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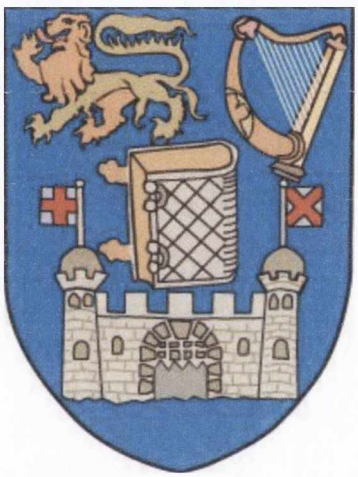
Stannyl Porphyrins, Ferrocenyl Porphyrins and Nonplanar Porphyrins:

Synthesis and Photophysical Properties



Submitted by

Muntaz Abu Bakar

BSc (Hons) in Chemistry, UTM, Skudai, Malaysia

MSc (Natural Product), UKM, Bangi, Malaysia

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

Doctor of Philosophy

Declaration

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Summary

The aim of this work was to synthesis the tin porphyrins, ferrocene porphyrins and nonplanar multiporphyrins arrays. The next step was to investigate their photophysical properties.

Free base tin porphyrins and a porphyrin dimer have been successfully synthesized *via* copper-free Stille coupling. This approach provides access to tin porphyrin synthons that were previously unavailable. Photophysical properties of these compounds were investigated. The stannyl porphyrins emitted in visible region and in all cases large Stokes shifts were observed. The emission intensities of the stannyl porphyrins were 100-fold higher than the starting bromoporphyrins. Measured fluorescence lifetime of the stannyl porphyrins and the dimeric porphyrin were comparable with commonly used PDT drug Foscan®.

To improve the synthetic access to ferrocene porphyrin type electron transfer compounds meso-ferrocenyl appended porphyrins and bisporphyrins were prepared using Suzuki coupling reactions of borylated porphyrins with appropriate ferrocene precursors. Yields were improved comparable to those previously reported in the literature. Photo physical studies were carried out for the ferrocene porphyrins and the dimers and the emission spectra showed that quenching process which was observed due to the interaction between the porphyrin and ferrocene group. The fluorescence lifetime were measured and have shorter lifetimes compared to the DPP

Novel dimeric, trimeric, and pentameric porphyrins containing a nonplanar porphyrin core have been successfully synthesized using transition metal catalyzed reactions on functionalized octaethylporphyrins. These porphyrins are sterically strained and this properties this is important to mimic the biological porphyrins due to their nonplanar conformation. Photophysical studies indicate great level of electronic coupling among the porphyrin subunits. Emission spectra showed a decreasing in the intensity of

multiporphyrins arrays and shorter lifetime compared to the 2,3,7,8,12,13,17,18-octaethylporphyrin **2** (OEP). Protonation of multiporphyrins arrays showed a bathchromic shift on the absorption maxima.

Publications

Sergeeva, N. N.; Bakar, M. A.; Senge, M. O. J. Synthesis of stannyl porphyrins and porphyrin dimers *via* stille coupling and their ^{119}Sn NMR and fluorescence properties. J. Org. Chem. **2009**, 74, 1488–1497.

Bakar, M. A.; Sergeeva, N. N.; Juillard, T.; Senge, M. O. Synthesis of ferrocenyl porphyrins *via* suzuki coupling and their photophysical properties. Organometallics. **2011**, 30, 3225–3228.

Conferences

Bakar, M. A.; Sergeeva, N. N.; Senge, M. O. Synthesis of ferrocenyl porphyrins *via* suzuki coupling and their photophysical properties. Recent Advances in Synthesis and Chemical Biology VIII" RCSI, Dublin, 18th December **2009**.

Ebrahim, M. M.; Bakar, M. A.; Senge, M. O. Synthesis of nonplanar porphyrins and arrays. : Centre for Chemical Synthesis and Chemical Biology "Recent Advances in Synthesis and Chemical Biology X" Health Science Centre, UCD, Dublin, 9th December **2011**.

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List of Schemes

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Abbreviations

Ac_2O	acetic anhydride
Ar	aromatic
$BF_3.OEt_2$	boron trifluoride etherate
br	broad
Bu	butyl
$CDCl_3$	deuterated chloroform
$(CH_2OH)_2$	dicloroethane
CsF	cesium fluoride
CuI	copper iodide
DCM	dichloromethane
d	doublet
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dd	doublet-doublet
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
equiv.	equivalent
H_2O	water
H_2SO_4	sulfuric acid
HCL	hydrochloric acid
HexylLi	hexyl lithium
HRMS	High resolution mass spectrometry
HSQC	Heteronuclear Single Quantum Coherence
Hz	Hertz
IPA	2-propanol
IUPAC	International Union of Pure and Applied Chemistry
J	coupling constant measured in Hertz
KF	potassium fluoride
KOH	potassium hydroxide
$LiAlH_4$	lithium aluminum hydride

m	multiplet
MALDI	matrix-assisted laser desorption/ionisation
MeOH	methanol
$MgSO_4$	magnesium sulphate
mp	melting point
MS	mass spectrometry
m/z	mass-to-charge ratio
NaCl	Sodium chloride
NaOH	sodium hydroxide
Na_2SO_4	Sodium sulphate
NBS	*N*-Bromosuccinimide
NH_4Cl	Ammonium chloride
NLO	nonlinear optics
NMR	nuclear magnetic resonance
OEP	2,3,7,8,12,13,17,18-octaethylporphyrin
P_2O_5	Phosphorus pentoxide
$PdCl_2(PPh_3)_2$	dichlorobis(triphenylphosphine)palladium(II)
$Pd_2(dba)_3$	tris(dibenzylideneacetone)dipalladium(0)
$Pd(PPh_3)_4$	tetrakis(triphenylphosphine)palladium(0)
PDT	photodynamic therapy
Ph	phenyl
PhLi	phenyl lithium
ppm	parts per million
PTSA.H_2O	*p*-toluenesulfonic acid
q	quartet
R_f	retention factor
RLi	organolithium reagent
s	singlet
S_NAr	nucleophilic aromatic substitution
t	triplet

t-BuLi	*tert*-butyl lithium
TEA	triethylamine
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMEDA	*N,N,N',N'*-tetramethylethylenediamine
TMS	trimethylsilane
TPP	5,10,15,20-tetraphenylporphyrin
TrPP	5,10,15-triphenylporphyrin
UV	ultraviolet
v/v	volume to volume
vis	visible
δ	chemical shift measured in parts per million (ppm)
ε	molar absorption coefficient
λ	wavelength measured in nanometre (nm)

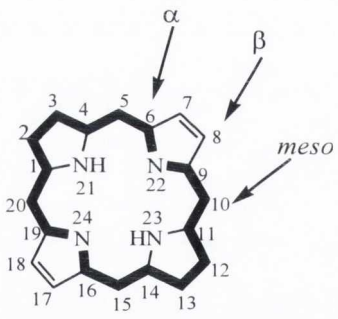
CHAPTER 1

INTRODUCTION

1.1 Background

The word porphyrin has its origins from ancient Greek, namely as *porphura* which is derived from an earlier semitic word to describe purple dye pigments.[1] Porphyrins are defined as "a large class of deeply coloured red or purple, fluorescent crystalline pigments, of natural or synthetic origin, having in common, a substituted aromatic ring consisting of four pyrrole-type residues, linked together by four methine bridging groups".[2] The structure was first proposed by Küster in 1912, and refined by Fischer in 1929 when he succeeded in the synthesis of Heme. Tetrapyrroles have numerous applications as biomimetic models and as useful components in material science. In recent years they have found applications of porphyrins in medicinal chemistry as photosensitizers in photodynamic therapy (PDT), for the treatment of tumour cells, psoriasis and for the treatment of certain forms of age-related macular degeneration (AMD).[3]

There are three different types of carbon atoms in a porphyrin unit and its positions are numbered according to IUPAC in **1**[4,5]

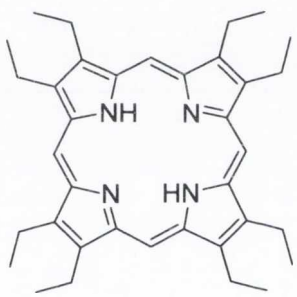


1

The positions 2, 3, 7, 8, 12, 13, 17 and 18 are known as the β position, 5, 10, 15 and 20 as the meso position and 1, 4, 6, 9, 11, 14, 16 and 19 as the α-position.[6] The four inner nitrogen atoms (21–24) can form complexes with a wide variety of metal ions.[7]

Only 18 out of 22 π-electrons take part in the aromatic system and therefore it follows the Hückel law for aromaticity (4n+2).[8,9] Four of the 22 π-electrons in free-base porphyrins possess more double bond character.[6] The remaining β-β double bonds are not involved in the aromatic system and so can undergo addition reactions to form hydroporphyrins without loss of the aromatic character.[10]

The β positions on the porphyrin periphery are available to undergo numerous addition and substitution reactions.[7] Which of the two sites, meso or β, is activated depends of the porphyrin. While addition to the α-position is rare, such occurrences result in ring-opening i.e. blatriene formation. Depending on the type of substituents in the meso-positions, applications can be found in different fields; porphyrins with electron withdrawing and electron donating groups can be used for non-linear optics (NLO) and polar and nonpolar substituents on one porphyrin find application in photodynamic therapy (PDT). Symmetric porphyrins are synthetically more accessible than asymmetric ones. Therefore the most widely investigated porphyrins are 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin (OEP) **2** and 5, 10, 15, 20-tetraphenylporphyrin (TPP) **3.**[11]



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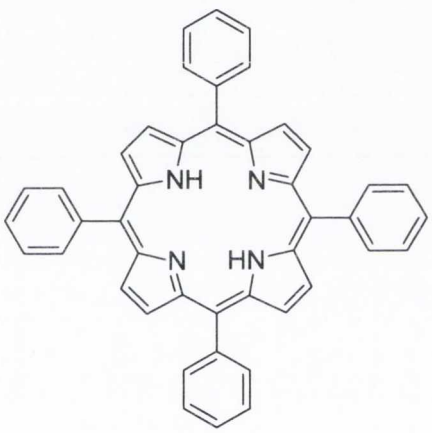


3

1.2 Reactivity

Essentially, porphyrins are aromatic molecules, and as such they should undergo the characteristic reactions of these compounds, i.e: electrophilic substitution reactions such as Vilsmeier formylations, nitrations, halogenation reactions and acylations; nucleophilic reactions such as those with organometallic reagents; and oxidation and reduction reactions. However, the chemistry of porphyrins is dominated by electrophilic substitution reactions and for many years nucleophilic attack was restricted to activated substrates.

Activation of the porphyrin was achieved by metallation with high-valent metals,[25,26] substitution of the β or meso positions with electron withdrawing groups,[27] and leaving groups[28,29] or deformation of the macrocycle.[30,31] Without prior activation, strong nucleophiles are needed to achieve addition at the *meso*-position. The lack of nucleophilic addition can be ascribed to low electrophilicity of the porphyrins (Figure 1.1), where nucleophilic attack can only be achieved with hard nucleophiles such as lithium reagents.

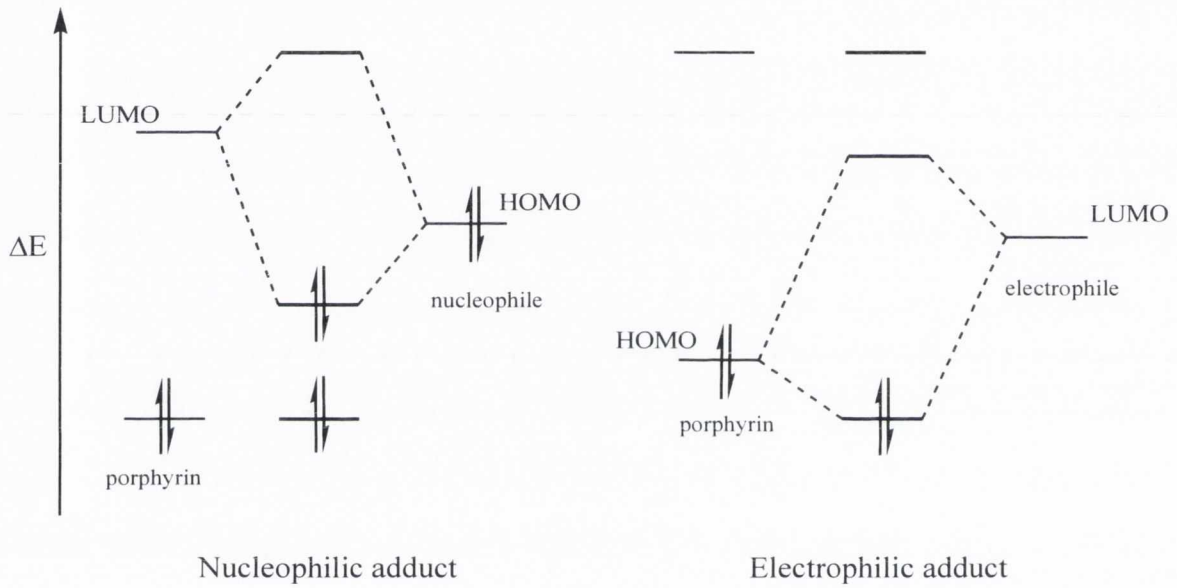


Figure 1.1 Orbital interactions of porphyrins with nucleophiles and electrophiles.

1.3 Photodynamic therapy

Photodynamic therapy (PDT) is a cytotoxic treatment modality based on photoactive substances of photosensitisers such as porphyrins that selectively retain in tumour tissues. Irradiation of the target tissues with appropriate wavelength of light activates the production of highly reactive oxygen and leads to a series of phototoxic reactions that cause selective death of tumor cells. Studies have been conducted on the treatment of a variety of malignant and pre malignant cancer conditions including head

and neck cancer,[1] lung cancer,[2] mesothelioma,[3] Barrett's esophagus,[4] prostate[5] and brain tumors.[6] PDT is also employed to treat non-cancerous conditions such as psoriasis[7] and age related macular degeneration (ARMD).[8]

The photochemical processes in PDT are represented by the Jablonski diagram (Figure 1.2).[9] Upon absorption of light with a suitable wavelength, the photosensitisers which have ground electronic singlet state (P^0) are excited to the first excited singlet-state ($^1P^*$). The photosensitiser can decay back to the ground state by emitting fluorescence photons enabling identification of tumour tissue. Alternatively, the $^1P^*$ photosensitisers can convert to the first excited triplet state, $^3P^*$ *via* intersystem crossing (ISC). The $^3P^*$ state is sufficiently long-lived that can be involved in chemical reactions. The $^3P^*$ photosensitisers can also return to the ground state by emitting phosphorescence.

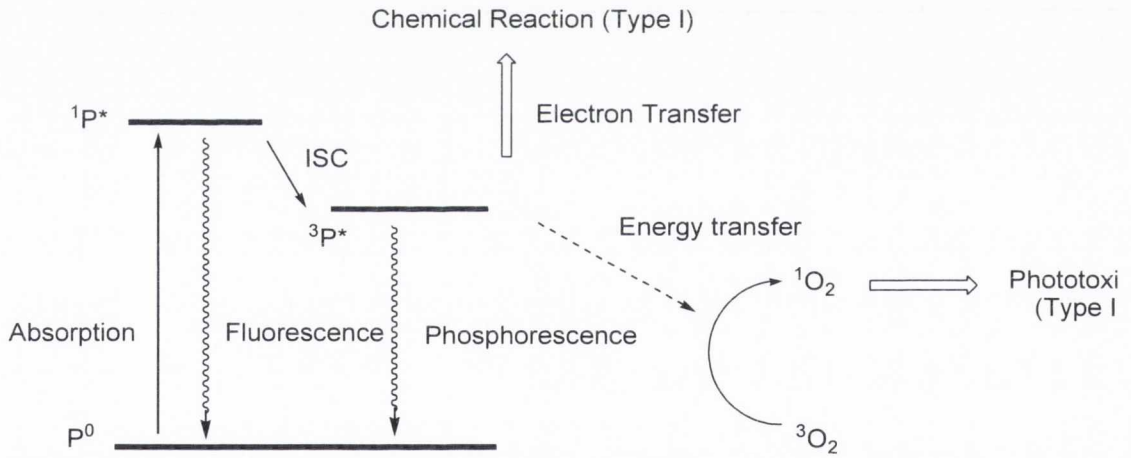


Figure 1.2 A simplified Jablonski diagram for PDT.

There are two types of photodynamic process that promote chemical reactions in a substrate including damage to living tissue; these are referred as type I and type II. Type I photoprocesses involves electron or hydrogen transfer reaction between excited state $^3P^*$ photosensitisers and other molecules. These excited photosensitisers can react directly with an organic substract (S) by electron exchange producing an oxidised substract (S^+) and a reduced photosensitiser (P^-). The reduced photosensitiser (P^-) can

react with oxygen to produce a less reactive superoxide anion (O_2^-), which can then form the highly reactive hydroxyl radical ($^{\cdot}OH$). The excited photosensitiser, $^3P^*$ also can react with superoxide radicals ($O_2^{\cdot}$) to produce superoxide anions (O_2^-) which can then form the highly reactive hydroxyl radical ($^{\cdot}OH$) that is harmfull to cells. The type II photoprocess is an electron spin exchange between $^3P^*$ photosensitisers and ground state oxygen, $^3O_2$. It produces the cytotoxic singlet-state of oxygen, $^1O_2$ that reacts with various biomolecules such as triacyl glycerols, cholesterols, phospholipids, histidine and nucleic acids. The extent of photodamage and cytotoxicity is dependent on the type of photosensitiser, its localisation, the total dose of administered photosensitiser, total light time exposure, the availability of oxygen and the time between the injection of drug and light exposure.

