \textit{J}= 5.0 Hz, H\textsubscript{β-pyrrolic}), 8.95-8.91 (m, 3H, H\textsubscript{β-pyrrolic}), 8.88 (d, 1H, \textit{J}= 5.0 Hz, H\textsubscript{β-pyrrolic}), 8.76 (d, 1H, \textit{J}= 5.0 Hz, H\textsubscript{β-pyrrolic}), 8.29-8.13 (m, 8H, H\textsubscript{o-Ar}), 7.81-7.64 (m, 13H, H\textsubscript{m,p-Ar} + H\textsubscript{vinyl}), 7.39-7.34 (m, 5H, H\textsubscript{Ar}). UV-vis...
(CH$_2$Cl)$_2$ $\lambda_{max}$ (log $\varepsilon$) 433 (5.47), 558 (4.41), 598 (4.14) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$ 803.0 (M$^+$). HRMS, $m/z$: calcd for MH$^+$ (C$_{36}$H$_{34}$N$_5$Zn): 804.2106, found: 804.5568.

**ZnTPP-CN=PhOMe, Zn90.**

(Z)-2-(2-cyano-2-(4-methoxyphenyl)ethenyl)-5,10,15,20-tetraphenylporphyrinato zinc(II).

Porphyrrin 90 (32 mg, 41 µmol) was reacted with Zn(OAc)$_2$·2H$_2$O. Zn90 was collected as a purple solid (28 mg, 82%). $^1$H-NMR (400 MHz, CDCl$_3$): δ9.50 (s, 1H, H$_{\beta}$-pyrrolic), 8.99 (d, 1H, $^3$J= 5.0 Hz, H$_{\beta}$-pyrrolic), 8.95-8.86 (m, 4H, H$_{\beta}$-pyrrolic), 8.75 (d, 1H, $^3$J= 5.0 Hz, H$_{\beta}$-pyrrolic), 8.26-8.17 (m, 6H, H$_{\beta}$-Ar), 8.15-8.10 (m, 2H, H$_{\alpha}$-Ar), 7.80-7.71 (m, 10H, H$_{m,p}$-Ar), 7.68-7.63 (m, 2H H$_{m}$-Ar) 7.47 (s, 1H, H$_{vinyl}$), 7.22 (d, 2H, $^3$J=9.0, H$_{AR}$), 6.83 (d, 2H, $^3$J=9.0, H$_{AR}$), 3.82 (s, 3H, H$_{OMe}$). UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$) 432 (5.59), 558 (4.56), 598 (4.28) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$= 833.2 (M$^+$). HRMS, $m/z$: calcd for M$^+$ (C$_{54}$H$_{35}$N$_5$OZn): 833.2133, found: 833.2130.

**ZnTXP-CN=PhCO$_2$H, 91.**

(Z)-2-(2-cyano-2-(4-carboxyphenyl)ethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II).

KOH (46 mg, 0.71 mmol) in MeOH (12 mL) /H$_2$O (1.2 mL) was added to a solution of Zn88 (40 mg, 0.041 mmol) in THF (12 mL). The mixture was heated to reflux for 22 h. Once cooled to RT,
H₂O (25 mL) and CH₂Cl₂ (25 mL) were added followed by 2M H₃PO₄ (430 µL, 0.86 mmol). The organic layer was extracted and washed with H₂O (2 x 40 mL). Reaction was concentrated in vacuo to give the desired product 91 (39 mg, 100%) as a purple solid. ¹H-NMR (400 MHz, acetone-d₆): δ 9.64 (s, 1H, Hβ-pyrrolic), 8.97 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.88 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.86-8.81 (m, 4H, Hβ-pyrrolic), 8.16 (d, 2H, ³J= 8.0 Hz, HAryl), 7.96 (s, 1H, HVinyl), 7.92 (s, 2H, H₀-xyl), 7.86-7.80 (m, 6H, H₀-xyl), 7.62 (d, 2H, ³J= 8.0 Hz, HAryl), 7.49-7.44 (m, 3H, H₇-xyl), 7.37 (s, 1H, H₀-xyl), 2.64 (s, 6H, HMe₄-xyl), 2.61 (s, 6H, HMe₄-xyl), 2.61 (s, 6H, HMe₄-xyl), 2.50 (s, 6H, HMe₄-xyl). UV-vis (DMF) λmax (log ε) 445 (5.05), 571 (4.05), 616 (3.88) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 862.3 (M⁺). HRMS, m/z: calcd for MH⁺ (C₆₂H₄₅N₅O₂Zn): 960.3256, found: 960.3373.

Porphyrin Arrays

(T₄MeP)₂-CN=Ph Dyad, 94.