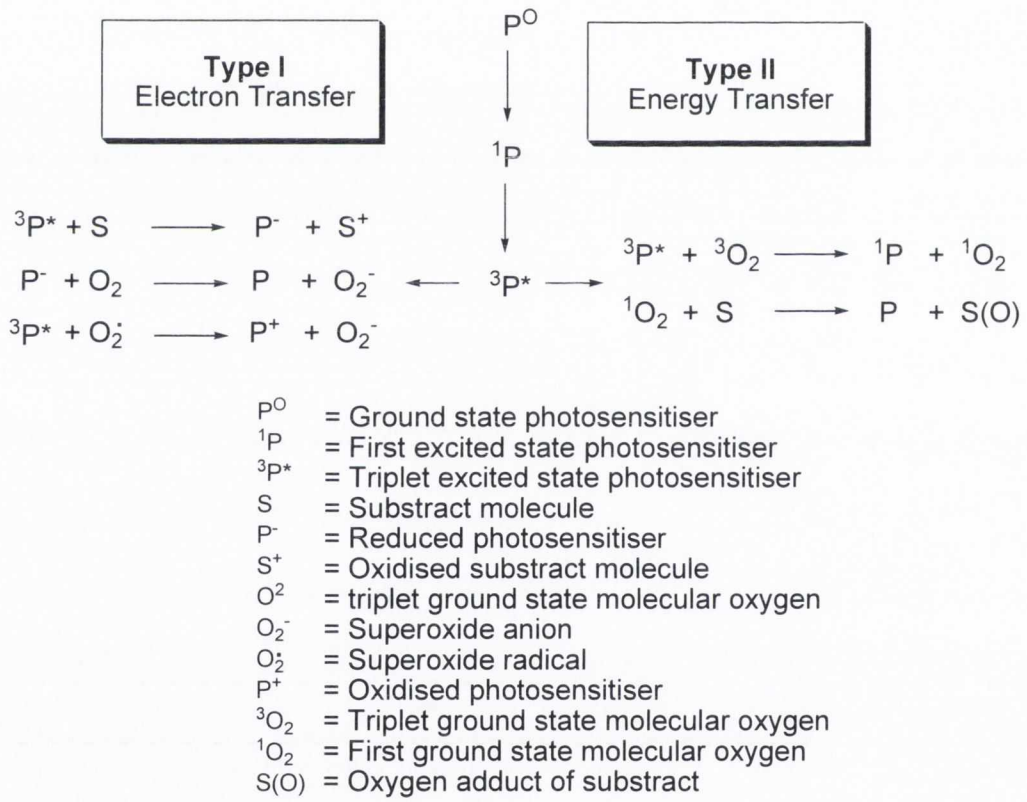
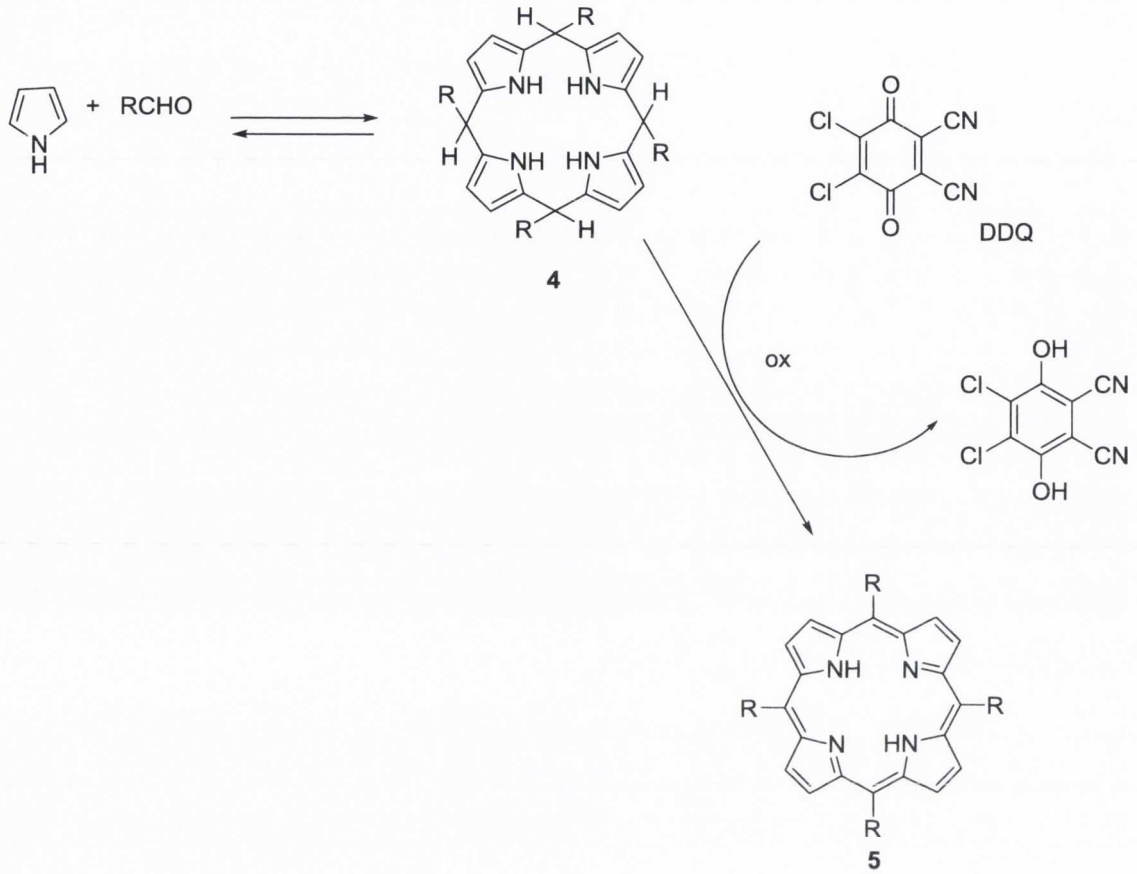


Figure 1.3 Type I and II photochemical reactions in PDT.

1.4 Synthesis of porphyrins and their precursors

A variety of meso substituted porphyrins can be prepared *via* the condensation of dipyromethanes with an aldehyde. The synthesis of dipyyromethanes can be non-trivial. The synthesis of 3,4-diethylpyrrole for example involves four steps.[12] This route has proven to be the most reliable and over the last 60 years, there have been many modifications to this reaction including those by Rothemund in 1974,[13] Adler *et al.* in 1967,[14] and Lindsey *et al.* in 1987.[15] Lindsey's method is most widely used now. Here, pyrrole and an aldehyde react reversibly in a one-pot synthesis at room temperature to form an equilibrium distribution of tetra-substituted porphyrinogen **4**. The addition of DDQ, an oxidising agent, irreversibly converts the porphyrinogen to the corresponding aromatic porphyrin (Scheme 1.1). Overall yields in this reaction can reach up to 40% depending on the aldehyde used.[16]

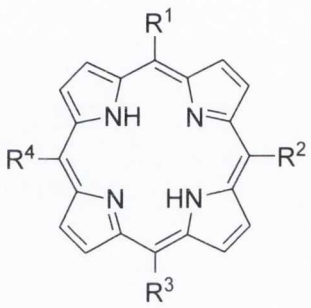


Scheme 1.1 Condensation reaction of pyrrole and aldehyde.

These symmetric porphyrins (A_4-type porphyrins) **5** are easily synthesised and are amenable further synthetic modification. The wide availability of aldehydes coupled with their ease of manipulation enables a range of porphyrins to be synthesised without elaborate multistep syntheses. Different groups on the aldehyde unit expose reactive sites on the porphyrin which allow for further synthetic extension. The substituent at the meso positions are generally alkyl or aryl groups but they can even include heterocyclic or organometallic groups and other porphyrins (bis-porphyrins).

Asymmetrically meso substituted analogues can be obtained using a mixed condensation reaction under the same principle used for asymmetric β substituted porphyrins. The mixed condensation of pyrrole with different aldehydes gives a series of products distinguished by their substitution pattern (Figure 1.4). The yield for any

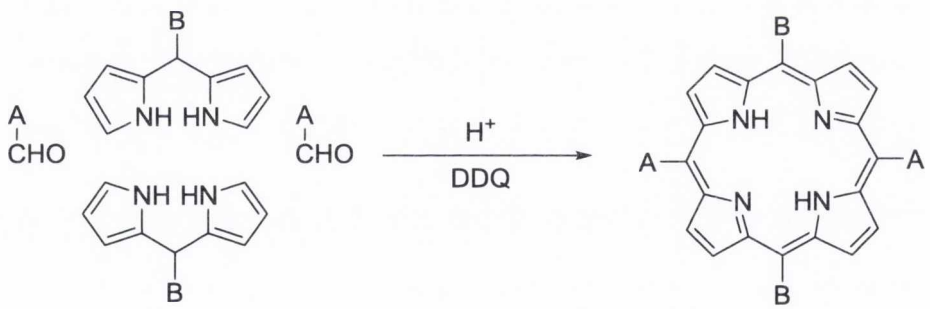
particular porphyrin *via* this method is very low and chromatographic purification can be very difficult. Therefore, depending on the substitution pattern required, different synthetic routes have been employed in order to improve the yields of the desired porphyrins.



A_4-type: $R^1=R^2=R^3=R^4$
A_3-type: $R^1=R^2=R^3$; $R^4=H$
A_3B-type: $R^1=R^2=R^3$;
5,15-A_2-type: $R^1=R^3$; $R^2=R^4=H$
5,10-A_2B_2-type: $R^1=R^2$; $R^3=R^4$
5,15-A_2B_2-type: $R^1=R^3$; $R^2=R^4$
5,15-A_2BC-type: $R^1=R^3$
ABCD-type:

Figure 1.4 Example of some substitution patterns resulting from mixed condensation using the "ABCD"-nomenclature introduced by Lindsey.[16]

The [2+2] MacDonald condensation is the most convenient route to the synthesis of A_2B_2- or A_2-type porphyrins.[17] Reaction of a dipyrromethane with an aldehyde affords A_2B_2 **7** and A_2-porphyrins **8** (Scheme 1.2).



6 **7** **8** B=H

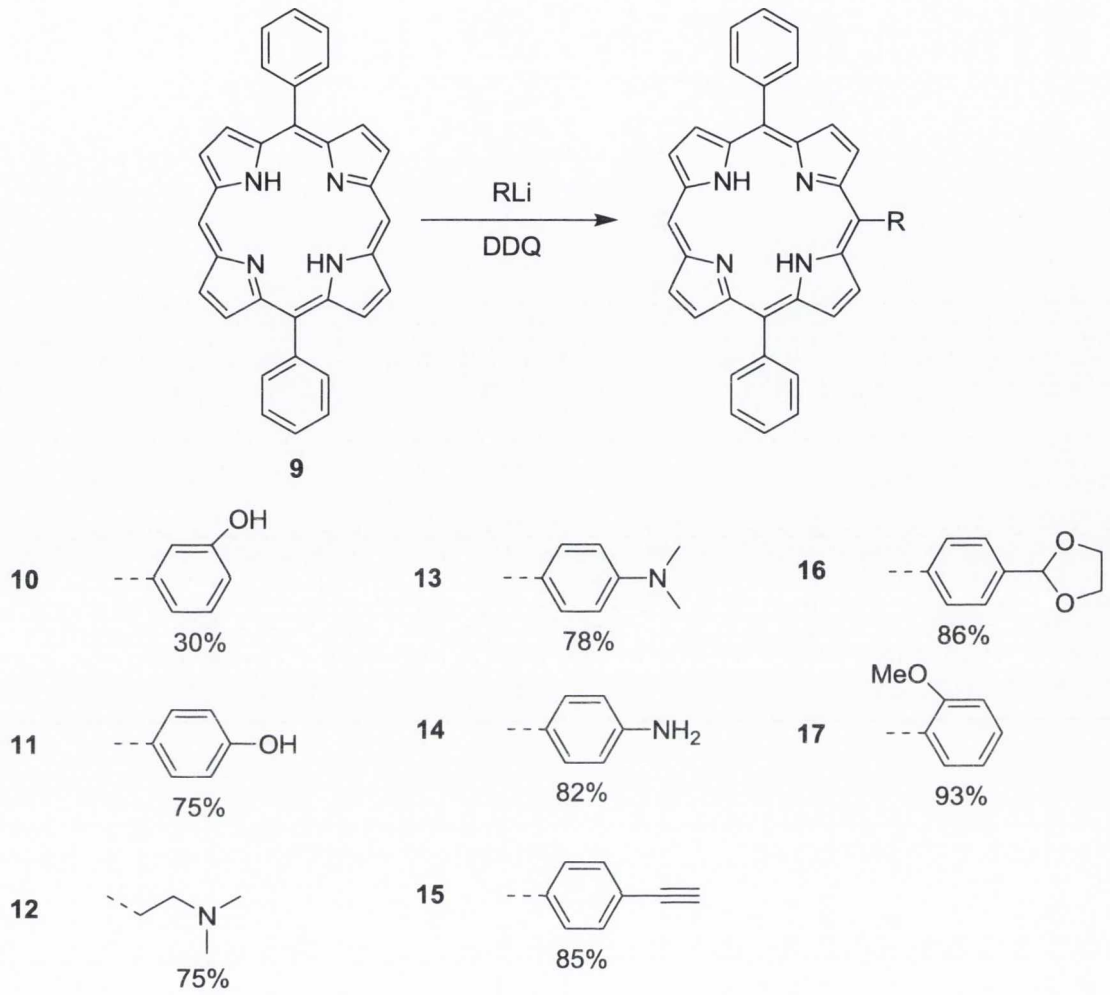
Scheme 1.2 Synthetic routes to (a) 5,15-A_2B_2- (and A_2-porphyrins) *via* a [2+2] MacDonald-type condensation reaction.

Halogenation of these systems allows for the introduction of different functional groups via C-C cross coupling reactions,[18] while reaction with organolithium reagents

yields A_3B- and A_2BC-porphyrins.[19] They satisfy an important criterion for the action of photosensitisers *in vivo* as amphiphilicity facilitates localisation in membrane structures of cells.[3]

One of the most successful approaches for modification of the porphyrin core is reaction with organolithium reagents which can be used to introduce a broad range of substituents with functional groups.[20] Up until recently the synthesis of these compounds required multisteps or mixed condensation reactions with a tedious purification. The nucleophilic reaction at the *meso* position proceeds *via* an addition-oxidation mechanism where the intermediates are thought to possess phlorin- or porphodimethene-type structures.[21] The specific reaction pathway primarily depends on steric constraints of the macrocycle and only partially on the steric bulk of the organolithium reagent. This methodology can be further developed for the preparation of mono-, di-, tri- and tetra-*meso*-substituted tetrapyrrole systems. This approach also offers a suitable pathway to the synthesis of ABCD-type porphyrins i.e. highly substituted porphyrins with a mixed substituent pattern. However, organolithium reagents are not tolerated by reactive functional groups and it is often difficult to prepare more complex reagents.

Senge *et al.* reported reaction of 5,15-diphenylporphyrin with corresponding functionalized organolithium reagents can yield *meso* substituted porphyrins in good yields 30-93%.[21,22] (Scheme 1.3). An excess of organolithium reagent was used (10-15 equiv.) to get a high yields of the desired products and to prevent the formation of ring-opened side products.



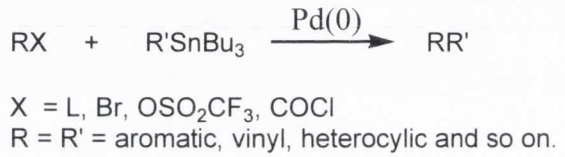
Scheme 1.3 Synthesis of unsymmetric A_2B-porphyrins *via* reaction with organolithium reagents.

1.5 Palladium mediated Stille coupling

Stille reaction defined as the cross coupling between organic electrophiles (usually unsaturated halides or triflates) and organostannanes, has recently become an extremely popular synthetic tool and further developments in this arena are consequently quite desirable.[23] From the literature many important advances have been reported, especially

on its scope and versatility with the development of efficient palladium catalysts and ligands.

One of the synthetic limitations in the Stille reaction would be its high steric demand, which often slows down the subsequent Sn/Pd transmetalation in the catalytic cycle. The reaction has been shown to tolerate many functional groups, such as amines, aldehydes, esters, and nitro groups.[24] The reaction normally can be used to obtain product in high yield. General scheme for the Stille coupling reaction showed in scheme 1.4.[24]



Scheme 1.4 General scheme for the Stille coupling reaction.

Normally Pd(II) or Pd(0) complex is introduced as the catalyst. If Pd(II) is used, it will initially reduced to Pd(0) by organotin compound. The resulting Pd(0) reacts with the organo halide to form the organopalladium halide (triflate) intermediate by oxidative addition. Transmetalation will take place in this intermediate. Finally, reductive elimination affords the product and Pd(0) species to complete the catalytic cycle. Figure 1.5 shows the mechanism for the Stille coupling reaction.[24]

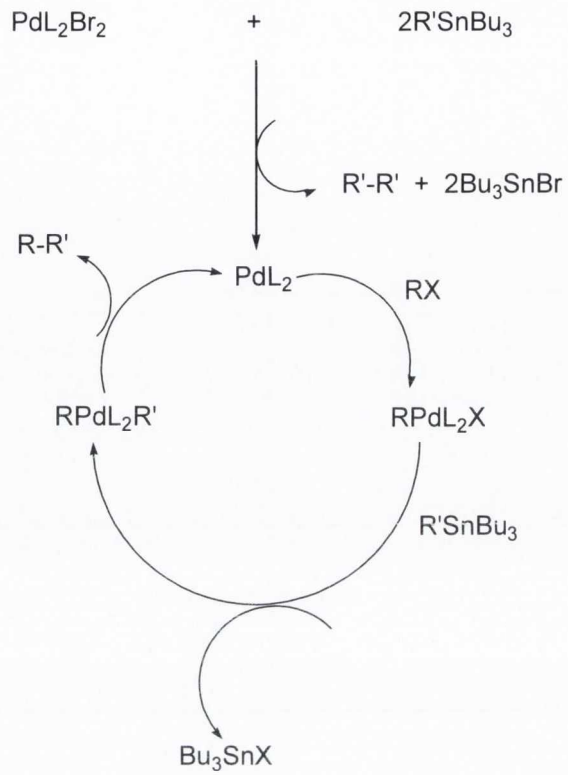
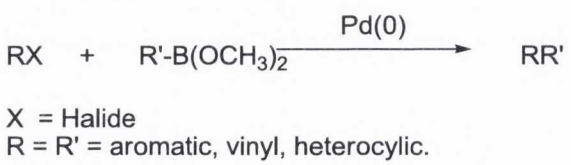


Figure 1.5 Mechanism for the Stille coupling reaction.

1.6 Suzuki coupling reaction

In the Suzuki coupling reaction an aryl or vinyl boronic acid are coupled with an aryl or vinyl halide using a palladium(0) catalyst (Scheme 1.5).



Scheme 1.5 General scheme for the Suzuki cross coupling reaction.

Suzuki coupling reaction has a same mechanism as Stille coupling reaction, which is Pd(II) will reduced to Pd(0). On this reaction involves oxidation-addition-transmetalation-reduction elimination sequence. Figure 1.6 shows the mechanism for the Suzuki cross coupling reaction.[25-29]

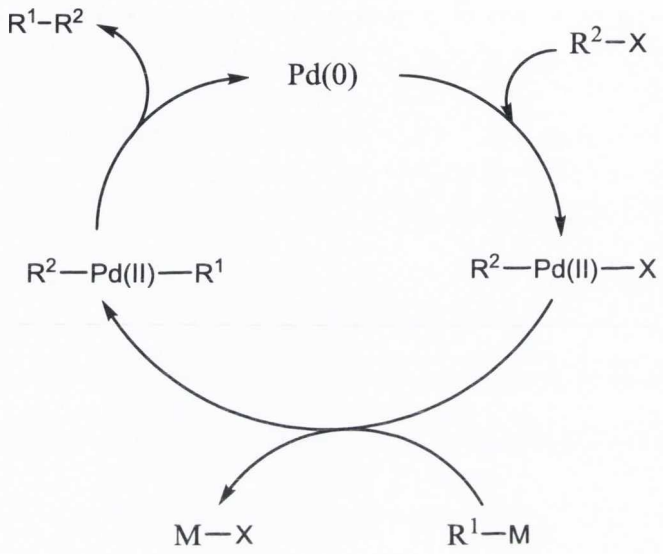
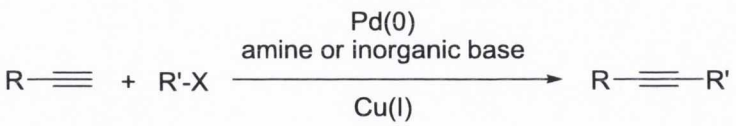


Figure 1.6 Mechanism for the Suzuki coupling reaction.

1.7 Sonogashira coupling reaction

Sonogashira reaction was classified as the reaction between terminal sp hybrized carbon from an alkyne with a sp^2 carbon of an aryl or vinyl halide. This reaction can be easily handled at room temperature in the presence of $PdCl_2(PPh_3)_2$ as a catalyst combined with co-catalyst CuI in TEA as a solvent[30] (Scheme 1.6).



R = Aryl, Hetaryl, Alkyl, SiR_3
R' = Aryl, Hetaryl, Vinyl
X = I, Br, Cl, OTf

Scheme 1.6 General scheme for the Sonogashira coupling reaction.