(Z,Z) 1,4-Bis(1-cyano-2-(5,10,15,20-tetra(4-methylphenyl)porphyrin)ethenyl). A solution of 2-formyl-5,10,15,20-tetrakis(4-methylphenyl)porphyrin 93 (60 mg, 86 µmol) 1,4-phenylenediacetonitrile (7 mg, 43 µmol) in CHCl₃ (3 mL) was stirred at RT under argon. Excess DBU (0.5 mL) was added and stirred for 4 h. The reaction mixture was directly purified by flash chromatography (silica, CH₂Cl₂:Hexane (7:3)) and concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product 94 (8 mg, 12%) as a purple solid. ¹H-NMR (400 MHz, CDCl₃): δ 9.56 (s, 2H, Hβ-pyrrolic), 8.97 (d, 2H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.90 (d, 2H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.87 (d, 2H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.84-8.78 (m, 6H, Hβ-pyrrolic), 8.23 (d, 4H, ³J= 8.0 Hz, H₇-Tol), 8.15-
8.07 (m, 12H, H_{o-Tol}), 7.68-7.64 (m, 6H, H_{m-Tol} and H_{vinyl}), 7.60-7.55 (m, 12H, H_{m-Tol}), 7.46 (s, 2H, H_{Ar}), 2.75 (s, 6H, H_{Me-Tol}), 2.71 (s, 12H, H_{Me-Tol}), 2.60 (s, 6H, H_{Me-Tol}), -2.55 (br s, 4H, NH). UV-vis (CH_{2}Cl_{2}) \( \lambda_{\text{max}} \) (log \( \varepsilon \)) 431 (5.49), 527 (4.68), 573.5 (4.31), 601 (4.25), 662 (4.02) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \( m/z = 1519.1 \) (M'). HRMS, \( m/z \): calcd for MH\(^{+}\) (C\(_{108}\)H\(_{81}\)N\(_{10}\)) : 1517.6646, found: 1517.7460.

\textbf{Zn(T4MeP)\(_{2}\)-CN=-Ph Dyad, Zn94.}

(Z,Z) 1,4-Bis(1-cyano-2-(5,10,15,20-tetra(4-methylphenyl)porphyrinato zinc(II))ethenyl).

Porphyridynad 94 (8 mg, 5.3 \( \mu \)mol) was dissolved in CHCl\(_{3}\) (4 mL) and stirred at RT. A solution of Zn(OAc)\(_{2}\)-2H\(_{2}\)O (3.0 mg, 14 \( \mu \)mol) in MeOH (0.5 mL) was added and stirred for 30 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture was concentrated \textit{in vacuo}. Crystallisation in CH\(_{2}\)Cl\(_{2}\)/MeOH gave the desired product \textbf{Zn94} (7 mg, 80%) as a purple solid. \(^1\)H-NMR (400 MHz, CDCl\(_{3}\)): \( \delta \) 9.64 (s, 2H, H\(_{\beta-\text{pyrrolic}}\)), 8.96 (d, 2H, \(^3\)J = 4.8 Hz, H\(_{\beta-\text{pyrrolic}}\)), 8.89 (d, 2H, \(^3\)J = 4.8 Hz, H\(_{\beta-\text{pyrrolic}}\)), 8.87-8.85 (m, 6H, H\(_{\beta-\text{pyrrolic}}\)), 8.81 (d, 2H, \(^3\)J = 4.8 Hz, H\(_{\beta-\text{pyrrolic}}\)), 8.19 (d, 4H, \(^3\)J = 7.8 Hz, H\(_{\text{Ar}}\)), 8.10-8.05 (m, 12H, H\(_{o-Tol}\)), 7.76 (s, 2H, H\(_{\text{vinyl}}\)), 7.62 (m, 4H, \(^3\)J = 7.8 Hz, H\(_{m-Tol}\)), 7.55-7.51 (m, 12H, H\(_{m-Tol}\)), 7.47 (s, 4H, H\(_{Ar}\)), 2.74 (s, 6H, H\(_{\text{Me-Tol}}\)), 2.71 (s, 6H, H\(_{\text{Me-Tol}}\)), 2.70 (s, 6H, H\(_{\text{Me-Tol}}\)), 2.59 (s, 6H, H\(_{\text{Me-Tol}}\)). UV-vis (CH\(_{2}\)Cl\(_{2}\)) \( \lambda_{\text{max}} \) (log \( \varepsilon \)) 437 (4.99), 560 (4.24), 602 (4.21) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \( m/z = 1647.1 \) (M'). HRMS, \( m/z \): calcd for M\(^{+}\) (C\(_{108}\)H\(_{76}\)N\(_{10}\)Zn\(_{2}\)) : 1640.4837, found: 1640.4902.
General Procedure- Monofunctionalised Porphyrins

A solution of 2-formylporphyrin (60 mg), 1,4-phenylenediacetonitrile (10 eq.), 1,8-diazabicycoundec-7-ene (DBU) (1.5 mL) and DCE (2.1 mL) was heated for 30 min at 100 °C and 250 W in a microwave reactor. The cooled reaction was then purified by column chromatography (silica, CH₂Cl₂) and crystallised in CH₂Cl₂/MeOH to give the desired compounds.

T4EP-CN=-PhCN, 96.

(Z)-2-(2-cyano-2-(cyanomethylphenyl)ethenyl)-5,10,15,20-tetra(4-ethylphenyl)porphyrin.

Porphyrin 96 was collected as a purple solid (48 mg, 68%). ¹H-NMR (400 MHz, CDCl₃): δ 9.45 (s, 1H, Hᵥ-pyrrolic), 8.96 (d, 1H, ³J= 5.0 Hz, Hᵥ-pyrrolic), 8.89 (d, 1H, ³J= 5.0 Hz, Hᵥ-pyrrolic), 8.84 (d, 1H, ³J= 5.0 Hz, Hᵥ-pyrrolic), 8.81-8.74 (m, 3H, Hᵥ-pyrrolic), 8.21 (d, 2H, ³J=7.5, Hᵥ-Ar), 8.12 (d, 2H, ³J=7.5, Hᵥ-Ar), 8.10 (d, 2H, ³J=7.5, Hᵥ-Ar), 8.04 (d, 2H, ³J=7.5, Hᵥ-Ar), 7.63 (d, 2H, ³J=7.5, Hᵥ-Ar), 7.60-7.54 (m, 4H, Hᵢ-Ar), 7.52 (s, 1H, Hᵥ-Ar), 7.46 (d, 2H, ³J=7.5, Hᵥ-Ar), 7.37 (d, 2H, ³J=8.0, Hᵥ-Ar), 7.30 (d, 2H, ³J=8.0, Hᵥ-Ar), 3.77 (s, 2H, Hᵥ-Ar), 3.04-2.96 (m, 6H, CH₂CH₃), 2.78 (q, 2H, ³J=7.5, CH₂CH₃), 1.55-1.50 (m, 9H, CH₂CH₃), 1.29 (t, 3H, ³J=7.5, CH₃CH₂), -2.58 (br s, 2H, NH). UV-vis (CH₂Cl₂) λₘₐₓ (log ε) 433 (4.66) 527 (3.68) 565 (3.37) 603 (3.29) 660 (3.16) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 893.0 (M⁺). HRMS, m/z: calcd for MH⁺ (C₆₃H₅₅N₆): 893.4332, found: 893.4310.
TXP-CN=PhCN, 97.

(Z)-2-(2-cyano-2-(cyanomethylphenyl)ethenyl)-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin.

Porphyrin 97 was collected as a purple solid (55 mg, 78%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 9.53 (s, 1H, H$_{β}$-pyrrolic), 9.00 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.90 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.86 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.82-8.77 (m, 3H, H$_{α}$-pyrrolic), 7.94 (s, 2H, H$_{β}$-xyl), 7.87-7.80 (m, 6H, H$_{β}$-xyl), 7.65 (s, 1H, H$_{β}$-vinyl), 7.46-7.35 (m, 7H, H$_{β}$-xyl + H$_{α}$-xyl), 7.23 (s, 1H, H$_{α}$-xyl), 3.84 (s, 2H, H$_{β}$-benzyl), 2.65 (s, 6H, H$_{β}$-xyl), 2.61 (s, 6H, H$_{β}$-xyl), 2.60 (s, 6H, H$_{β}$-xyl), 2.48 (s, 6H, H$_{β}$-xyl), -2.60 (br s, 2H, NH). UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log ε) 435 (5.49), 527 (4.48), 568 (4.07), 604 (4.01) 662 (3.94) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z = 893.8 (M$^+\$). HRMS, m/z: calcd for MH$^+$ (C$_{63}$H$_{53}$N$_6$): 893.4332, found: 893.4468.

TPP-CN=PhCN, 98.

(Z)-2-(2-cyano-2-(cyanomethylphenyl)ethenyl)-5,10,15,20-tetraphenylporphyrin.