Two cycles take place in the mechanism of sonogashira reaction, which is the first cycle, cycle A known as 'palladium-cycle'is classical from C-C cross-coupling formation.[31] Reduction of Pd(II) to Pd(0) from formation complex of $[Pd(O)L_2]$ by the catalysts $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$.[32] Beside that, inorganic base such as amine can take part the reduction of Pd(II) to Pd(0) by formation of iminium cations.[33]

Second cycle, cycle B know as 'copper-cycle' which is π-alkyne copper complex make alkyne terminal proton become more acidic by formation of copper acetylide.[34] Complete mechanism of Sonoghashira coupling reaction has been showed in Figure 1.7.

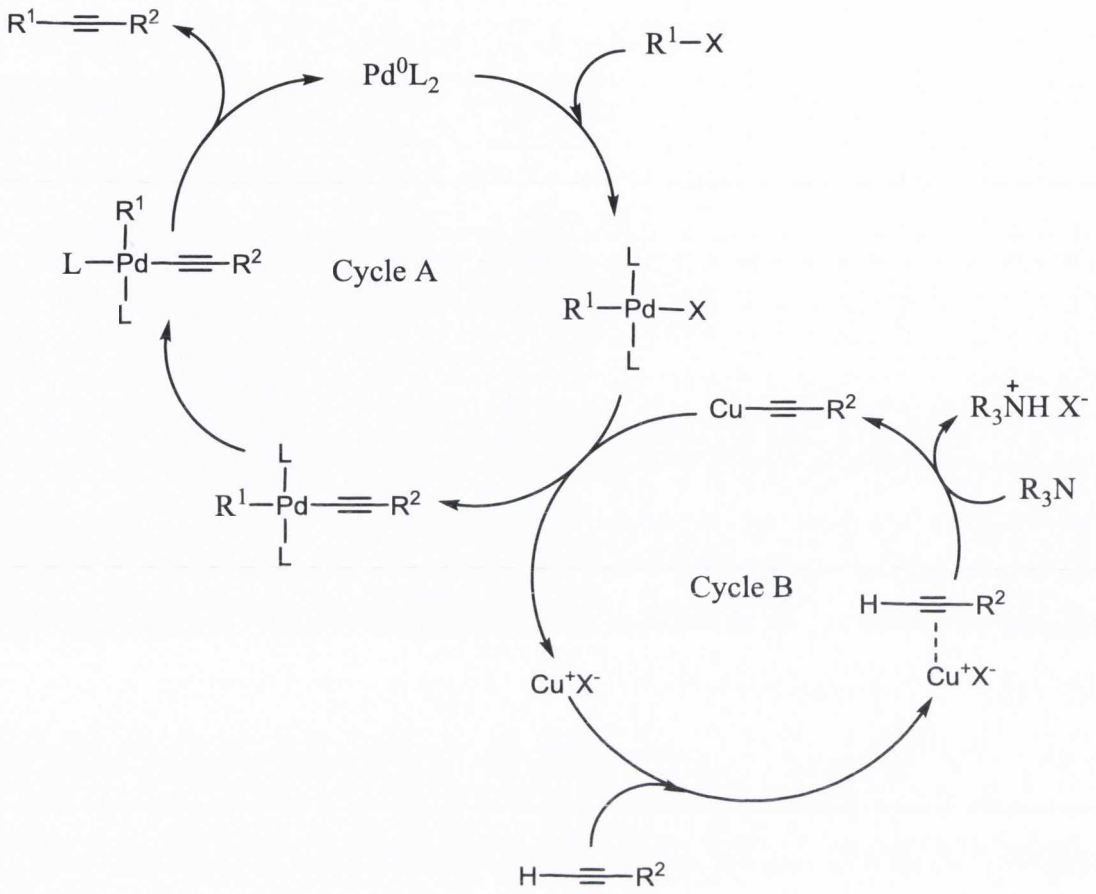


Figure 1.7 Mechanism for the Sonogashira coupling reaction.

However to avoid a formation of the homocoupling products, copper-free variation to the Sonogashira reaction has been introduced. This reaction still followed the original mechanism the different only the new intermediate which is can deprotonated the terminal alkyne proton and subsequent ligand exchange with the leaving group has been introduced. This happen since the amine associated with this reaction are not basic enough to deprotonated the reacting alkyne. [34]

1.8 Organotin compound

Organotin compounds or stannylenes (R_2Sn) have found wide agricultural and industrial application. Recent studies have shown their potential use as antifungal agents and their relatively high in vitro antitumor activity.[35-38]

Sn is an element in Group IV of the periodic table. This elements has four valence electrons and normally two of their p electron are used to form covalent bonding and the other lone pair to form an adduct with a Lewis acid. Besides that, Sn also do have low-lying empty p and d orbitals that can be used to form a complex. Figure 1.8 shows a several hybrization geometries of Sn.[39]

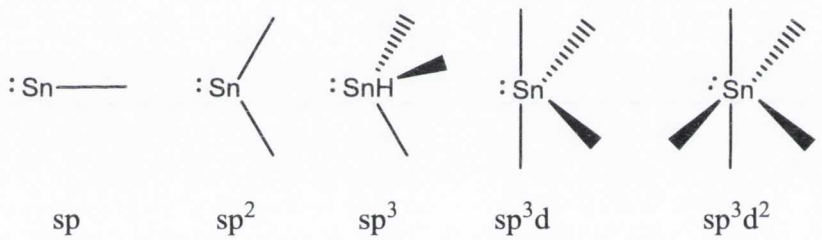


Figure 1.8 Hybrization geometries for stannylenes.

It can form stable adducts with strong base or strong acid such as amines and ethers[40] or boron halides.[39,41] Its also can form stable adducts with weak base or weak acid such as halides[42,43] or transition metals.[44,45]

Tin has three isotopes with $I=^1/_2$, which is two of the isotopes ^{119}Sn and ^{117}Sn have reasonable abundances and used as the main factor to investigated the NMR splitting.[46,47] While ^{115}Sn has low abundances and normally not take part on the NMR pattern. Even though combination of this three isotopes have been used to characterized NMR of the tin compounds, ^{119}Sn is the dominant and the most have been observed due to its higher receptivity.[48]

Besides that, coupling constant also one of the important matter that has to be looked over for determination the tin complex structure. Normally coupling constants for trans are higher than cis. This is because coupling constant depends on the geometry of the structure.[49,50]

1.9 Ferrocene

Ferrocene **18** is an organometallic compound, which is known as sandwich compound since its structure contains a metal in the middle of two coplanar cyclopentadienyl rings.[51] This compound shows aromatic character that has been used to investigated electronic structure in organometallics compounds.[52-54]

18

Beside that, ferrocene can be be used in various field such as catalyst on the carbon nanotubes production[55] and also found as useful for anticancer activity.[56]

1.10 Nonplanar porphyrins

Highly substituted porphyrins which are substituted on β and *meso* position of porphyrin make this macrocycle shows the nonplanar properties.[57] Besides that, the nonplanarity also can be induced by substituted on the core porphyrin, make larger heteroatoms from changing on the macrocycle. It also can be achieved by interrupting the aromatic conjugation in the system, reduction and strapping the macrocycle[57] (Figure 1.9).

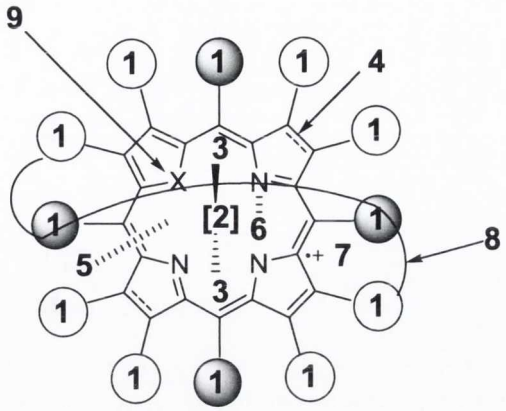


Figure 1.9 Possibilities for chemically altering the macrocycle and core conformation of porphyrins. Variation can be achieved by different means : 1) introduction of sterically demanding substituent; 2) metalation; 3) axial ligands; 4) degree of reduction; 5) interruption of the conjugated system; 6) N-alkylation, arylation or protonation; 7) cation radical formation; 8) "strapping" of the macrocycle *via* covalent linkage of the *meso*- or β-pyrrole position; 9) heteroatom substitution.

To differentiate between the non planar macrocycle, conformation plays the main role. There have four different type of distortion mode which is name as saddle-shaped, ruffled, dome and wave to confirm the conformation in the macrocycle[58] (Figure 1.10).

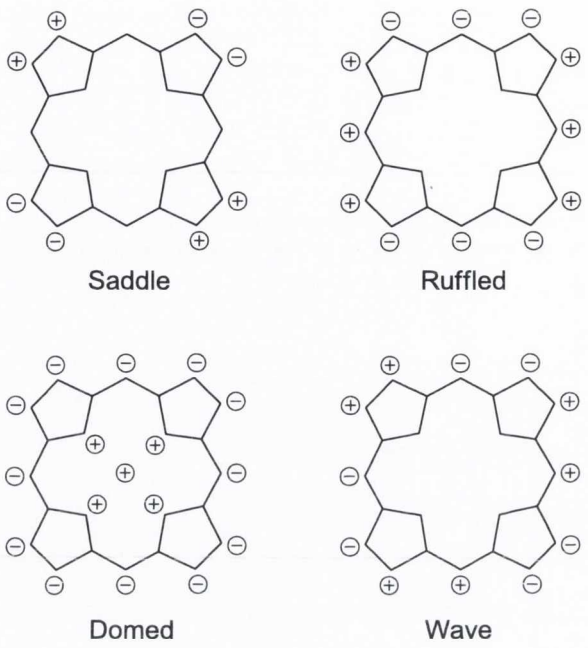


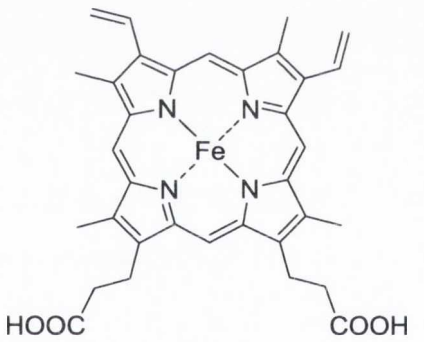
Figure 1.10 View of the four main distortion modes observed for porphyrin. Only the most significant displacements are shown. (+) indicates the displacement above the mean plane, (-) indicates the displacement below the mean plane.

Metalloporphyrin involving the small central metal ion like Ni(II) always showed saddle-shaped or ruffled distortion mode. Observation of alternate displacement of pyrrole ring above and below mean plane while C_m position remain more or less in plane confirmed as saddle-shaped conformation this happen because the short bond formed between the metal-nitrogen. While observation of alternating displacement of the C_m position above and below the mean plane confirmed as ruffled conformation and this happen because of the twisting of the bond between the metal-nitrogen.[59]

Metalloporphyrin involving large central ion such as Tl(II) showed doming distortion mode. Beside that, this type of distortion also can be found in five-coordinated complexes, when the axial ligand causes an out-of-plane displacement of the central metal.[60,61] This can be observed through displacement of the macrocycle atoms in opposite direction of metal displacement.

The fourth distortion mode known as "wave" and always be found as a local energy minimum conformer or lowest energy structure in molecular mechanism calculation.[62] These four types of distortion modes are a good system to classify different porphyrin conformation. In some cases, combination of these four distortion mode can give the conformation of the macrocycle.[63]

Nonplanarity plays a important role in terms of biological relevant. Since last decade, scientist always investigated how the multitude of biological reaction can be catalyzed by tetrapyrrole containing pigment protein complexes.[64] For example, heme **19** is a important class of porphyrins containing iron was involved for oxygen transport, storage (myglobin, hemoglobin) and for the incorporation of molecular oxygen into organic substrate. In other hand, for example in photosynthesis (chlorophyll **20**) the same cofactor will function as an antenna pigment (exciton transfer) in light harvesting complexes or as a reaction center pigment (charge separation).[65,66]



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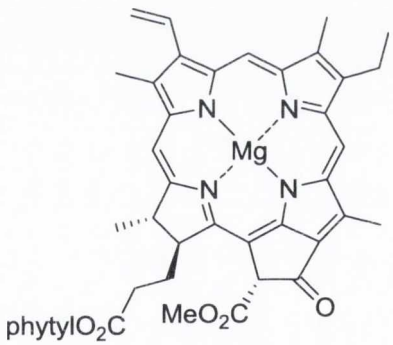


20

The differences in physicochemical properties of this protein complexes cannot be explain by looking into the sequence itself, the major reason that contributed to this factor is the close interplay between bound cofactor and respective apoprotein that exhibit a flexible conformations.[67]

Analysis of the various porphyrin-protein structure show that the physiochemical studies always can be correlated with the results of the conformation for the chlorophyll in the photosynthesis antenna and reaction center complexes.[68-70] Same

as Heme, which is the environment, spin state and axial ligands, planar and nonplanar porphyrin always contributed to the motion and flexibility of the macrocylce.[71,72] Other example such as Vitamin B_{12} derivatives and others corrins always found with the high degree of conformational flexibility,[73] while very specific conformational changes have been identified for the sirohemes present in nitrite and sulfite reductase.[57]

1.10 Objectives

The Stille reaction has been used in porphyrin chemistry to introduce some functional groups into the macrocycle. However, the literature only reports examples associated with C-C bond formations starting from porphyrin bromides and the nonporphyrin tin counterparts. The synthesis of porphyrin dimers is often performed via metal catalyzed reactions, e.g., Suzuki or Sonogashira coupling. Only a few examples have been reported so far for the synthesis of porphyrin dimers and functional polymers using a Stille approach. Moreover, to protect the porphyrin core from undesired metalation by copper (from CuI often used as a co-catalyst to increase the reaction rate or to improve the solubility of the starting porphyrins) the synthesis generally requires prior porphyrin metalation, preferably with zinc, that later has to be removed from a coupling product if necessary. At present, there is no universal procedure for Stille coupling reactions of porphyrins in terms of the reaction conditions. Reported protocols employ a variety of solvents, catalysts, and additives for the reactions.

The aim of this work to development a novel synthetic approach for the synthesis of free base stannyl porphyrins that can be used as coupling partners in Stille reactions. Depending on the reaction conditions either stannyl or dimeric porphyrins can be prepared and their physicochemical properties investigated.

In other hand, to improve the synthetic access to ferrocene porphyrin type electron transfer compounds meso-ferrocenyl appended porphyrins and bisporphyrins were prepared using Suzuki coupling reactions of borylated porphyrins with appropriate

ferrocene precursors. Yields were improved comparable to those previously reported in the literature. Photo physical studies were carried out for the ferrocene porphyrins and the dimers.

While to mimic the biological porphyrins due to their nonplanar conformation, the sterically strained novel dimeric, trimeric, and pentameric porphyrins containing a nonplanar porphyrin core have been synthesized using transition metal catalyzed reactions on functionalized octaethylporphyrins. Photophysical studies were carried out to the series for porphyrins.

CHAPTER 2

TIN PORPHYRINS AND THEIR PHOTOPHYSICAL PROPERTIES

Metal-catalyzed coupling reactions are an attractive synthetic tool for C-C bond formation and are used for modification of various organic molecules, especially heterocycles. Organotin compounds have found wide agricultural and industrial applications.[35-38] Recent studies have shown their potential use as antifungal agents and their relatively high *in vitro* antitumor activity. Stille coupling represents a simple approach to the synthesis of novel materials, including tin reagents and coupling products.[74-79]

Porphyrins has variety of applications in such as optoelectronics and nanotechnology as sensors and storage devices, photocatalysts in green chemistry, and photodynamic therapy agents for cancer treatments in medicine.[80-94] Development of new and more efficient methods to modify the porphyrin core to yield macrocycles with novel and improved physicochemical properties are required for these and other possible applications.

The Stille reaction has been used before in porphyrin chemistry to introduce some functional groups into the macrocycle.[95-98] However, the literature only reports examples associated with C-C bond formations starting from porphyrin bromides and the nonporphyrin tin counterparts.

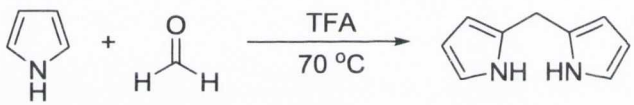
The synthesis of porphyrin dimers is often performed *via* metal catalyzed reactions like Suzuki or Sonogashira coupling.[99-102] Only a few examples have been reported so far for the synthesis of porphyrin dimers[103,104] and functional polymers[24,105] using a Stille approach. Moreover, to protect the porphyrin core from undesired metalation by copper (from CuI often used as a co-catalyst to increase the reaction rate[75,76] or to improve the solubility of the starting porphyrins) the synthesis generally requires prior porphyrin metalation, preferably with zinc, that later has to be removed from a coupling product if necessary.

At present, there is no universal procedure for Stille coupling reactions of porphyrins in terms of the reaction conditions. Reported protocols employ a variety of

solvents, catalysts, and additives for the reactions.[37] Depending on the reaction conditions either stannyl or dimeric porphyrins can be prepared and their physicochemical properties investigated.

2.1 Synthesis of starting material

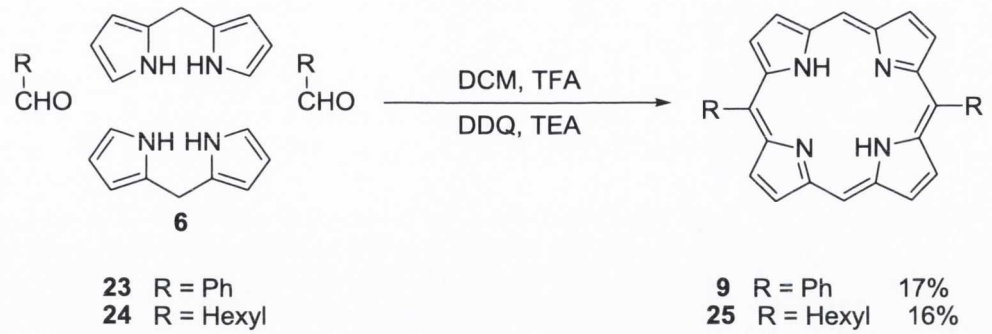
For this project, 5,15-diphenylporphyrin (DPP) **9** was used as a starting material.. These were synthesized by condensation of dipyrromethane (DPM) **6** and an appropriate aldehyde. Compound **6** was first synthesized from pyrrole **21** and paraformaldehyde **22** in 80% yield[107] as illustrated in Scheme 2.1.



21 **22** **6**

Scheme 2.1 Synthesis of dipyrromethane.

Compounds **9** and **25,** each with two free *meso*-positions available for subsequent functionalization, were synthesized using the appropriate aldehyde, DPM **6** as a precursor and TFA as a catalyst.[108,109] The product was purified using column chromatography and recrystalization with DCM:MeOH resulting in the isolation of **9** and **25** (Scheme 2.2).

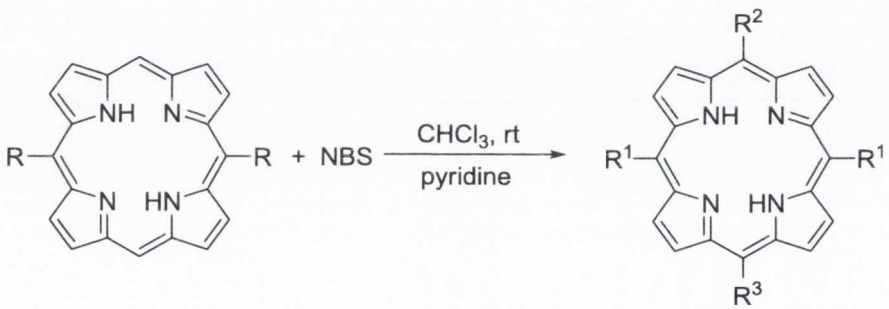


23 R = Ph
24 R = Hexyl

9 R = Ph 17%
25 R = Hexyl 16%

Scheme 2.2 Synthesis of DPP and 5,15-dihexylporphyrin.

Bromination with NBS have been used for meso disubstituted porphyrins to obtain the dibromo and monobromo porphyrins **26-28** (Scheme 2.3 and Table 2.1) in to 25-100% yields.[108]



9 R = Ph
25 R = Hexyl

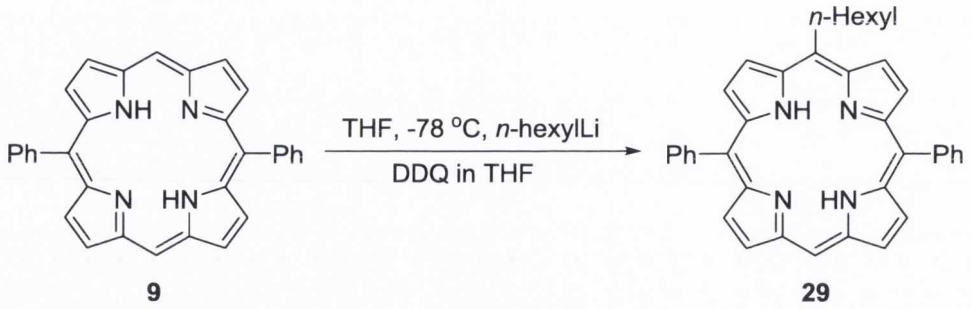
26 R^1 = Ph; R^2 = Br; R^3 = H 27%
27 R^1 = Ph; R^2 = R^3 = Br 100%
28 R^1 = Hexyl; R^2 = Br; R^3 = H 87%

Scheme 2.3 Synthesis of the bromoporphyrins.

Table 2.1 Synthesis of bromoporphyrins **26-28**

Porphyrin	Bromoporphyrins
9	**26**
9	**27**
25	**28**

Compound **29** was obtained by treatment of **9** with *n*-hexylLi under -78 °C in THF (Scheme 2.4).



9 **29**

Scheme 2.4 Synthesis of the 5-hexyl-10,20-diphenylpoprphyrin.

2.2 Synthesis of tin compounds

For this project four types of non-porphyrin reagents were synthetically tested. Tin compounds can be easily prepared starting from the corresponding bromides and can then be used for C-C bond formation in the presence of a catalyst.[107] Moreover, the precursors are commercially available, and the tin reagents are cheap to prepare compared to the related boronates widely utilized for Suzuki coupling.[108] The mono and bis-tin aromatic compounds **31**, **34** and **35** were synthesized on a large scale *via* organolithium reactions starting from commercially available mono or dibromoarenes **30**, **32**, **33** and tri(*n*-butyl)tin chloride (Scheme 2.5). In addition, use of commercially available **36**.

The reactions were carried out with an excess of *tert*-buLi (2.5 equiv. to that of monobromide) followed by addition of tri(*n*-butyl)tin chloride. The reaction of 1-bromonaphthalene gave the tin compound **31** in 94 %. The 1,4- and 1,3-bistin substituted compounds **34** and **35** were prepared in 54 % and 63 % yield, respectively using a similar method as for **31** but with the different dibromide.

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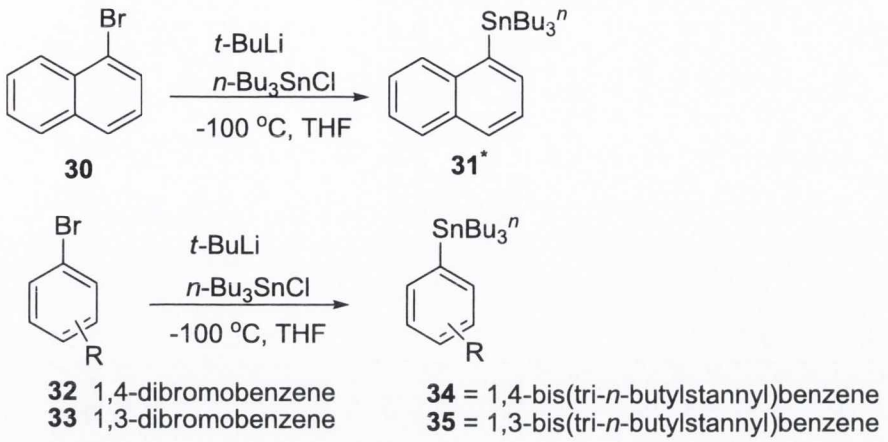
* Work carried out by Dr. N. N. Sergeeva

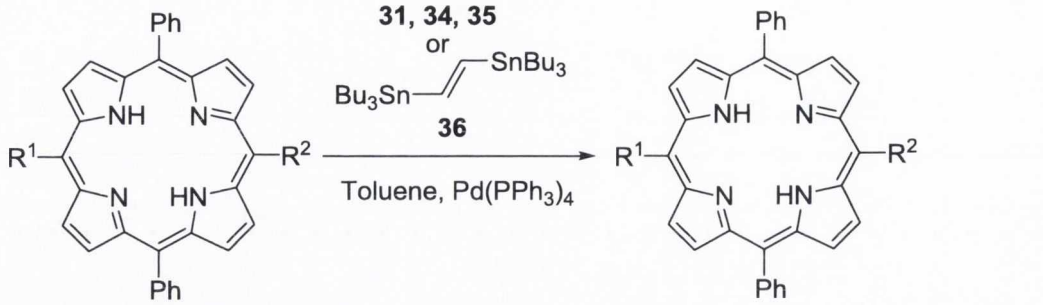


Scheme 2.5 Preparation of the mono- and bis-tin reagents **31**, **34** and **35**.

2.3 Synthesis of tin porphyrins and a dimer

Synthesis of tin porphyrins required the use of **26-28** as starting materials. The porphyrin bromides **26-28** are thermally stable and easily accessible molecules. No reaction was observed upon treatment of **28** with organotin compound due to the solubility problem. However, by using **26** and **27** as starting material with the corresponding tin reagents **31, 34**, **35** and **36**, the tin porphyrins **37-40** were obtained in up to 55 % yield.[101]

Importantly, the purifications of all tin complexes has to be carried on aluminum oxide; use of silica gel caused a rapid hydrolysis of the tin groups. 5,15-Dibromo-10,20-diphenylporphyrin **27** reacted with 1,4-bis(tri-*n*-butylstannyl)benzene **34** and tri-*n*-butylstannylnaphthalene **31** to give compounds **37** and **39.** The same approach can be used to synthesize **38** and **40** *via* a reaction of **26** with **35** and **36** (Scheme 2.6 and Table 2.2).



26 R^1 = Br, R^2 = H
27 R^1 = R^2 = Br

37 R^1 = Ph, R^2 = (4-*n*-$Bu_3SnC_6H_4$)- 53%
38 R^1 = H, R^2 = (3-*n*-$Bu_3SnC_6H_4$)- 21%
39 R^1 = R^2 = (1-naphthalenyl)- 50%
40 R^1 = H, R^2 = (*n*-$Bu_3SnCH{=}CH$)- 55%

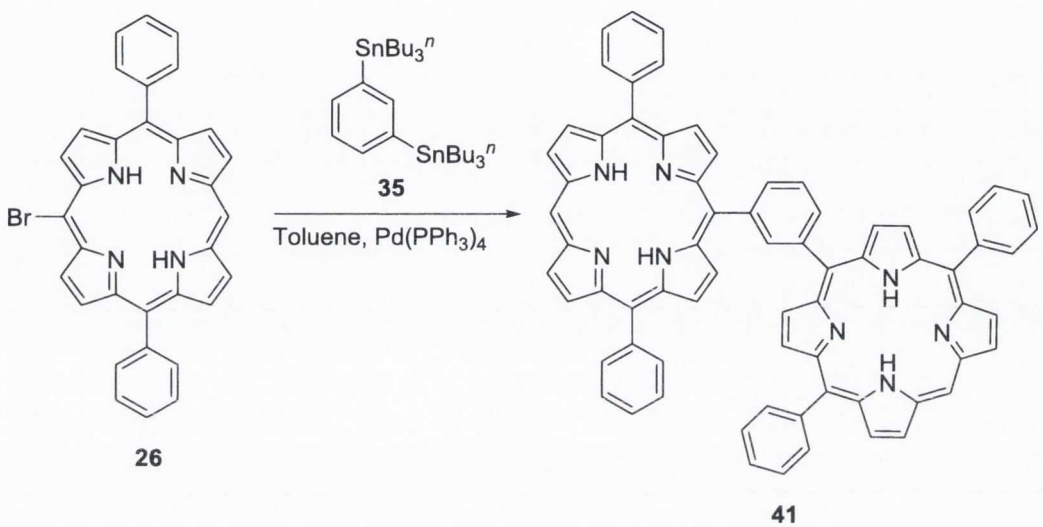
Scheme 2.7 Synthesis of the tin porphyrins **37-40**.

Table 2.2 Synthesis of tin porphyrins **31-34**

Porphyrin	Tin compounds	Tin porphyrins
27	**34**	**37**
26	**35**	**38**
27	**31**	**39**
26	**36**	**40**

Moreover, the porphyrin free bases can be used under these reaction conditions and no palladium insertion was observed during these transformations for the whole series. The reactions exclusively gave tin products, when two (for mono-substitution) or four (for bisproducts) equivalents of the tin compounds were used. No dimer formation was detected. Generally, these reactions proceeded until formation of the desired products only, and in the cases of lower yields the starting materials were recovered. Noteworthy, conditions involving CsF and CuI in most cases resulted in complex mixtures with a very low yield of the tin adducts.

This methodology can be further extended and used for the synthesis of porphyrin dimers. This was achieved by reducing the number of tin reagent equiv. to 0.5 equiv. The reaction mixtures were purified on silica gel to give compound **41** in 28 % yield via Stille coupling reaction of **26** with **35** (Scheme 2.7).[101]



Scheme 2.7 Synthesis of the dimer **41**.

2.4 NMR studies of tin compounds

Tin has three NMR active nuclei (spin 1/2) with relatively high natural isotope abundance of ^{115}Sn (0.34%), ^{117}Sn (7.68%), and ^{119}Sn (8.59%).[110] According to the literature, tin NMR studies were only carried out for a series of the porphyrinatotin(IV) complexes with axial ligation at tin(IV), to investigate their axial environmental surroundings.[110] ^{119}Sn (8.59 %) has a nuclear spin of ½ will gives a narrow NMR signal and is slightly more sensitive than ^{117}Sn or ^{115}Sn nuclei.[110] For the tin porphyrins, main attention was given to the use of ^{119}Sn NMR spectroscopy.

The tin reagents **31, 34**, **35** and **36**, and the tin porphyrins **37** and **40** exhibited resonances in the approximate range of δ -35 to -65 ppm compared to the starting

compound *n*-Bu_3SnCl with a chemical shift of 144.9 ppm. The data for the proton decoupled ^{119}Sn NMR are summarized in Table 2.3 and illustrated in Figure 2.1.

Table 2.3 ^{119}Sn NMR data (in ppm) for the tin reagents **31, 34**, **35** and **36** and tin porphyrins **37** and **40**.

Reagent	**^{119}Sn**
***n*-Bu_3SnCl**	144.9
31	-39.7
34	-43.9
35	-43.3
36	-63.3
Porphyrin	
37	-45.1
40	-40.5

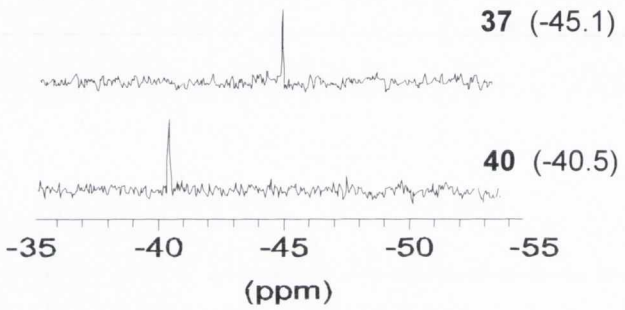


Figure 2.1 Proton decoupled ^{119}Sn NMR spectra for the porphyrins **37** and **40**.

The ^{119}Sn NMR resonances of the organostannanes can be correlated with the substitution pattern at the tin atom. Thus, the visible changes in the chemical shifts are observed in the case of the double bond pattern of **36** compared to aromatic substituents for the **31** and further for **34**. In all cases, resonances for the tin atoms of the porphyrins appear slightly downfield from the corresponding tin reagents.

Normally determination of the organotin compound structure depends on the Sn chemical shifts. However, more information describing the detailed proton-tin spin-spin interactions for the systems in which two pairs of H and Sn nuclei (H^1/Sn^1 and H^2/Sn^2, respectively) correlated to one another by a number of $^nJ(H\text{-}^{117/119}Sn)$ couplings. The spectra become more complicated because the ^{117}Sn and ^{119}Sn have the same spin and

are also present in almost equal isotopic ratios. Moreover, a little difference in *J* values are observed for the ^{117}Sn and ^{119}Sn nuclei.

The appearance of the two sets of the satellite signals centred with a major (H,H)-resonance singlet (6.96 ppm) for the symmetric olefin **36** (Figure 2.2A) obscures determination of the *J* (Sn,H). The lower part of the Figure 2.2A shows the spectrum obtained in homonuclear decoupling mode where the frequency of the field has been set at 6.96 ppm (double bond *singlet*).

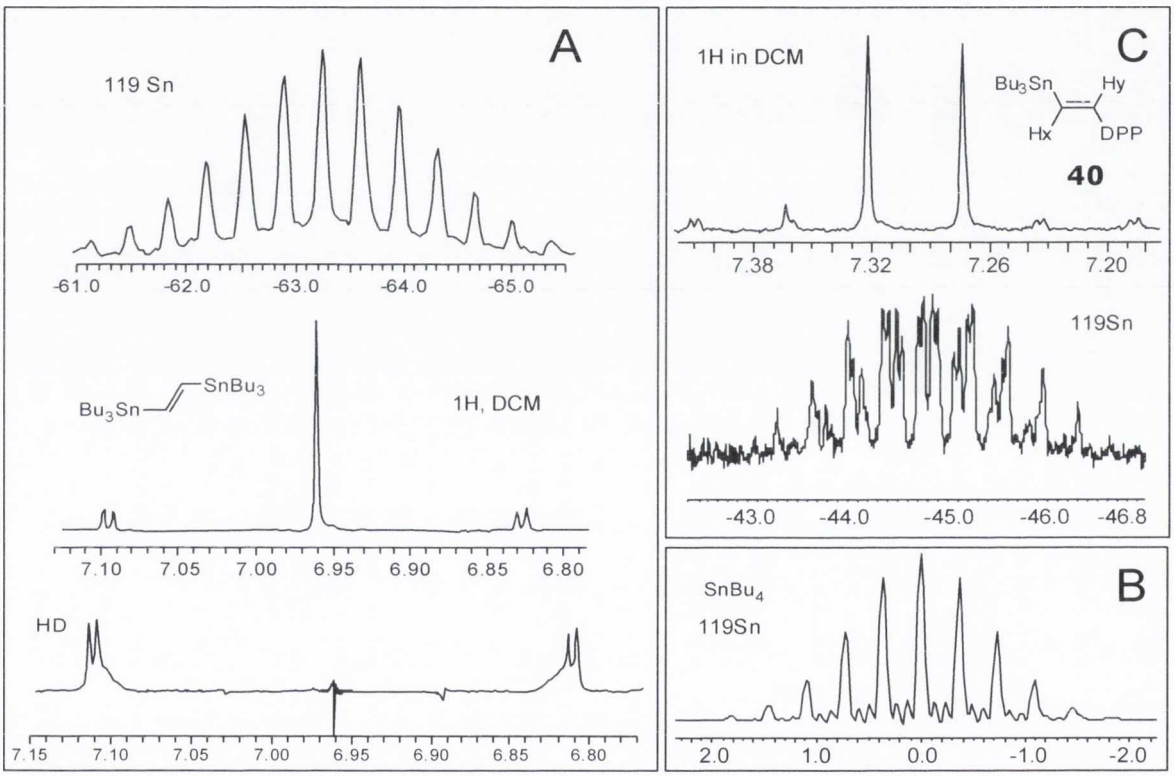


Figure 2.2 A) The proton coupled ^{119}Sn (149.3 MHz) and ^{1}H (400 MHz) NMR spectra in CD_2Cl_2; **B**) ^{119}Sn, ^{1}H, and homonuclear decoupling (at 6.96 ppm) for the compound **36**; **C**) ^{119}Sn spectrum of the external reference compound *n*-Bu_3Sn; ^{1}H (for H_x) and ^{119}Sn for the porphyrin **40**.

From Figure 2.2B it be can proven that the resonances, because the doublet satellites are not collapsed (SnH) with a *J* value for $^{117/119}$Sn-^{1}H ca. 106 Hz. On the other

hand, *n*-Bu_3Sn spin-spin coupling (Sn,H) can be calculated and the value is around 54 Hz for ^{119}Sn-^{1}H and from the literature the values for ^{117}Sn-^{1}H is around 52 Hz.[111] Figure 2.2C presents ^{1}H (only the resonance at 7.28 ppm (H_x) is shown) and proton coupled ^{119}Sn spectra. In this case a number of the spin-spin coupling systems can be considered as three separate resonances centred around 7.28 ppm of ^{1}H NMR which is (i) protons attached to non-NMR active tin ± 80 %; (ii) protons attached to NMR active tin i.e ^{1}H-^{119}Sn; (iii) protons attached to NMR active tin i.e ^{1}H-^{117}Sn. In the first case, the signal is a *doublet* with $J \sim 19.3$ Hz for *trans* spin-spin (H,H) coupling. In the other two cases, the signal is *double doublet,* which is a (Sn,H) spin coupling of 71.5 Hz and a (H,H) spin coupling of $J \sim 19.3$ Hz (Figure 2.3).

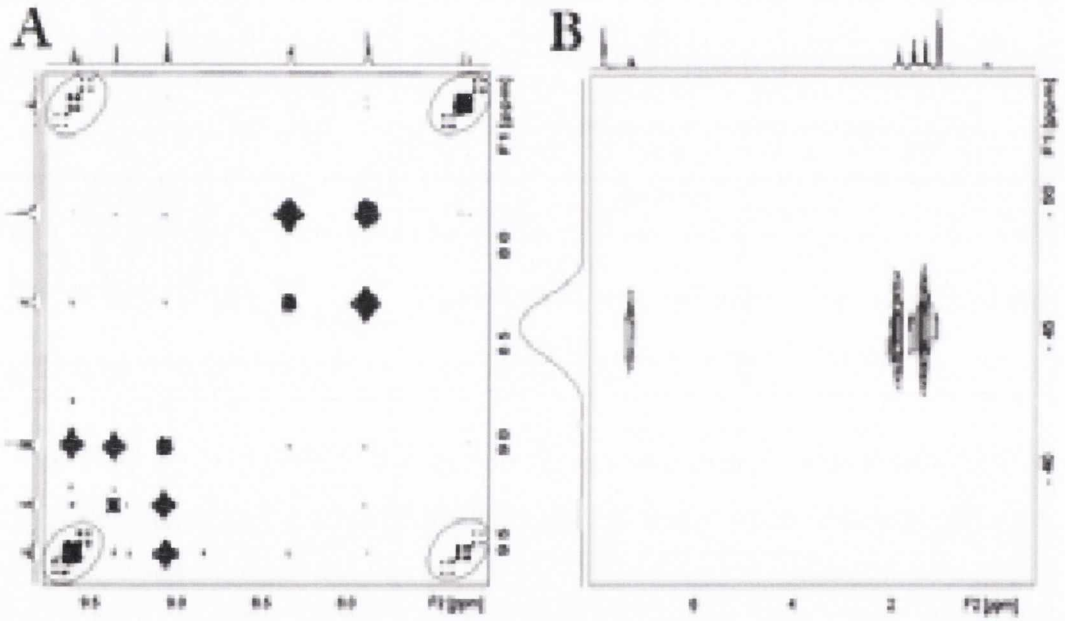


Figure 2.3 2D (H,H) TOCSY (600 MHz, $CDCl_3$): (A) double bond Hx and Hy, aromatic and porphyrin Hs [7-9 ppm]; (B) ^{1}H, ^{119}Sn HSQC spectra for **40**.