Porphyrin 98 was collected as a purple solid (58 mg, 80%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 9.50 (s, 1H, H$_{β}$-pyrrolic), 8.95 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.88 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.83 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.79 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.77 (d, 1H, $^3$J = 5.0 Hz, H$_{β}$-pyrrolic), 8.73 (d, 1H,
$^3J = 5.0 \text{ Hz, } H_{\beta\text{-pyrrolic}}, \ 8.32-8.28 \ (m, 2H, H_{o\text{-ph}}), \ 8.23-8.18 \ (m, 6H, H_{o\text{-ph}}), \ 7.84-7.70 \ (m, 12H, H_{m,p\text{-ph}}) \ 7.63 \ (s, 1H, H_{\text{Vinyl}}), \ 7.38-7.34 \ (m, 4H, H_{AR}), \ 3.82 \ (s, 2H, H_{\text{benzylic}}), \ -2.58 \ (br \ s, 2H, NH). \ \text{UV-vis (CH}_2\text{Cl}_2) \ \lambda_{\text{max}} (\log \varepsilon) \ 431 \ (5.22), \ 525 \ (4.20), \ 567 \ (3.82), \ 602 \ (3.76), \ 660 \ (3.57) \ \text{nm. MALDI-TOF MS (1,8,9-anthracenetriol):} \ m/z = 782.3 \ (M^+). \ \text{HRMS, } m/z: \ \text{calcd for } MH^+ \ (C_{55}H_{37}N_6) \ 781.3080, \ \text{found:} \ 781.3079.$

**FeTPP-CN=-PhCN, Fe98.**

(Z)-2-(2-cyano-2-(cyanomethylphenyl)ethenyl)-5,10,15,20-tetraphenylporphyrinato iron(III) chloride.

Acetonitrile (10 mL) was refluxed under argon for 2 h to remove any dissolved oxygen. The reaction’s temperature was then lowered to 70°C and iron(II) chloride (190 mg, 0.96 mmol) added. A solution of 98 (34 mg, 0.044 mmol) in degassed CHCl$_3$ (5 mL) was then added to the reaction over 5 min. The reaction was then heated back up to reflux, stirred for 3 h and then left exposed to air overnight at RT. The reaction mixture was then concentrated *in vacuo*, redissolved in CH$_2$Cl$_2$ and washed with 0.1M HCl (3 x 25 mL). The reaction mixture was purified by column chromatography (silica, 100% CH$_2$Cl$_2$ – 98% CH$_2$Cl$_2$: 2% MeOH) and filtered through filter paper to give the desired compound Fe98 as a purple/brown solid (22 mg, 58%). UV-vis (CH$_2$Cl$_2$)$\lambda_{\text{max}} (\log \varepsilon) 433 \ (4.94), \ 515 \ (4.06), \ 668 \ (3.36) \ \text{nm. MALDI-TOF MS (1,8,9-anthracenetriol):} \ m/z = 835.7 \ (M^+-Cl). \ \text{HRMS, } m/z: \ \text{calcd for } MH^+-Cl \ (C_{55}H_{35}FeN_6) \ 834.2194, \ \text{found:} \ 834.2316.$
T3EP-CN=-PhCN, 99.

(Z)-2-(2-cyano-2-(cyanomethylphenyl)ethenyl)-5,10,15,20-tetra(3-methoxycarbonylphenyl)porphyrin.

Porphyrin 99 was collected as a purple solid (30 mg, 43%). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 9.36 (s, 1H, H$_{\beta$-pyrrolic}), 8.97-8.7.0 (m, 10H, H$_{\alpha$-pyrrolic and H$_{\alpha$-Est}), 8.55-8.47 (m, 4H, H$_{\alpha$-Est}), 8.43-8.29 (m, 4H, H$_{\alpha$-Est}), 7.79 (m, 4H, H$_{m$-Est}), 7.52-7.31 (m, 5H, H$_{vinyl and H_{Ar}}$), 4.01-3.98 (m, 12H, CO$_2$CH$_3$), 3.83 (s, 2H, H$_{benzylic}$), -2.61 (br s, 2H, NH). MALDI-TOF MS (1,8,9-anthracenetriol): $m/z$= 1014.4 (M$^+$).

HRMS, $m/z$: calcd for MH$^+$ ($C_{63}$H$_{45}$N$_6$O$_6$): 1013.3299, found: 1013.3330.


(Z,Z) 1-(1-cyano-2-(5,10,15,20-tetra(4-ethylphenyl)porphyrin)ethenyl)-4-(1-cyano-2-(5,10,15,20-tetra(3,5-dimethylphenyl)porphyrin)ethenyl).

Chemical Formula: $C_{41}H_{50}N_{10}$
Exact Mass: 1628.78
Molecular Weight: 1630.11
A solution of 2-formyl-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin 17 (12 mg, 15 μmol), cyano porphyrin 96 (5.5 mg, 6.2 μmol) and DBU (0.2 mL) in DCE (0.2 mL) was heated to 120°C, 250 W for 30 min in a microwave reactor. The cooled reaction was then purified by flash chromatography (silica, CH₂Cl₂:Hexane (4:1)) and crystallisation from CH₂Cl₂/MeOH, to give the desired product 101 (8 mg, 80%) as a purple/brown solid. ¹H-NMR (400 MHz, CDCl₃): δ 9.60 (s, 1H, Hβ-pyrrolic), 9.55 (s, 1H, Hβ-pyrrolic), 9.03-8.97 (m, 2H, Hβ-pyrrolic), 8.93-8.78 (m, 10H, Hβ-pyrrolic), 8.28-8.24 (m, 2H, Hα-Ar), 8.17-8.11 (m, 6H, Hα-Ar), 7.98 (s, 2H, Hα-Xyl), 7.87-7.82 (m, 6H, Hα-Xyl), 7.72-7.66 (m, 4H, Hm-Ar and Hvinyl), 7.63-7.55 (m, 6H, Hm-Ar), 7.53-7.34 (m, 8H, Hp-Ar and Hα), 3.02 (m, 6H, CH₂CH₃), 2.86 (q, 2H, J= 7.5 Hz, CH₂CH₃), 2.69 (s, 6H, HMe-Xyl), 2.62 (s, 6H, HMe-Xyl), 2.61 (s, 6H, HMe-Xyl), 1.56 (m, 9H, CH₂CH₃), 1.36 (m, 3H, CH₂CH₃), -2.53 (br s, 2H, NH), -2.57 (br s, 4H, NH). UV-vis (CH₂Cl₂) λₘₐₓ (log ε) 435 (4.96), 527 (4.00), 563 (3.99), 606 (3.92), 662 (3.33) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1633.56 (M⁺). HRMS, m/z: calcd for MH⁺ (C₁₁₆H₉₇N₁₀Zn): 1629.7898, found: 1629.7880.

**ZnTXP-CN=Ph=CN-T4EP dyad, 102.**

(Z,Z) 1-{1-cyano-2-{5,10,15,20-tetra(4-ethylphenyl)porphyrinato zinc(II)}ethenyl}-4-{1-cyano-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin)ethenyl}.

A solution of 2-formyl-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc 100 (13 mg, 16 μmol), cyano porphyrin 96 (5.5 mg, 6.2 μmol) and sodium methoxide (10 mg) in THF (0.3mL) was heated to 120°C, 250 W for 60 min in a microwave reactor. The cooled reaction was then purified by flash chromatography (silica, CH₂Cl₂:Hexane (9:1)) and crystallisation from CH₂Cl₂/MeOH, to
give the desired product 102 (7 mg, 70%) as a purple/brown solid. $^{1}$H-NMR (400 MHz, CDCl$_3$): δ 9.71 (s, 1H, H$_{\beta}$-pyrrolic), 9.55 (s, 1H, H$_{\beta}$-pyrrolic), 9.06 (d, 1H, $^{3}$J$_{1}$= 5.0 Hz, H$_{\beta}$-pyrrolic), 9.01-8.78 (m, 11H, H$_{\beta}$-pyrrolic), 8.28 (d, 2H, $^{3}$J$_{2}$= 9.0 Hz, H$_{o}$-Ar), 8.18-8.09 (m, 6H, H$_{o}$-Ar), 7.96 (s, 2H, H$_{o}$-Xyl), 7.85-7.81 (m, 6H, H$_{o}$-Xyl), 7.80 (s, 1H, H$_{vinyl}$), 7.72-7.67 (m, 3H, H$_{m}$-Ar and H$_{vinyl}$), 7.63-7.55 (m, 6H, H$_{m}$-Ar), 7.48-7.34 (m, 8H, H$_{p}$-Xyl), 6.91 (d, 2H, $^{3}$J$_{3}$= 7.0 Hz, H$_{ar}$), 6.58 (m, 2H, H$_{ar}$), 3.04 (m, 6H, CH$_2$CH$_3$), 2.85 (q, 2H, $^{3}$J$_{4}$= 7.5 Hz, CH$_2$CH$_3$), 2.68 (s, 6H, H$_{Me-Xyl}$), 2.61 (s, 6H, H$_{Me-Xyl}$), 2.60 (s, 6H, H$_{Me-Xyl}$), 2.52 (s, 6H, H$_{Me-Xyl}$), 1.57 (m, 9H, CH$_2$CH$_3$), 1.29 (m, 3H, CH$_3$CH$_3$), -2.53 (br s, 2H, NH). UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log ε) 435 (5.25), 562 (4.37), 606 (4.28) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1695.1 (M$^+$). HRMS, m/z: calcd for MH$^+$ (C$_{116}$H$_{95}$N$_{10}$Zn): 1691.7033, found: 1691.8030.