From the $SnBu_3$ fragment the same result can be obtained for the alkyl region (1-2 ppm). Here three sets of the resonance signals can be observed and *J* can be estimated as 8.2 Hz for the (H,H) of $Sn(CH_2Pr)_3$ and ca. 50 Hz for ($^{117/119}Sn$-^{1}H) spin-spin couplings. This is from the data for Bu_4Sn (Figure 2.3). Thus, the complexity of the

proton coupled ^{119}Sn NMR spectrum of the compound **40** can be explained as a number of the spin-spin coupling contributions originating from *ddt* (Figure 2.2C).

Determination of the position and the values of ^{n}J in ^{13}C revealed two interesting features. The isotopic difference of the order of ~2 Hz in ^{1}H NMR is also preserved in the ^{13}C NMR and a strong shift up-field for -Sn(CH$_2$Pr)$_3$ (10.2 ppm, the first ^{13}C resonance signal) that was confirmed by DEPT and HSQC (similar results were found for the compound **36** as well). It is known that J coupling constants for directly bonded (Sn,C) are very large; the values of the J ($^{117/119}$Sn-^{13}C) are *ca.* 336 Hz for the ^{1}J, ~53 Hz for the ^{2}J and ~21 Hz for the ^{3}J.

2.5 Photophysical studies of the tin porphyrins and the dimer

The absorption and emission spectra and the fluorescence lifetimes were measured out for all of the tin porphyrins and dimer. The porphyrins were excited at the energies of the Soret bands, resulting in a deviation of the mirror image rules of the emission spectra. Such exceptions of the mirror rules are often associated with the different geometry of the excited state compared to the ground states.[112] All tin porphyrins exhibit a larger bathochromic shift of the last Q-bands ~650 nm in CH_2Cl_2 compared to ~635 nm in THF. However, due to their relatively low solubility in CH_2Cl_2, and in some cases unwanted protonation (dication formation) in this solvent, the spectra for these compounds were recorded in THF (Figure 2.4).

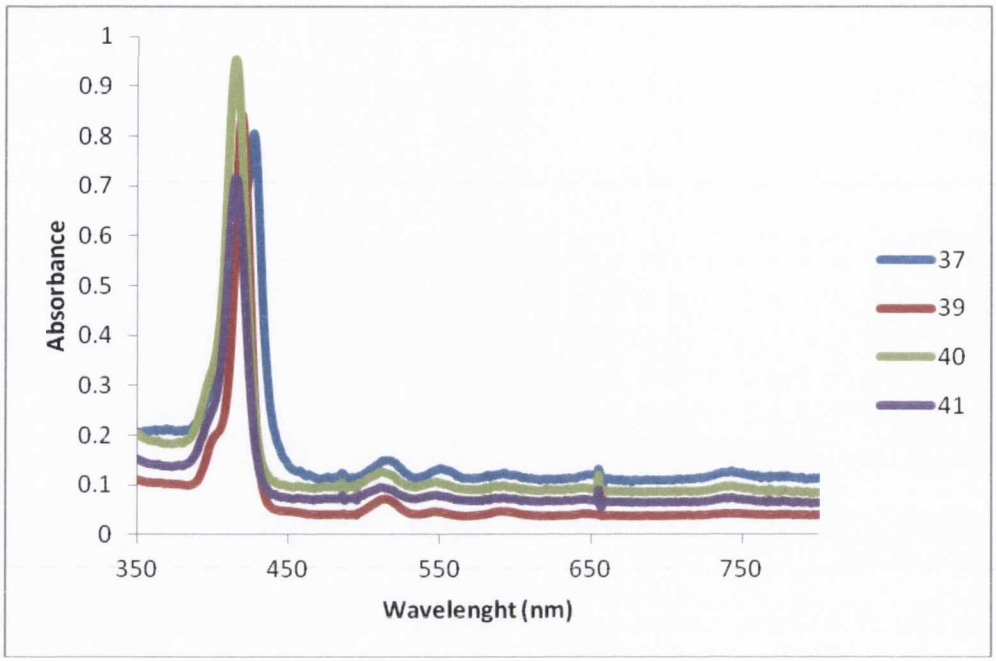


Figure 2.4 Absorption spectra of the porphyrins **37**, **39**, **40** and **41** (3.33×10^{-3}M in THF).

The tin compounds showed a much higher emission intensity compared to the corresponding bromides (as an example, the bromoporphyrin **27** is shown in Figure 2.5.

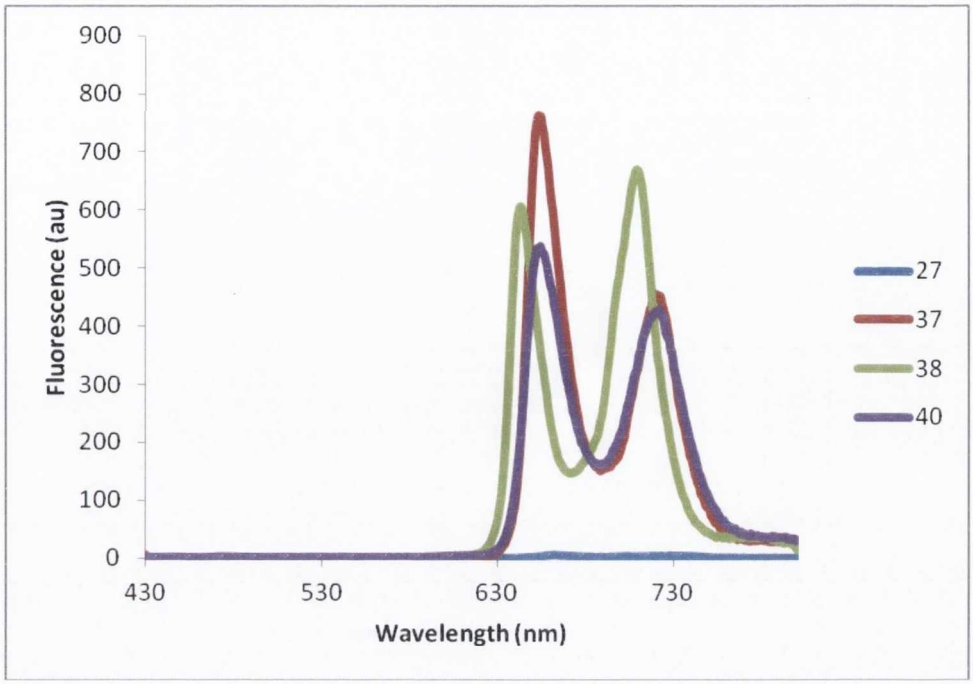


Figure 2.5 Emission spectra at the excitation energies of the Soret bands for the porphyrins **27, 37**, **38**, **40** (1.85×10^{-3}M in THF).

The porphyrins were excited at the energies of the Soret bands and then the emission was detected in the UV-vis region. In all cases large Stokes shifts were observed (Table 2.3). Fluorescence lifetime measurements were carried out in THF and excitation of the porphyrins was performed by 635 nm laser with pulse rate of <200 ps. The laser (635 nm) targeted the lower-energy Q-band in the absorption spectra, which originates from the lowest singlet excited state S_1. Fluorescence lifetime results are presented in Table 2.4.

Table 2.4 Photophysical data of the compounds **37**, **38**, **39**, **40** and Foscan® in THF.

Entry	Absorption λ_{max}/nm [log (ξ)]	Excitation λ_{ex}/nm	Emission at 298K Λ_{em}/nm (τ_f, ns)
Foscan®	373 (5.0), 408 (5.4), 419 (5.4), 516 (4.7), 541 (4.7), 600 (4.6), 652 (4.9)	373	655 (8.8)
37	417 (5.3), 427 (5.4), 516 (4.7), 551 (4.6), 593 (4.5), 648 (4.5)	417, 427	652, 722 (9.5 ± 0.1)
38	412 (5.4), 440 (5.1), 509 (4.6), 545 (4.5), 585 (4.5), 643 (4.6)	412	643, 709 (10.1 ± 0.1)
39	415 (5.6), 511 (4.8), 547 (4.7), 592 (4.7), 645 (4.6)	415	653, 721 (7.7 ± 0.1)
40	408 (5.8), 420 (5.7), 508 (4.9), 540(4.7), 584 (4.7), 640 (4.5)	409	643, 709 (10.9 ± 0.1)

Concentration for all samples: 7.39×10^{-7} $molL^{-1}$ in THF; *Laser: 370 nm (pulse <1 ns); 635 nm (<200 ps)

Photophysical properties of the tin porphyrins and the dimer were compared with the lifetime of Foscan® (2,3-dihydro-5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin) in THF at the same concentration. Foscan is an approved drug in photodynamic therapy.[3,109,112] This comparison showed that the Q-bands in the absorption spectra for the porphyrin synthesized and the lifetimes of the novel compounds are comparable to Foscan®. So, the same region of the optical spectrum (a last Q-band) and a longer fluorescence lifetime of these novel porphyrins make them the promising test compounds for use in PDT.

2.6 Conclusion

Meso functionalised porphyrins and organotin reagents were prepared via condensation, bromination and organolithium reactions. Tin porphyrins **37-40** were successfully synthesized in 20-55% *via* Stille coupling reaction and using palladium as catalyst. These compounds are stable and can be stored in solid form for several months. They show a significant synthetic potential and could be used as building blocks in coupling reactions. On the other hand by using a same method and reducing the tin-reagent equivalents, dimer porphyrin **41** was synthesized in 28%.

^{119}Sn NMR studies can be used for analysis and characterization of the tin porphyrins. It conveniently gives a narrow signal and the spectra can be recorded within a short period of time. However, tin NMR active nuclei give extremely complicated spectra where ^{1}H and $^{117/119}$Sn multiples arise from the different types of spin-spin couplings.

Photophysical analyses were carried out for the series of the tin porphyrins and the dimer. Emission spectra for the tin porphyrins were recorded in THF and showed an increased intensity for the latter compared to the starting bromides. The fluorescence lifetimes were measured for the tin porphyrins and the dimer compared with commonly used PDT drug Foscan®.

CHAPTER 3

FERROCENE PORPHYRINS AND THEIR PHOTOPHYSICAL PROPERTIES

Porphyrins[113-122] and ferrocenes[123-125] are most commonly used for applications in molecular electronic devices,[126-129] or as models for multiple-electron transfer reactions,[130,131] and also as porphyrins known as a suitable agents for the photodynamic treatment of cancer.[132-136]

Due to their promising photochemical properties, donor-acceptor systems with a direct meso-ferrocene linkage have found frequent use in recent studies.[121,137-144] However, despite this interest the synthetic chemistry of these compounds is lagging behind developments

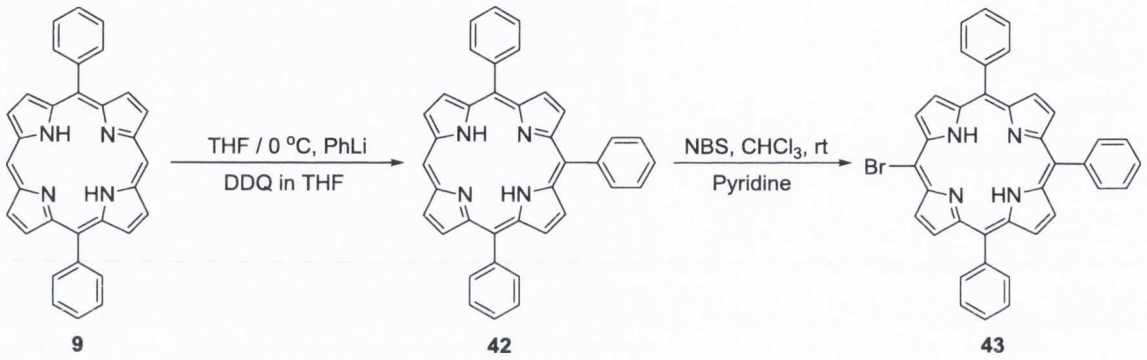
Previously all ferrocene porphyrins with one, two or four ferrocene units directly attached on the *meso-* position of porphyrin have been synthesized *via* condensation reactions using appropriate aldehydes, pyrroles and or dipyrromethanes. [121,131,137-141,145-155] These reactions are prone to scrambling and give widely varying yields ranging from 0.5 to 40 % depending on the system used and mostly at the lower end of the scale.

Here we introduce a new method of synthesizing symmetrical and unsymmetrical ferrocene porphyrin compounds (one or two ferrocene units directly attached to the meso position of porphyrin) and ferrocene-bridged bisporphyrin *via* Suzuki coupling reaction by new borylated porphyrin as a starting material.

The porphyrins synthesized were fully characterized by spectral analysis, including ^{1}H and ^{13}C NMR, UV and MALDI-TOF MS. Photophysical properties of the novel porphyrins prepared including absorption, emission, and fluorescence lifetimes were investigated. Fluorescence analyses indicated that quenching process occurring due to the interaction between porphyrin and ferrocene. A fluorescence lifetime measurement of ferrocene porphyrins was detected in the region of 7.4 – 10.3 ns.

3.1 Synthesis of starting material

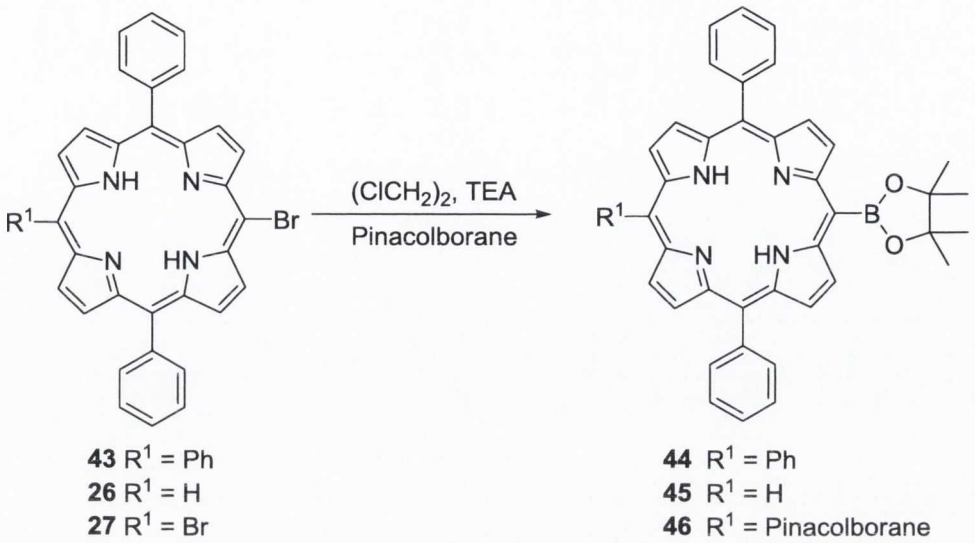
Compounds **42** has been synthesized *via* organolithium reagent, which was obtained by treatment of **9** with PhLi at 0 °C in THF and compound **42** has been treated with NBS to obtain the bromoporphyrin **43** (Scheme 3.1).



9 **42** **43**

Scheme 3.1 Synthesis of the 5,10,20-triphenylpoprphyrin **42** and 5-bromo-10,15,20-triphenylporphyrin **43**.

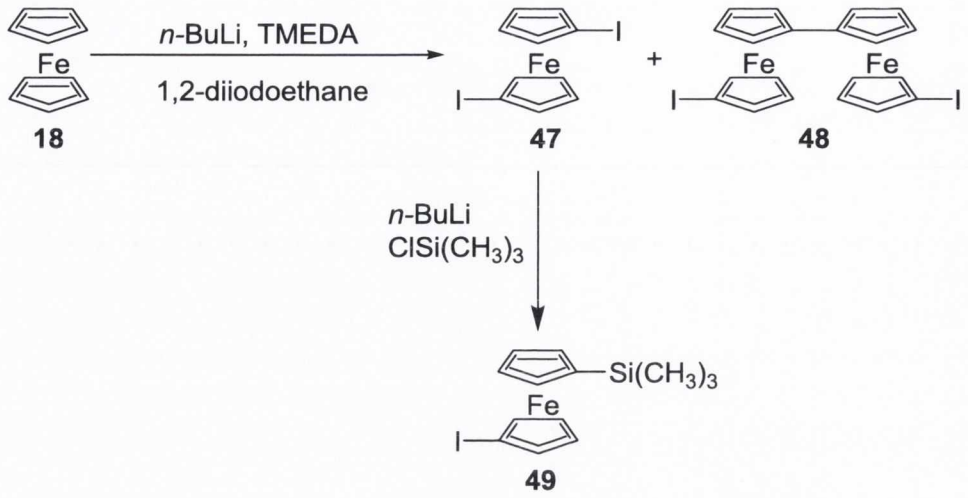
The suzuki cross-coupling reaction has been shown to be an efficient method for coupling of borylated porphyrins with aryl halides.[145-150] Novel borylated porphyrins **44-46** were synthesized from bromoporphyrins[152] **26**, **27** and **43** via Pd-catalyzed reaction with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane).[153,154] The reactions were carried out with excess of pinacolborane (20 equiv. to the brominated porphyrin or 40 equiv. in the synthesis of compound **46**) yielded **44-46** in 87%, 91% and 40% yields, respectively by the reaction shown in Scheme 3.2.



Scheme 3.2 Preparation of borylated porphyrins **44-46**.

3.2 Synthesis of ferrocene compounds

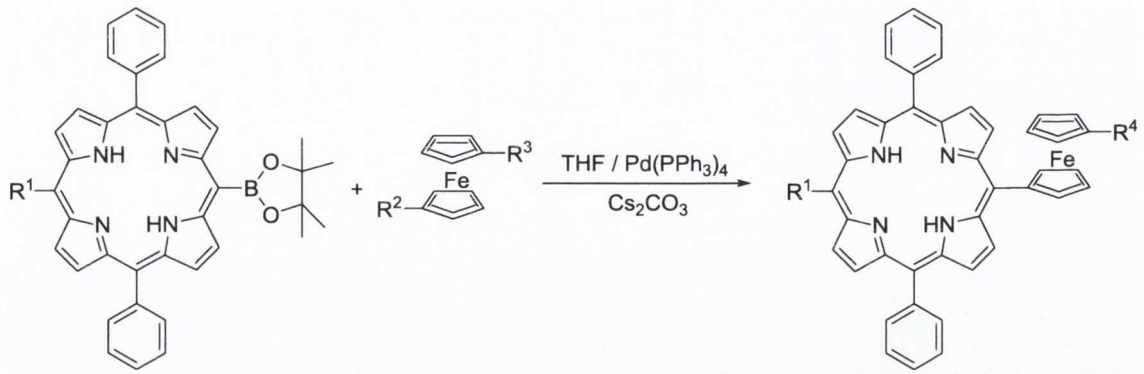
The mono- and bis-ferrocene compounds were synthesized on a large scale *via* organolithium reactions starting from commercially available ferrocene. Using excess of *n*-BuLi (2.2 equiv. to the ferrocene compound) in 1,2-diiodoethane provided **47** in 68% and **48** in 28% yield. Compound **49** was obtained 61% yield, by the reaction shown in Scheme 3.3 with 1:1 equiv. of *n*-BuLi followed by chlorotrimethylsilane. Their structures were verified by spectroscopic analysis including ^{1}H NMR.[142-144]



Scheme 3.3 Preparation of mono- and bis-ferrocene reagents **47-49**.

3.3 Synthesis of ferrocene porphyrin compounds

Compounds **44-46** were reacted with compounds **18**, **47-49** under Suzuki cross coupling conditions with the stronger base Cs_2CO_3 and $Pd(PPh_3)_4$ as the catalyst.[156] The catalyst for all these reactions was freshly made[155] and the residue purified by column chromatography on silica gel (hexane:DCM 1:1 v/v). The desired ferrocene porphyrin compounds **50-57** were isolated in 22% - 38% (Scheme 3.4 and Table 3.1).



44 R^1 = Ph
45 R^1 = H
46 R^1 = Pinacolborane

18 $R^2 = R^3 = H$
47 $R^2 = R^3 = I$
48 $R^2 = I$, R^3 = Fc-I
49 $R^2 = I$, $R^3 = Si(CH_3)_3$

37% **50** R^1 = Ph, $R^4 = Si(CH_3)_3$
29% **51** R^1 = Ph, R^4 = Fer-I
22% **52** R^1 = Ph, R^4 = I
23% **53** R^1 = H, $R^4 = Si(CH_3)_3$
38% **54** R^1 = H, R^4 = Fc-I
37% **55** R^1 = H, R^4 = I
23% **56** R^1 = H, R^4 = H
29% **57** R^1 = Fc-I, R^4 = I

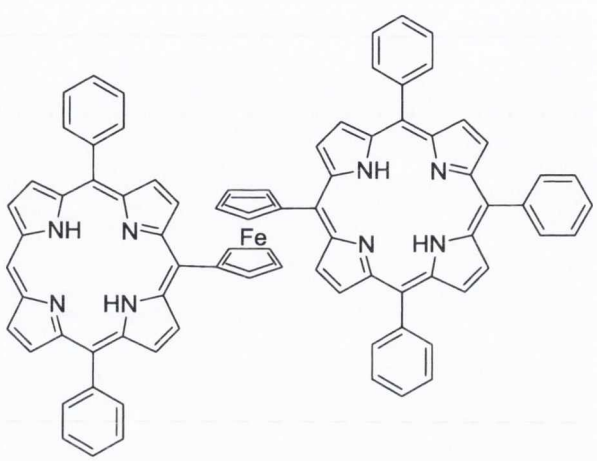
Scheme 3.4 Synthetic route for the preparation of ferrocene porphyrin compounds **50-57**.

Table 3.1 Synthesis of ferrocene porphyrins **50-57**

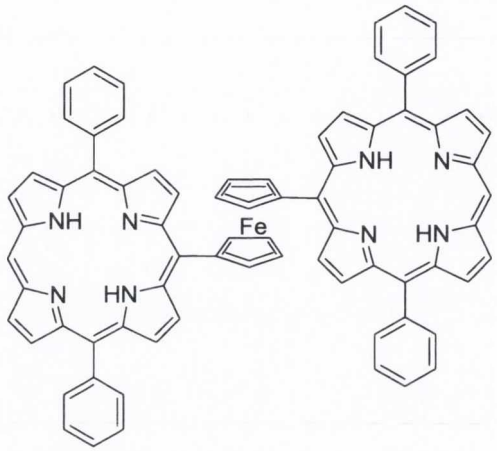
Porphyrin	Ferrocene	Ferrocene porphyrins
44	**49**	**50**
44	**48**	**51**
44	**47**	**52**
45	**49**	**53**
45	**48**	**54**
45	**47**	**55**
45	**18**	**56**
46	**47**	**57**

By using the same approach, a ferrocene-bridged bisporphyrin (dimer) can be synthesized by coupling 1.0 equiv. of compound **55** with 1.0 equiv. of borylated porhyrins **44** or **45**. The reaction mixtures were purified by column chromatography (silica gel) using hexane:DCM (2:3 v/v) as eluents to give the compounds **58** and **59** in

30% and 28% yield respectively. However, a symmetric dimer **59** also has been isolated from the reaction mixture of compound **55** in 9% yields.



58 (28%)



59 (30%)

All ferrocene porphyrin compounds are stable and have good solubility in common organic solvents. The structures of the ferrocene porphyrin compounds, **50-55**, **57-59** were elucidated by ^{1}H NMR, ^{13}C NMR, UV-vis and MALDI-TOF mass spectrometric analysis. All the analytical and spectral data were consistent with the predicted structures. While compound **56** was previously synthesized and compare by literature.[132]

^{1}H NMR data for the ferrocene porphyrins and the dimers were summarized in the Table 3.1. For example compound **57** with two unit ferrocene attached to the meso position of the DPP show β proton at the range 9.82-8.70 ppm (doublet, J = 4.0 Hz). For free base porphyrin such as DPP indicated β proton as a doublet at ~ 9.50 ppm (J = 4.0 Hz), means β proton for the ferrocene pophyrin compound shifted to the lower field. This is due to the increased anisotropic effect and van der Waals deshielding that comes from ferrocenyl group.

For the ferrocene unit the signal indicated at the range 5.53 – 4.05 ppm and the inner –NH protons for all the ferrocene porphyrin compounds are shifted up-field and appear as a broad singlet at ~ 2.60 ppm. However for the compound **57** (-1.66 ppm) the

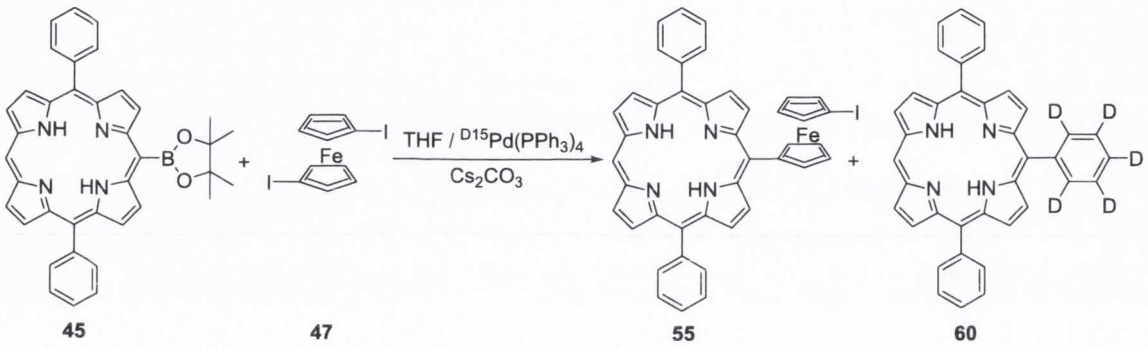
inner –NH appears at 0.97 ppm downfield compared to other ferrocene porphyrin compounds. Its shows when more ferrocene units are substituted on the porphyrin, the inner –NH proton will be less shielded, because the ferrocene unit will decrease the π-orbital overlap in the porphyrin core and the π current inside the porphyrin ring.

Table 3.2 ^{1}H NMR data of the ferrocene porphyrin compounds.

Compounds	meso, β and aromatic	Ferrocene unit	NH
50	10.00 (d, J = 3.5 Hz, 2H), 8.78 (m, 6H) 8.22 (m, 6H), 7.78 (m, 9H)	5.56 (t, J = 1.8 Hz, 2H), 4.82 (t, J = 1.8 Hz, 2H), 4.24 (m, 4H)	-2.28 (br, 2H)
51	9.96 (br, 2H), 8.77 (m, 6H) 8.23 (m, 6H), 7.78 (m, 9H)	5.47 (br, 2H), 4.63 (br, 2H), 4.53 (br, 2H), 4.19 (m, 4H), 4.08 (s, 4H), 3.89 (s, 2H)	-2.29 (br, 2H)
52	10. 09 (d, J = 7.8 Hz, 2H), 8.78 (m, 5H), 8.22 (m, 5H), 7.78 (m, 9H), 7.56 (m, 2H)	5.59 (t, J = 1.8 Hz, 2H), 4.84 (t, J = 1.7 Hz, 2H), 4.48 (t, J = 1.7 Hz, 2H), 4.10 (t, J = 1.8 Hz, 2H)	-2.30 (br, 2H)
53	10.10 (br, 3H), 9.27 (d, J = 4.9 Hz, 2H), 8.93 (d, J = 3.9 Hz, 2H), 8.86 (d, J = 4.9 Hz, 2H), 8.26 (dd, J = 2.0 Hz, 3.0 Hz, 4H), 7.82 (m, 6H)	5.59 (br, 2H), 4.87 (br, 2H), 4.21 (br, 4H)	-2.62 (br, 2H)
54	10.09 (s, 1H), 10.02 (br, 2H), 9.27 (d, J = 4.6 Hz, 2H), 8.93 (d, J = 4.7 Hz, 2H), 8.83 (d, J = 4.7 Hz, 2H), 8.27 (d, J = 4.7 Hz, 4H), 7.82 (m, 6H)	5.44 (s, 2H), 4.61 (s, 2H), 4.50 (s, 2H), 4.18(s, 4H), 4.08 (d, J = 1.8 Hz, 4H), 3.89 (s, 2H)	-2.63 (br, 2H)
55	10.12 (s, 1H), 10.03 (br, 2H), 9.27 (d, J = 4.9 Hz, 2H), 8.89 (dd, J = 3.9 Hz,	5.60 (s, 2H), 4.84 (s, 2H), 4.48 (s,	-2.65 (br, 2H)

	4.9 Hz, 4H), 8.26 (d, *J* = 5.8 Hz, 4H), 7.82 (m, 6H)	2H), 4.09 (s, 2H)	
56	10.10 (m, 3H), 9.26 (d, *J*= 4.7 Hz, 2H), 8.94 (d, *J*= 4.7 Hz, 2H), 8.85 (d, *J*= 4.7 Hz, 2H), 8.27 (m, 4H), 7.82 (d, *J*=6.5 Hz, 6H)	5.59 (s, 1H), 5.53 (s, 1H), 4.86 (s, 1H), 4.77 (s, 1H), 4.21 (s, 1H), 4.11 (s, 2H), 4.05 (s, 2H)	-2.59 (s (br), 1H)
57	9.82 (dd, *J* = 4.9 Hz, 5.2 Hz, 4H), 8.70 (t, *J* = 4.1 Hz, 4H), 8.20 (m, 4H), 7.79 (m, 6H)	5.53 (d, *J* = 1.8 Hz, 3H), 4.82 (dt, *J* = 1.8 Hz, 12.2Hz, 3H), 4.42 (t, *J* = 1.8 Hz, 2H), 4.33 (br, 2H), 4.14 (s, 4H), 4.02 (t, *J* = 1.8 Hz, 2H)	-1.66 (br, 2H)
58	10.05 (s,1H), 9.84 (m, 4H), 9.19 (m, 2H), 8.72 (m, 7H), 8.44 (m, 3H), 8.23 (m, 4H), 7.91 (m, 10H), 7.45 (m, 11H)	5.65 (br, 4H), 4.96 (br, 4H)	-2.75 (br, 2H), -3.04 (br, 2H)
59	10.07 (s,2H), 9.90 (br, 4H), 9.21 (d, *J* = 4.0 Hz, 4H), 8.69 (d, *J* = 4.0 Hz, 4H), 8.03 (d, *J* = 3.5 Hz, 4H), 7.56 (m, 12H), 7.39 (m, 8H)	5.59 (s, 4H), 4.86 (s, 4H)	-2.96 (br, 4H).

All reactions for the synthesis of ferrocene porphyrin compounds yielded side products. When using **44** as a starting material TPP (**3**) was obtained while use of **45** as a starting material gave TrPP (**42**) as a side product. To prove the phenyl group is desired from the catalysts, four reactions with different type of catalysts were carried out as shown in Scheme 3.5.



45 47 55 60

Scheme 3.5 Synthesis of compound **55** using $^{D15}Pd(PPh_3)_4$.

For the first reaction commercially available $Pd(PPh_3)_4$ was used, for the second and third reaction, freshly made labeled phenyl $^{D15}Pd(PPh_3)_4$ and $Pd(PPh_3)_4$ were prepared while for the fourth reaction was carried out using $Pd(dba)_2$ as the catalyst.

The first reaction with **45** gave **55** and 5,10,15-triphenylporphyrin in 22 and 28 % yield, respectively. Reactions with $Pd(P(C_6D_5)_3)_4$ gave 22 % of **55**, 22 % of deborylated 5,15-diphenylporphyrin (DPP) and 9 % of 5,10,15-triphenylporphyrin. Incorporation of phenyl residues from the catalyst into the 5,10,15-triphenylporphyrin was proven by MALDI-TOF mass spectrometry (Figure 3.1). The *m/z* value of 543.2471 for the compound derived from the reaction with deuterated catalyst corresponded to the formula $C_{38}D_5H_{21}N_4$. Besides that, it also can proof that by using freshly made $Pd(PPh_3)_4$ catalysts, amount of produced TrPP can be minimize. Reaction with $Pd(dba)_2$ gave no product, only starting material was recovered

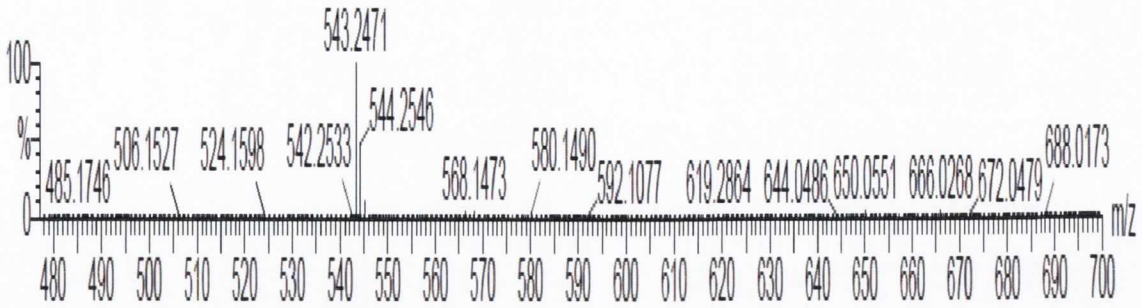


Figure 3.1 Mass spectra shown Chemical Formula : $C_{38}H_{21}D_5N_4$, Exact mass 543.2471 found 543.2471.

3.4 Photophysical studies of ferrocene porphyrins (monomeric and dimeric)

Photophysical studies were performed for all ferrocene porphyrins (Table 3.3). The visible absorption spectra of the porphyrin conjugates are characterized by the typical Soret band and Q-bands; absorption of the ferrocene unit at 292 and 441 nm is very low.[157-159] For example, compound **55** with a ferrocene unit at the meso position exhibits the Soret band at 415 nm and Q bands at 509, 584 and 661 nm. The ferrocene-bridged bisporphyrins **59** exhibited the Soret band at 417 nm and Q bands at 516, 549, 593, 651 and a weak absorption at 742 nm.

The Soret and Q bands in all the ferrocene porphyrin compounds are significantly red shifted compared to DPP (405, 502, 534, 575 and 631 nm). It shows that the ferrocene unit can extend the π conjugation of the central porphyrin core and strong electronic coupling between porphyrin conjugated system and the ferrocene moiety.[160] Beside that, the broadening of this signal indicates a partial mixing of π-π^* with an intramolecular charge-transfer.[161-163]

Table 3.3 UV-visible absorption, fluorescence emission and fluorescence lifetime spectral data of ferrocene porphyrin compounds with DPP.

Compound	[a] Absorption λ_{max}/nm	[b] Emission λ_{em}/nm	[b] Fluorescence lifetime (τ_f, ns)[a]
DPP	405, 502, 534, 575,631	635, 700	12.3 ± 0.1
50	420, 517, 595, 653	656, 723	7.4 ± 0.1
51	418, 515, 549, 592, 649	654, 720	8.6 ± 0.1
52	419, 513, 581, 669	647, 712	8.8 ± 0.1
53	416, 507, 588, 668	651, 710	8.1 ± 0.1
54	413, 509, 542, 586, 642	653, 719	9.2 ± 0.1
55	415, 509, 584, 661	647, 711	10.3 ± 0.1
56	418, 507, 600, 671	653, 717	7.5 ± 0.1
57	417, 516, 549, 593, 651, 742	653, 718	8.6 ± 0.1
58	416, 513, 547, 591, 647, 742	648, 709	9.3 ± 0.1
59	413, 510, 551, 588, 643, 741	648, 709	9.5 ± 0.1

[a] UV-visible measurement was carried out in THF (3.33×10^{-3}M).

[b] Fluorescence lifetime measurements were carried out in THF (5.56×10^{-4}M) and excitation of the porphyrins was performed by 370 nm laser with pulse rate of < 1 ns.

Figure 3.2 shows the relative steady state fluorescence spectra for DPP, **55** and **57-59** in THF. DPP was excited at 405 nm (Soret band) and compounds **55**, **57-59** were excited at 415 nm, 417 nm, 416 nm and 413 nm respectively. Two emission bands at 635-650 nm and 700-716 nm were observed. The relative intensity of ferrocene compounds has been significantly quenched from one ferrocene unit attached to porphyrin (**55**) to ferrocene-bridged bisporphyrin (**58** and **59**) and the intensity completely quenched when two ferrocene units are attached to porphyrin (**57**) when compared to DPP.

These quenching processes take place when ferrocene is attached on to meso position of the porphyrin and it is suggest that this quenching process takes place

because the electron transfer from ferrocene to the singlet excited state of the porphyrin ring through a rapid electron-transfer mechanism.[159,164] The mechanism of quenching of the excited states of porphyrins by ferrocene depends on energy transfer, heavy atom metal effects and redox mechanism.[164-171]

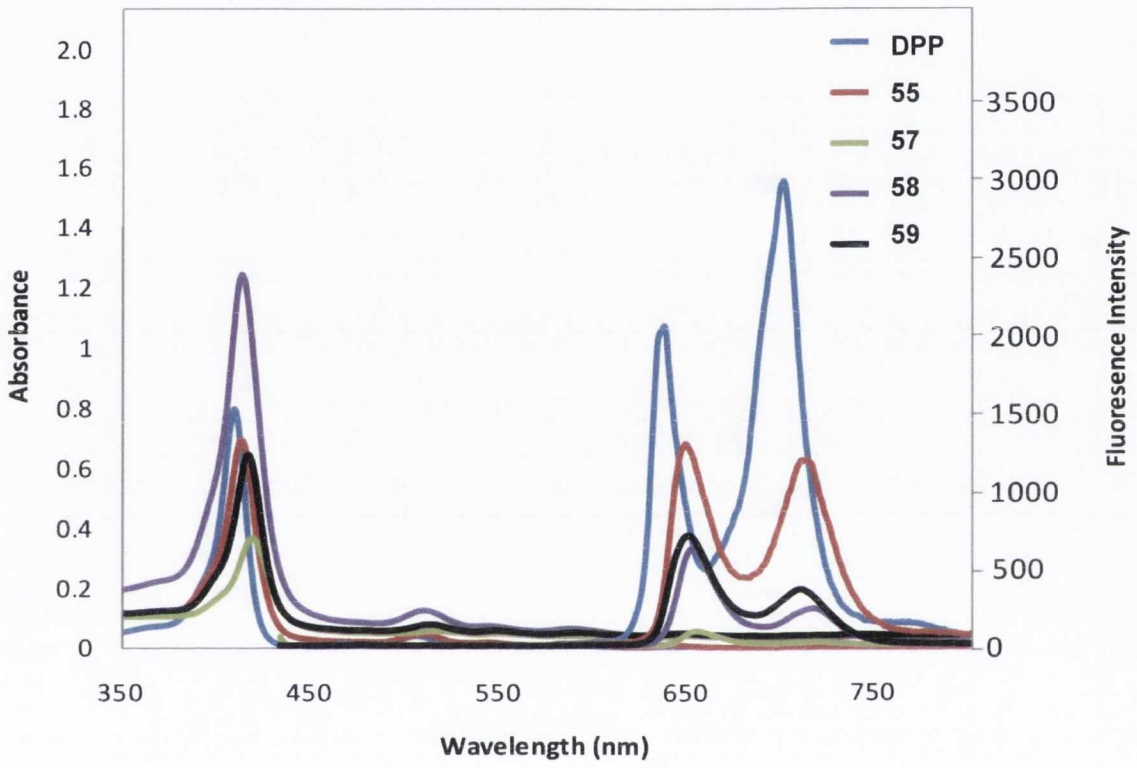


Figure 3.2 Absorption and fluorescence spectra at the excitation energies of the Soret bands of the porphyrins DPP, **55**, **57-59** (3.33×10^{-3}M in THF for absorption and 5.56×10^{-4}M in THF for fluorescence).