TXP-CN=-Ph-=CN-FeTPP dyad, 103.

(Z,Z) 1-(1-cyano-2-(5,10,15,20-tetraphenylporphyrinato iron(III))ethenyl)-4-(1-cyano-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin)ethenyl).

A solution of 2-formyl-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin 17 (13 mg, 40 μmol), cyano porphyrin Fe98 (6 mg, 6.9 μmol), DBU (0.2 mL) in DCE (0.4 mL) was heated to 120°C, 250 W for 20 min in a microwave reactor. The cooled reaction was then purified by flash chromatography (silica, CH$_2$Cl$_2$:MeOH (1:0 to 97:3)) and crystallisation from CH$_2$Cl$_2$/MeOH, to give the desired product 103 (5 mg, 45%) as a brown/purple solid. UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log ε) 425 (5.49), 520 (4.67), 595 (4.35), 657 (4.08) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 1574.5 (M$^+$-Cl). HRMS, m/z: calcd for MH$^+$ (C$_{106}$H$_{79}$FeN$_{10}$): 1606.5527, found: 1606.6536.
ZnTXP-CN=Ph-CN-ZnT4EP dyad, 104.

(Z,Z) 1-(1-cyano-2-(5,10,15,20-tetra(4-ethylphenyl)porphyrinato zinc(II))ethenyl)-4-(1-cyano-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II))ethenyl).

Porphyrin dyad 101 (4 mg, 2.5 µmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (4 mL) and stirred at RT. A solution of Zn(OAc)\textsubscript{2}·2H\textsubscript{2}O (1.4 mg, 6.3 µmol) in MeOH (0.4 mL) was added and stirred for 30 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture was concentrated in vacuo. Crystallisation in CH\textsubscript{2}Cl\textsubscript{2}/MeOH gave the desired product 104 (4 mg, 100%) as a purple solid. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.74 (s, 1H, H\textsubscript{β-pyrrolic}), 9.69 (s, 1H, H\textsubscript{β-pyrrolic}), 9.08 (d, 1H, \(^3\)J= 5.0 Hz, H\textsubscript{β-pyrrolic}), 9.05 (d, 1H, \(^3\)J= 5.0 Hz, H\textsubscript{β-pyrrolic}), 9.00-8.83 (m, 10H, H\textsubscript{β-pyrrolic}), 8.28-8.23 (m, 2H, H\textsubscript{o-Ar}), 8.16-8.10 (m, 6H, H\textsubscript{o-Ar}), 7.98 (s, 2H, H\textsubscript{o-Xyl}), 7.85-7.78 (m, 6H, H\textsubscript{o-Xyl}), 7.70-7.66 (m, 2H, H\textsubscript{m-Ar}), 7.62-7.54 (m, 8H, H\textsubscript{m-Ar} and H\textsubscript{vinyl}), 7.52-7.35 (m, 8H, H\textsubscript{o-Xyl} and H\textsubscript{Ar}), 3.03 (m, 6H, CH\textsubscript{3}CH\textsubscript{3}), 2.88 (q, 2H, \(^3\)J= 7.5, CH\textsubscript{2}CH\textsubscript{3}), 2.69 (s, 6H, H\textsubscript{Me-Xyl}), 2.62 (s, 6H, H\textsubscript{Me-Xyl}), 2.61 (s, 6H, H\textsubscript{Me-Xyl}), 2.53 (s, 6H, H\textsubscript{Me-Xyl}), 1.56 (m, 9H, CH\textsubscript{3}CH\textsubscript{3}), 1.38 (m, 3H, CH\textsubscript{2}CH\textsubscript{3}). UV-vis (CH\textsubscript{2}Cl\textsubscript{2}) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 420 (4.89), 559 (3.78), 606 (3.92) nm. MALDI-TOF MS (1,8,9-anthracenetriol): \textit{m}/\textit{z}= 1752.61\textsuperscript{1}, exact mass: 1752.61, molecular weight: 1762.61.
TXP-CN\text{-}=\text{Ph}=-\text{CN-FeTPP} \text{ dyad, 105.}

(Z,Z) 1-(1-cyano-2-(5,10,15,20-tetraphenylporphyrinato iron(III))ethenyl)-4-(1-cyano-2-(5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrinato zinc(II))ethenyl).