The fluorescence lifetimes for all the ferrocene porphyrins are summarized in Table 3.2. It shows that all ferrocene porphyrin compounds have shorter lifetimes compared to the DPP. This suggests an efficient photoinduced electron transfer from ferrocene to the excited singlet state of porphyrin.[172]

3.5 Conclusion

In conclusion, meso functionalized porphyrins and ferrocene reagents were prepared *via* condensation, bromination, borylated and organolithium reactions. Nine novel free base ferrecone porphyrins (**50-55**, **57**) including dimers (**58**, **59**) including with one known ferrocene porphyrin **56** were successfully synthesized *via* Suzuki-coupling reaction using palladium as a catalyst in 28-30 % yields.

Synthesis of the ferrocene porphyrins yielded unsual but common type of side product. This has been explained by the unlikely fragmentation of the porphyrin that arises from the reaction using palladium as a catalyst and the structure was confirmed by MALDI-TOF mass spectrometry.

All the compounds were fully characterized by spectral analysis, including ^{1}H and ^{13}C NMR, UV and MALDI-TOF MS. Photo physical studies were carried out for the ferrocene porphyrins and the dimers. Emission spectra showed that quenching process which was observed due to the interaction between the porphyrin and ferrocene group. The fluorescence lifetime was measured and have shorter lifetimes compared to the DPP.

CHAPTER 4

NONPLANAR PORPHYRINS AND PHOTOPHYSICAL PROPERTIES

Since last two decades, nonplanar porphyrins become an interesting to the chemists not only as biomimetic model compounds but also for their novel chemical reactivity and for their remarkable physicochemical properties.[173] Synthetic nonplanar porphyrins allow an understanding of the role of the macrocycle distortion to the chromophore properties in intact pigment protein complexes.[173] A prime strategy to access such molecule has been achieved by substituted the porphyrin periphery with sterically demanding substituents to afford the so-called 'highly substituted porphyrins'.[57]

2,3,7,8,12,13,17,18-Octaethylporphyrin **2** (OEP), is one of the most widely studied compounds because of good solubility, stability and high symmetry. OEP is fully substituted with ethyl group on the β positions and has four free meso positions for functionalization. When substituted in the meso position, the molecule become sterically strained and this properties is important to mimic the biological porphyrins such as heme and cholorophyll due to their nonplanar conformation.[57]

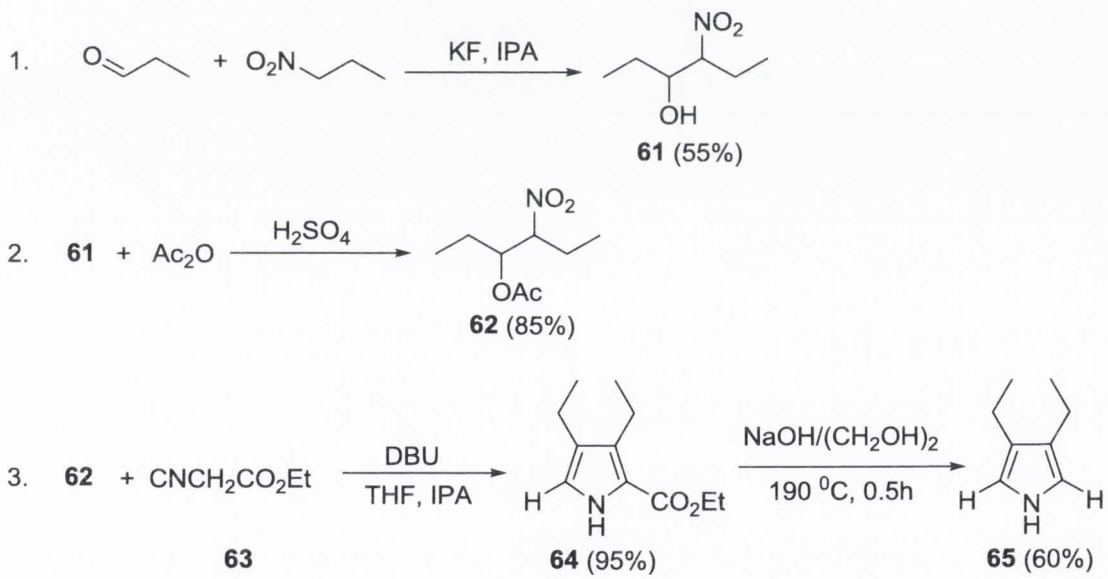
Multiporphyrin arrays incorporating nonplanar porphyrins another way to mimic biological porphyrin system. They are widely used in optical applications (nonlinear optics[174] and optical limiting[175]), medicine (photodynamic therapy[176] and DNA cleavage[177,178]), molecular sensing[179] and molecular recognition. [180]

Previously no multiporphyrin arrays containing β- and meso substituted porphyrins linked by phenylacetylene or phenyl linkers had been synthesized. However, we synthesized multiporphyrin arrays contained meso substituted porphyrins linked by phenylacetylene.[181] By using the same approached, novel dimeric, trimeric, and pentameric porphyrins containing a nonplanar porphyrin core have been successfully synthesized using transition metal catalyzed reactions on functionalized octaethylporphyrins.

4.1 Synthesis of meso functionalized Octaethylporphyrins

Synthesis of 3,4-diethylpyrrole **65** takes four main steps which are presented in scheme 4.1.[12] First step, yields 4-nitro-3-hexanol **61** in 55% yield and in the second step, an 85% yield of 4-acetoxy-3-nitrohexane **62** was obtained..

Through Barton-Zard reaction[182], ethyl-3,4-diethylpyrrole-2-carboxylate **64** was successfully synthesized in 95% yield, by reaction of **62** with ethyl isocyanoacetate **63**. **63** were synthesized although this compound is commercially available since it is very expensive. This compound were synthesized according to the literature procedure.[183,184] Reduction of ester **64** by sodium hydroxide obtained 3,4-diethylpyrrole in 60% yield.

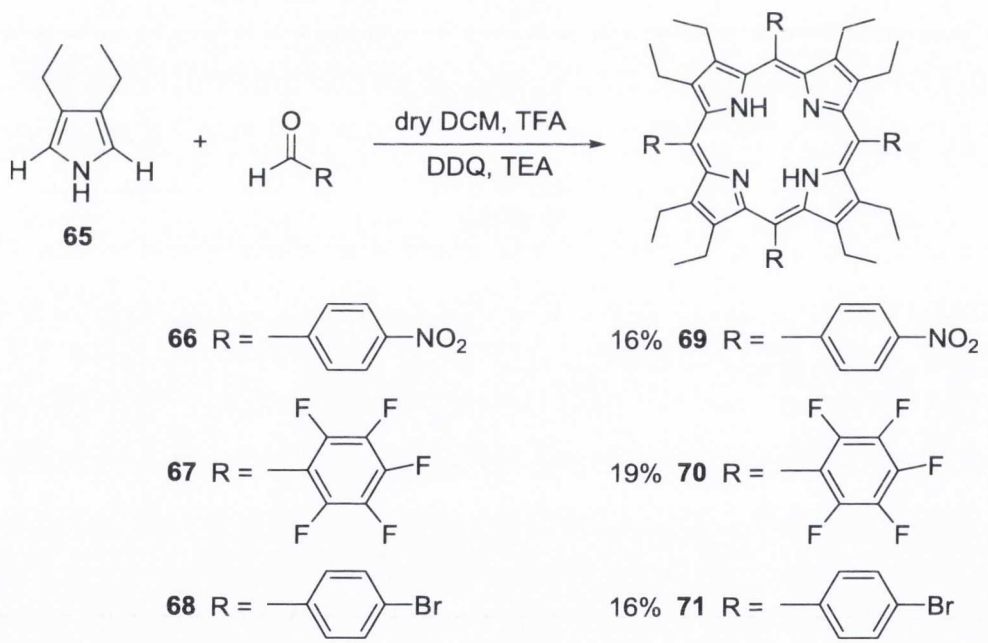


Scheme 4.1 Synthesis of 3,4-diethylpyrrole.

4.1.1 Functionalization of meso positions by condensation reaction

'Symmetrical'highly substituted porphyrins were synthesized via condensation reactions using the same approach as that used for the synthesis of **9**, which is condensation of 3,4-diethylpyrrole **65** with an appropriate aldehyde.

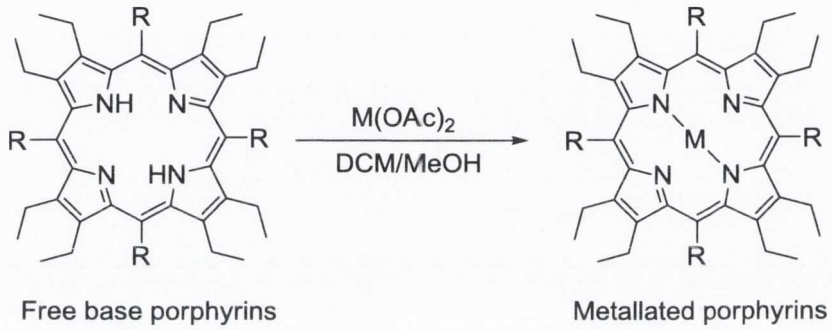
Compounds **69**, **70** and **71** with all *meso* functionalization were synthesized *via* modification of the Lindsey method[15] using various aromatic aldehydes, **65** as a precursor and TFA as a catalyst. The reaction was shielded from light and was left to stir overnight. After this time DDQ and TEA was added and the mixture stirred for a further hour. The product was filtered through neutral alumina and eluted with DCM. Further purification using column chromatography and recrystalization with DCM:MeOH resulted in the isolation of **69**, **70** and **71** in 16-19 % yield (Scheme 4.2).



Scheme 4.2 Synthesis of nonplanar free base porphyrins.

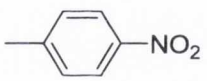
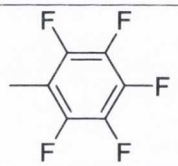
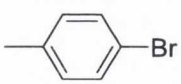
These sterically crowded compounds can be used for further reactivity and supramolecular porphyrin assemblies.

Copper and zinc metallated porphyrins were synthesized by treating the free base porphyrins with $Cu(OAc)_2$ or $Zn(OAc)_2$ in DCM:MeOH 10:1, and with stirring at room temperature for 2h. In other hand, nickel metallated porphyrins were synthesized by reflux of the free base porphyrins with $Ni(OAc)_2$ in toluene overnight[185] (Scheme 4.3and Table 4.1).



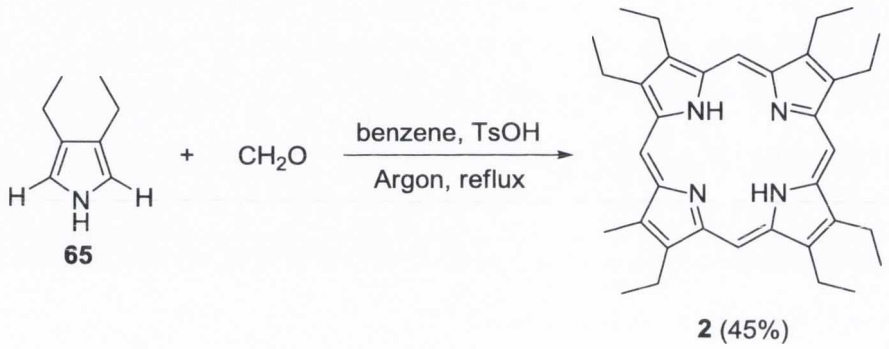
Scheme 4.3 Synthesis of metalated porphyrins.

Table 4.1 Summary of metalated porphyrins.

	M = Cu	M = Zn	M = Ni
R = 	**72** (81%)	**73** (95%)	**74** (82%)
R = 	**75** (93%)	**76** (80%)	**77** (64%)
R = 	**78** (75%)	**79** (90%)	**80** (70%)

4.1.2 Functionalization on meso position *via* S_NAr reaction

OEP **2** was synthesized by reaction of 3,4-diethylpyrrole **65** with formaldehyde and *p*-toluenesulfonic as a catalyst.[12] Residue was purified by chromatography using neutral alumina and eluted with hexane:DCM 2:1 (v/v) and gave **2** as a purple crystals in 45% (Scheme 4.4).



Scheme 4.4 Synthesis of octaethylporphyrin **2**.

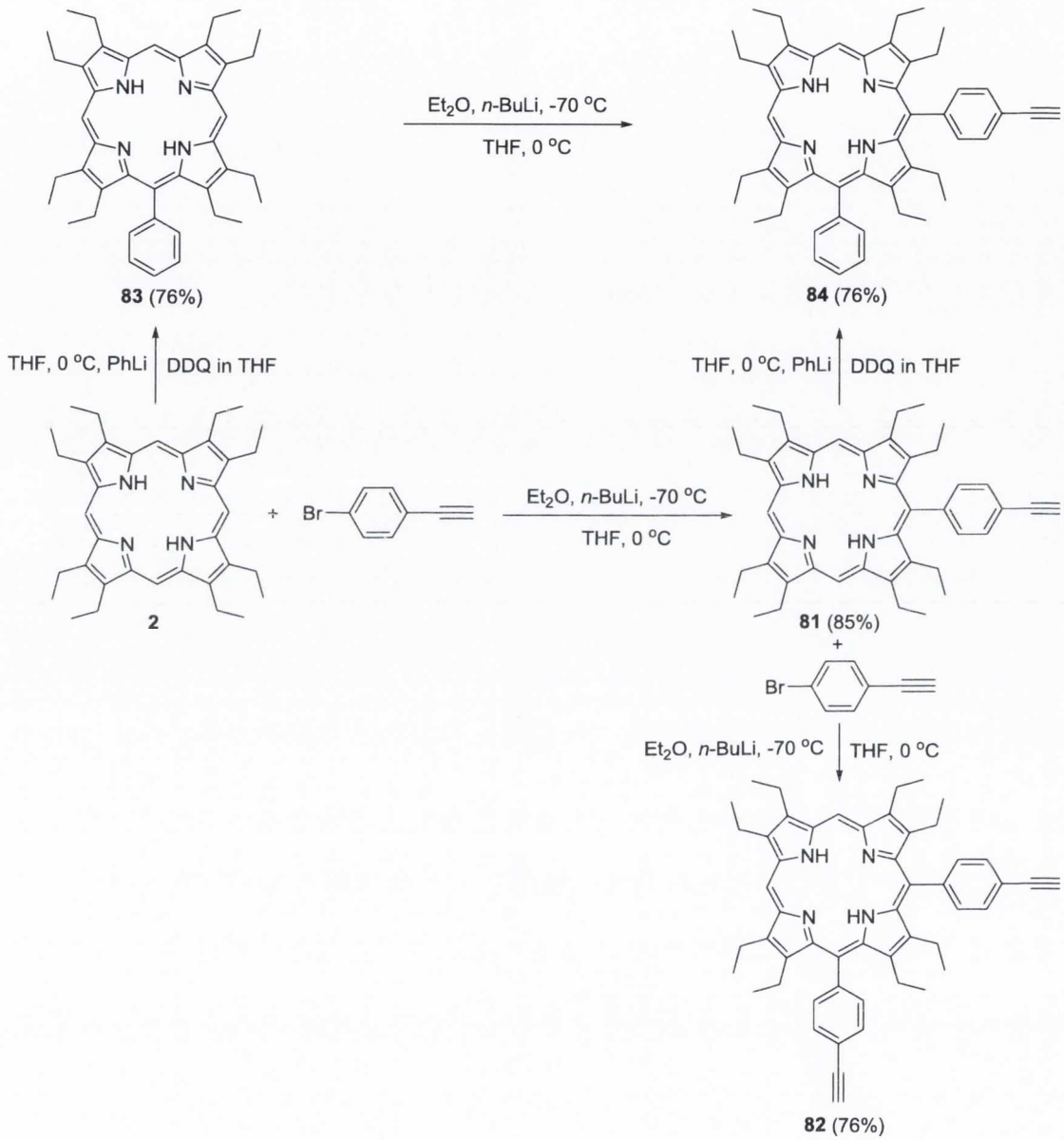
OEP can also be synthesized in a better yield (65%) starting from ethyl-3,4-diethylpyrrole-2-carboxylate **64** according to the literature.[182]

Next step involved the reaction of OEP with organolithium reagent to obtain functional groups suitable for C-C coupling in later reactions. Mono- (**81**) and disubstituted OEP (**82**) was synthesized on a large scale *via* organolithium reactions starting from commercially available 1-bromo-4-ethynylbenzene (Scheme 4.5).

The reaction were carried out with an excess of *n*-BuLi (20 equiv.) followed by addition of OEP (1.0 equiv.) in THF. The mixture were purify column chromatography using neutral alumina and hexane:DCM 1:1 (v/v) as a eluent to yield 85% of **81** and 13% of starting material.

The same approach was used for the synthesis of disubstituted OEP (**82**) by using **81** as a starting material and the desired compound was obtained in 76% yield.[186]

Compound **84** was obtained in 76% yield by treatment of **2** with PhLi at 0 °C in THF[187] (Scheme 4.5).