Porphyrin dyad 103 (5 mg, 3.1 µmol) was dissolved in CH$_2$Cl$_2$ (4 mL) and stirred at RT. A solution of Zn(OAc)$_2$·2H$_2$O (1.4 mg, 4.3 µmol) in MeOH (0.4 mL) was added and stirred for 30 min. MALDI mass spectrometry indicated reaction completion and the reaction mixture was concentrated in vacuo. Crystallisation in CH$_2$Cl$_2$/MeOH gave the desired product 105 (5 mg, 100%) as a purple solid. UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 433 (5.06), 526 (4.05), 566 (3.65), 603 (3.58), 662 (3.52) nm. MALDI-TOF MS (1,8,9-anthracenetriol): $m/z = 1638.2$ (M$^+$). HRMS, $m/z$: calcd for M$^+$ (C$_{108}$H$_{76}$ClFeN$_{10}$Zn): 1667.4584, found: 1667.4596.

2,2',2''-(Benzene-1,3,5-triyl)triacetonitrile, 106.

Sodium cyanide (1.24 g, 25 mmol) was dissolved in DMSO (50 mL) and stirred at 40°C. By a dropping funnel, 1,3,5-tris(bromomethyl)benzene (2.90 g, 8 mmol) in DMSO (10 mL) was added over 1.5 h. The reaction was stirred for a further 16 h then poured into ice cold H$_2$O (200 mL).
The white precipitate was filtered off and washed with H₂O. Drying in vacuo resulted in 106 (0.97 g, 62%) being collected as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ (s, 3H, Hₐ𝐾), (s, 6H, CH₂CN). All spectra were in agreement with reported data.¹⁴⁸

TPP-CN=⁻PhCN₂, 107.

(Z)-2-(2-cyano-2-(3,5-dicyanomethylphenyl)ethenyl)-5,10,15,20-tetraphenylporphyrin.

A solution of porphyrin 11 (30 mg, 47 µmol), 2,2',2''-(benzene-1,3,5-triyl)triacetonitrile 106 (92 mg, 0.47 mmol), 1,8-diazabicycoundec-7-ene (DBU) (1.5 mL) and DCE (2.0 mL) was heated for 40 min at 120°C and 250 W in a microwave reactor. The cooled reaction was then purified by column chromatography (silica, CH₂Cl₂: Hexane (4:1, 1:0)) and crystallised in CH₂Cl₂/MeOH to give 107 (18 mg, 46%). ¹H-NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H, Hβ-pyrrolic), 8.96 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.89 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.84 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.78 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.76 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.73 (d, 1H, ³J= 5.0 Hz, Hβ-pyrrolic), 8.32-8.28 (m, 2H, H₀-Ph), 8.24-8.18 (m, 6H, H₀-Ph), 7.84-7.72 (m, 12H, Hₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚₚ₂

UV-vis (CH₂Cl₂) λₑₓₜ (log ε) 423 (4.45), 524 (3.49), 569 (3.12), 600 (3.07), 660 (2.92) nm. MALDI-TOF MS (1,8,9-anthracenetriol): m/z= 821.1 (M⁺). HRMS, m/z: calcd for MH⁺ (C₅₇H₃₇N₇): 820.3189, found: 820.3190.
Vinyl Linked Porphyrins

**TPP-=-Ph, 108.**

(Z)-2-(2-phenylethenyl)-5,10,15,20-tetraphenylporphyrin.

A solution of porphyrin phosphonium salt 25 (30 mg, 32 µmol) and benzaldehyde (17 mg, 0.16 mmol) were stirred in degassed CHCl₃ (5 mL) under argon at reflux. DBU (15 µL, 96 µmol) in degassed CHCl₃ (1 mL) was added over 10 min and the reaction was stirred for a further 30 min. On cooling to RT the reaction mixture was then concentrated *in vacuo* and purified by flash chromatography (silica, CH₂Cl₂). The major band was collected and concentrated *in vacuo*. Crystallisation from CH₂Cl₂/MeOH gave the desired product 108 (19 mg, 83%) as a purple powder. ¹H-NMR (400 MHz, CDCl₃): δ 8.99 (s, 1H, H⁺-pyrrolic), 8.83-8.69 (m, 6H, H⁺-pyrrolic), 8.27-8.17 (m, 8H, H₀-Ph), 7.83-7.70 (m, 12H, H mù,p-Ph), 7.36-7.25 (m, 6H, H AR and H vinyl), 6.99 (d, 1H, ³J= 16.1 Hz, H vinyl), -2.58 (br s, 2H, NH). UV-vis (CH₂Cl₂) λ_max (log ε) 422 (5.12), 523 (4.20), 561 (3.77), 598 (3.60), 657 (3.33) nm. HRMS, m/z: calcd for MH⁺ (C₅₂H₃₇N₄): 717.3018, found: 717.3023.

**ZnTPP-=-Ph, 109.**

(Z)-2-(2-phenylethenyl)-5,10,15,20-tetraphenylporphyrinato zinc(II).

Porphyrin 108 (18 mg, 23 µmol) was dissolved in CH₂Cl₂ (5 mL) and stirred at RT. A solution of Zn(OAc)₂·2H₂O (9 mg, 40 µmol) in MeOH (0.5 mL) was added and stirred for 40 min. MALDI mass
spectrometry indicated reaction completion and the reaction mixture was concentrated *in vacuo*. Crystallisation in CH$_2$Cl$_2$/MeOH gave the desired product 109 (18 mg, 100%) as a purple powder. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 9.10 (s, 1H, H$_{\beta\text{-pyrrolic}}$), 8.95-8.80 (m, 6H, H$_{\beta\text{-pyrrolic}}$), 8.27-8.16 (m, 8H, H$_{\text{o-Ph}}$), 7.84-7.70 (m, 12H, H$_{m,p\text{-Ph}}$), 7.36-7.22 (m, 6H, H$_{AR}$ and H$_{vinyl}$), 7.03 (d, 1H, $^3$J$=16.1$ Hz, H$_{vinyl}$). UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 424 (5.19), 555 (4.10), 591 (3.67) nm. HRMS, $m/z$: calcd for MH$^+$ (C$_{52}$H$_{34}$N$_4$Zn): 778.2075, found: 778.2094.
6.5 Synthesis of a Covalently Linked Porphyrin Hydrogel

**T4CP, 110.**

5,10,15,20-tetra(4-carboxyphenyl) porphyrin

4-Carboxybenzaldehyde (8.00 g, 53 mmol) and pyrrole (3.56 g, 53 mmol) were added to refluxing propionic acid (250 mL). The reaction was refluxed for 60 min and once cooled to RT was filtered thru a sintered funnel and washed with MeOH. The remaining powder was subsequently dried to give 110 (2.362 g, 23%) as a purple powder. $^1$H-NMR (400 MHz, DMSO-$d_6$): δ 8.84 (s, 8H, H$_\beta$-pyrrolic), 8.37 (d, 8H, $^3$J= 8.0 Hz, H$_{o-Ar}$), 8.31 (d, 8H, $^3$J= 8.0 Hz, H$_{m-Ar}$), -2.84 (br s, 2H, NH). Spectral data in agreement with literature.$^{[185]}$
4-carboxyphenyl porphyrin 110 (1.98 g, 2.5 mmol) was dissolved in excess thionyl chloride (60 mL) under argon and stirred for 16 h. The excess thionyl chloride was then removed *in vacuo*, leaving a green solid. The porphyrin was dissolved in dry CH₂Cl₂ (150 mL) and a solution of Jeffamine T403 and triethylamine (2.2 mL) in dry CH₂Cl₂ (30 mL) added at 0°C under argon. The reaction was stirred for 30 min and was then allowed to warm to RT and stir for a further 24 h. The reaction mixture was then washed with sat. aq. NaHCO₃ (2 x 25 mL) and H₂O (2 x 25 mL) and the organic layer removed. The solvent was then removed *in vacuo* to give 111 (1.15 g) as a sticky purple solid. ¹H-NMR (400 MHz, CDCl₃): δ 8.9-8.8 (m, 8H, Hβ-pyrrolic), 8.3-8.1 (m, 16H, HPh), 3.8-2.8 (m, HJeffamine), 1.8-0.7 (m, HJeffamine), -2.8 (br s, 2H, NH).

Porphyrin-PEGDGE hydrogel, 112.

Porphyrin-Jeffamine 111 (0.4 g, 0.17 mmol) was dissolved in DMF (1 mL) using heating and sonication. PEGDGE (0.34 g, 0.68 mmol) was added to the solution, stirred to ensure complete mixing and poured into 15 mm diameter molds. The samples were then placed in a laboratory
temperature and humidity cabinet (40 °C, 45% relative humidity) for 5 days. Upon gelation, the samples were swollen in milli-Q H$_2$O with daily solvent replacement and weighing of samples.

**Porphyrin-Jeffamine-PEGDGE hydrogel, 113.**

Porphyrin-Jeffamine 111 (0.2 g, 0.086 mmol), Jeffamine T403 (0.64 g, 1.6 mmol) and PEGDGE (1.4 G, 2.8 mmol) were dissolved in DMF (7 mL). The solution was poured in 15 mm diameter molds and placed in a laboratory temperature and humidity cabinet (40 °C, 45% relative humidity) for 7 days. Upon gelation, the samples were swollen in milli-Q H$_2$O with daily solvent replacement and weighing of samples.
Chapter 7

References


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