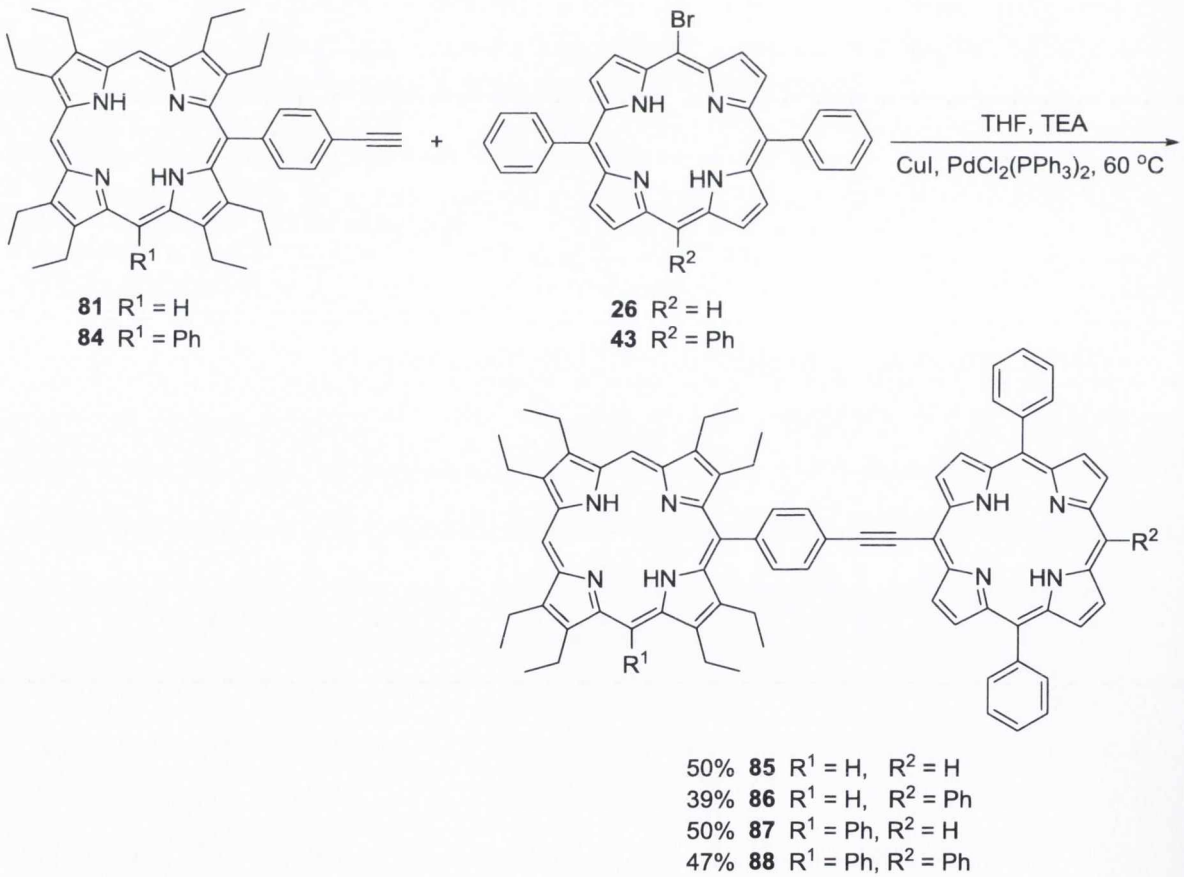
Scheme 4.5 Synthesis of mono- and disubstitued OEP.

Compound **84** can also be synthesized by treated OEP with PhLi to produce compound **83** in 80% yield and then this product was reacted with bromo-ethynylbenzene to give **84** in 63% yield.

4.2 Synthesis of nonplanar multiporphyrin arrays

4.2.1 Synthesis of dimers

The Sonogashira coupling reaction has been widely applied to porphyrin systems.[188,189] The first time palladium catalyzed coupling of aryl or alkenyl halide with terminal alkynes by Sonogashira was reported in 1975.[190] Dimeric systems bridged by a phenylacetylene linker were synthesized *via* Sonogashira coupling reaction. By using 1.0 equiv. of meso substituted OEP (**81** or **84**) with 1.0 equiv. of bromoporphyrin (**26** or **43**) in the presence of $PdCl_2(PPh_3)_2$ as a catalyst in THF yield **85-88** in 39% - 50% yield and no Copper inserted compound -or meso-meso linked compound has been recovered from this reaction (Scheme 4.6 and Table 4.2).



81 R^1 = H
84 R^1 = Ph

26 R^2 = H
43 R^2 = Ph

50% **85** R^1 = H, R^2 = H
39% **86** R^1 = H, R^2 = Ph
50% **87** R^1 = Ph, R^2 = H
47% **88** R^1 = Ph, R^2 = Ph

Scheme 4.6 Synthesis of dimeric compounds bridged by phenylacetylene linkers.

Table 4.2 Synthesis of dimeric compounds bridged by phenylacetylene linkers.

Porphyrin 1	Porphyrin 2	Dimeric
81	**26**	**85**
81	**43**	**86**
84	**26**	**87**
84	**43**	**88**

At first this reaction were carried out at the room temperature, because the starting material was free base porphyrin and to prevent the formation of Copper metallated porphyrin. However, the reaction did not work as only starting material appeared on the TLC after leaving the mixture for two days. Then the mixture was heated to 60 ^{o}C in a closed system and after 2h, green coloured spot can be observed on the TLC even though there still has a intense spot corresponding to the starting material and the reaction was left overnight The mixture was purified through column chromatography and eluted with hexane:DCM starting from 4:1(v/v) and increased slowly until the target compounds were obtained.

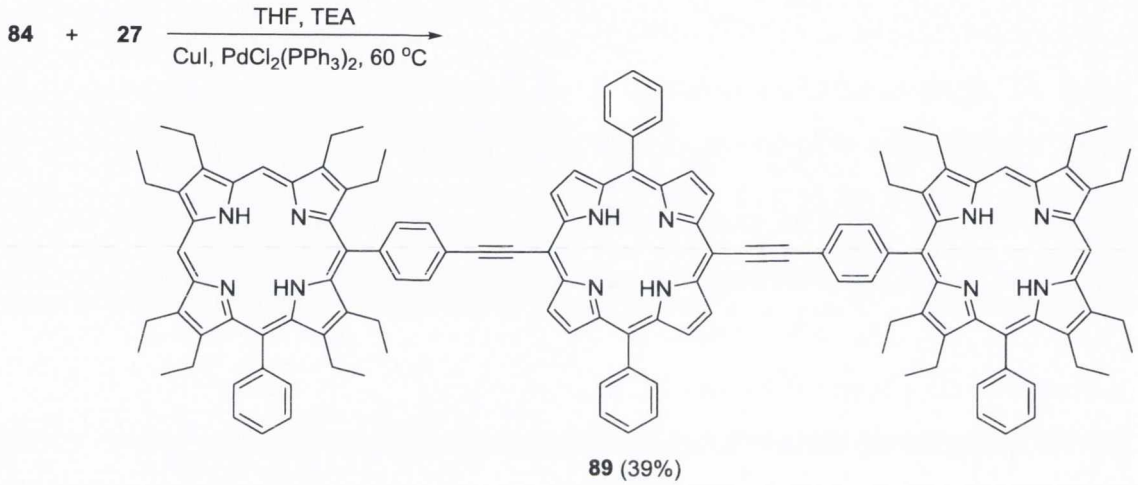
These dimeric compounds contain free meso position both on octaethylporphyrin and in the β-unsubstituted porphyrin residue. Thus, further substitution chemistry can be explored.

4.2.2 Synthesis of trimers

Using the same strategy as for the dimers, trimeric porphyrin compounds can also be synthesized. Two types of trimers linked by phenylacetylene have been successfully synthesized, called a linear type and an angular or bent type trimers.

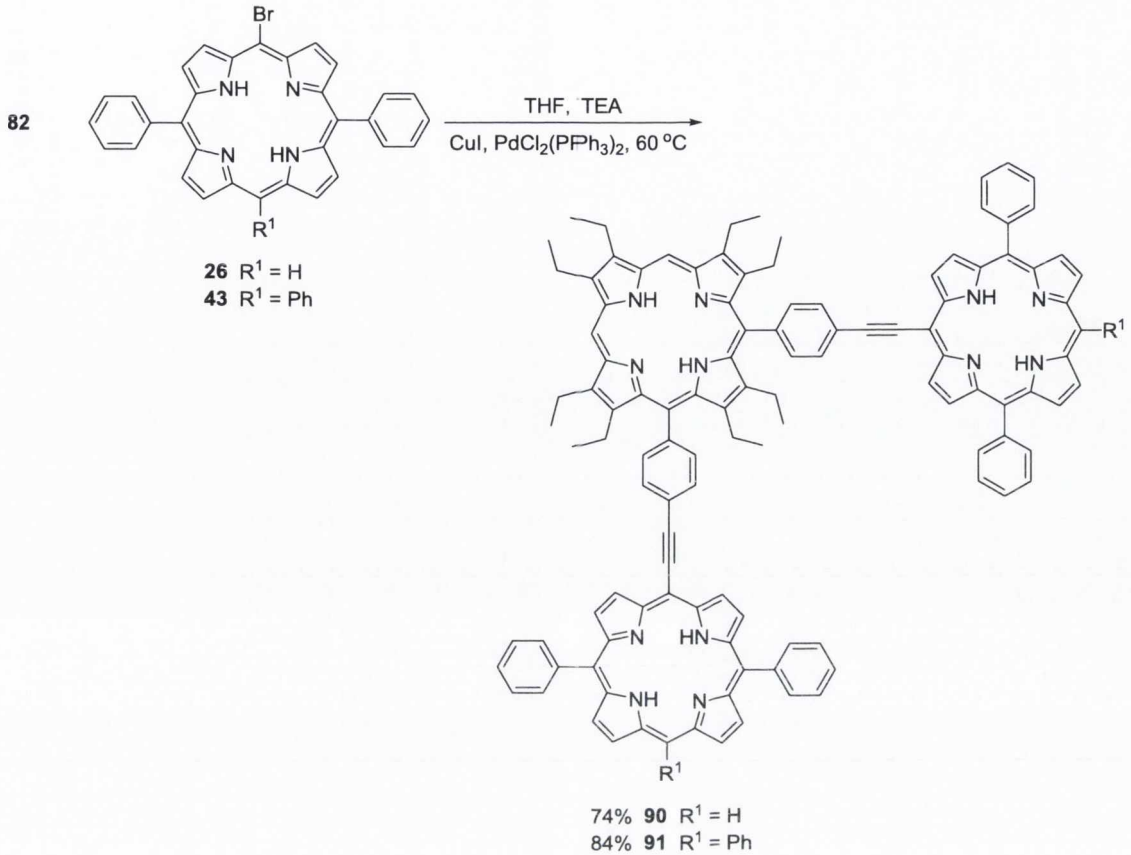
The linear type trimer **89**, was synthesized by using 2.0 equiv. of meso substituted OEP **84** with 1.0 equiv. of **27** in the presence of 0.2 equiv of CuI and 0.1

equiv of $PdCl_2(PPh_3)_2$ (Scheme 4.6). The mixture was purified by column chromatography using hexane:DCM as a eluent and a total of four fractions were separated. From the TLC and ^1H NMR data, the first two fractions were confirmed to be the starting materials (**84** and **27**), the third fraction was identified as **87** in 15% and the last fraction was the desired product **89** in 39% yield (Scheme 4.7).



Scheme 4.7 Synthesis of trimeric compound bridged by a phenylacetylene linker.

Likewise, respectively bent type trimers (**90** and **91**) were synthesized in good yields of 74% and 84%, by using 1.0 equiv. of *meso* substituted OEP **82** and 2.0 equiv. of bromoporphyrins (**26** or **43**). There was no *meso-meso* linked porphyrin recovered from this reaction (Scheme 4.8 and Table 4.3).



Scheme 4.8 Synthesis of trimeric compounds bridged by phenylacetylene linkers.

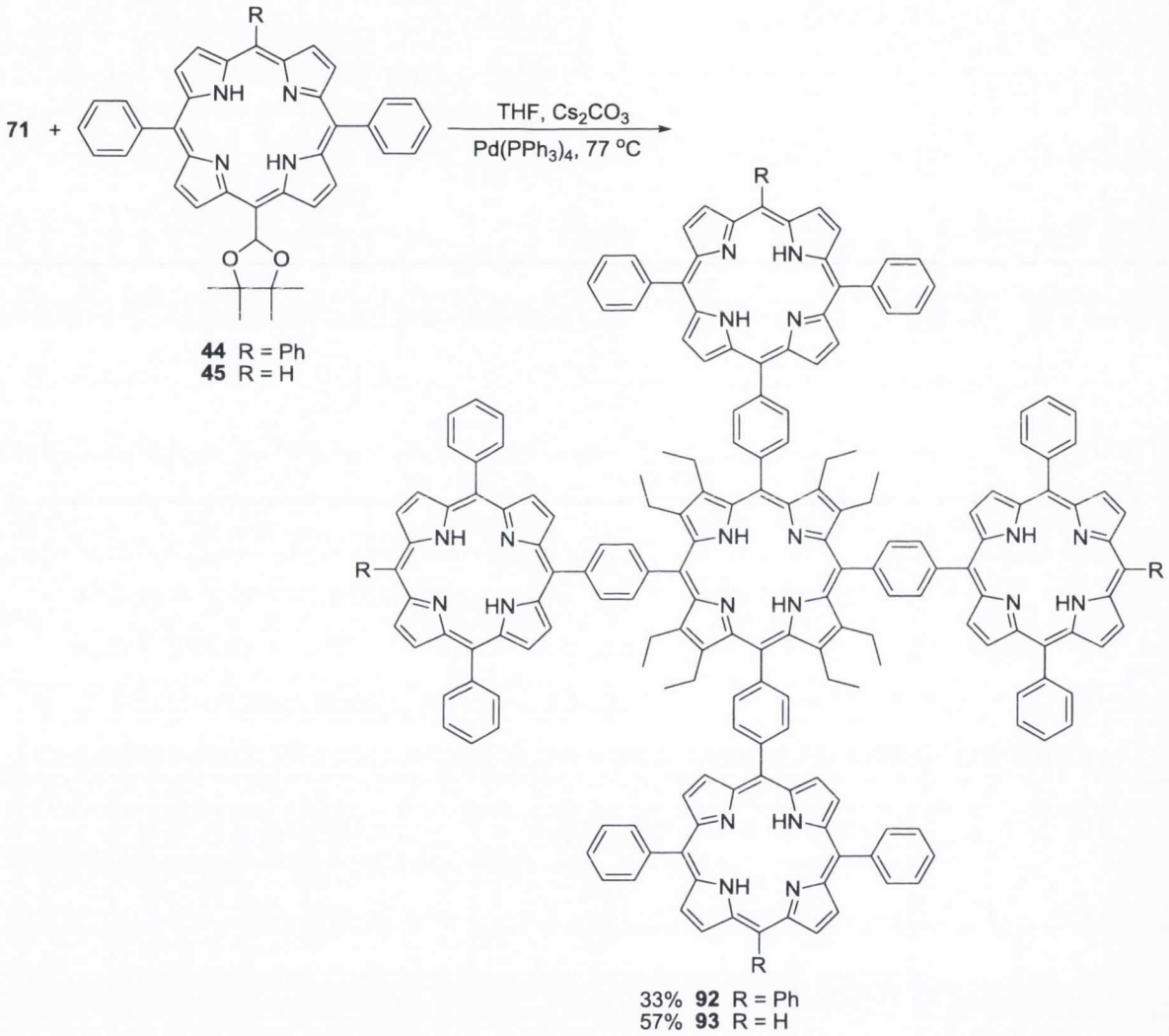
Table 4.3 Synthesis of trimeric compounds bridged by phenylacetylene linkers.

Porphyrin 1	Porphyrin 2	Dimeric
82	**26**	**90**
82	**43**	**91**

4.2.3 Synthesis of pentamers

Pentameric type porphyrins or more commonly known as star-shaped pentads,[191,192] were synthesized *via* Suzuki cross coupling reaction by reaction 1.0 equiv. of **2** with 4.0 equiv of borylated porphyrins (**44** or **45**) in the presence of $Pd(PPh_3)_4$ and Cs_2CO_3 in THF and under reflux condition at 77 °C. The reaction mixture

was refluxed under the same condition for four days to ensure the reaction was completed. Since for the first, second and third days the intense spot of starting material can see on the TLC. After four days-, the reaction was quenched by cooling to room temperature and filteration through silica and washing with DCM. Purification of the residue yielded **92** and **93** in 33% and 57%, respectively (Scheme 4.9).



Scheme 4.9 Synthesis of star-shaped porphyrins.

4.3 NMR Studies

Porphyrin are diamagnetic compounds, due to this make this compounds are very different with other compounds in terms of their ^{1}H NMR. Their chemical shifts is strongly dependent on the orientation and distance of the proton in relation to the delocalization pathway of the π-electron of the porphyrin. Porphyrin periphery are the deshielding region of the ring current effect whereas proton above or inside the porphyrin macrocycle are in the shielding region.[193] This can be observed in the ^{1}H NMR spectra of free base porphyrins (Figure 4.1).

OEP **2** has four planes of symmetry. When compared to the chemical shifts of the protons in pyrrole, the N-protons in porphyrins displayed upfield shifts of ca. 12 ppm. Ethyl group that substituted on the β position of porphyrin shows one triplet signal at 1.95 ppm indicated for eight CH_3 fragment and one quartet signal at 4.1 ppm for eight CH_2 fragment. The meso proton resonated at 10.13 ppm as a sharp singlet signal. The N-H proton, in the core of the porphyrin were shielded by the ring current and shifled upfield at -3.72 ppm.[12]

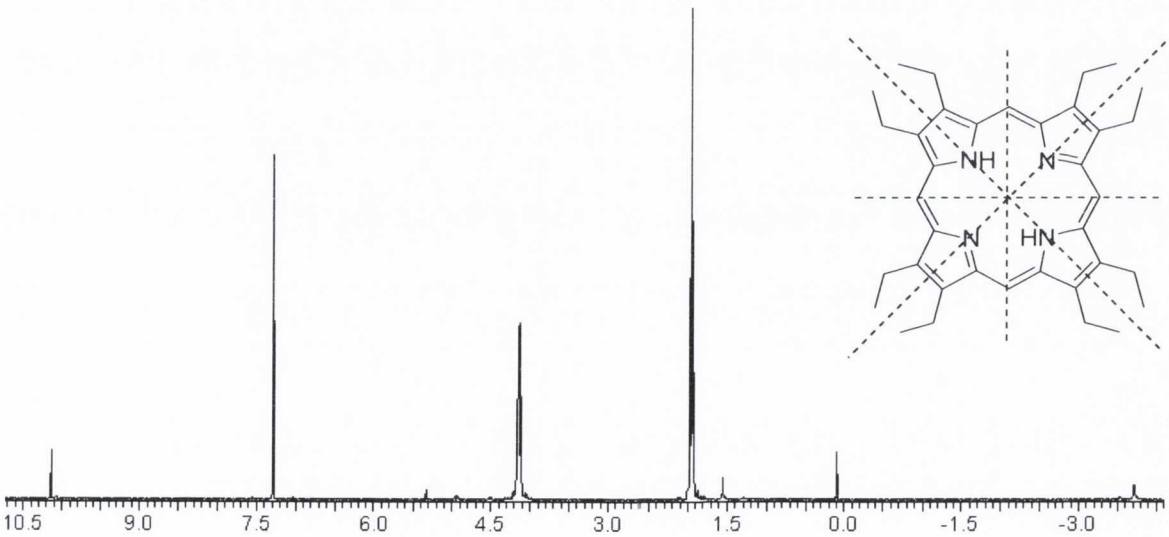


Figure 4.1 ^{1}H NMR spectrum OEP **2** in $CDCl_3$.

Normally for meso substitued porphyrins, the chemical changes that are observed are influenced by three main features. 1) The ring current is reduced, 2) the signal from the methine proton 'opposite' the *meso* substituent is more strongly shifted to higher field than the signal from the 'adjacent' methines, 3) protons in the vicinity of the substituent experience direct magnetic anisotropic effects, which are apparent in the NMR spectra.[194]

Previously Senge and co-workers, prepared 5-butyl, 5-10-dibutyl, 5,10,15-tributyl and 5,10,15,20-tetrabutyl octaethylporphyrin nickel (II) and discussed how the increase in the number of substituting group on the OEP will increase the distortion of the compounds.[21,22,195,196] In 2004, Syrbu *et al* discussing more detail on substituting phenyl group on the meso position of the OEP and how the increase on the phenyl substituted will effect on the ^{1}H NMR signal.[197] This showed how the increase of the substituted group will make the compounds become more sterically hindered and will effect the planarity of the compound. Besides that, when the distortion increases, the aromaticity of the compounds decreases. [197]

The ^{1}H NMR data for compounds **2** (monomer), **88** (dimer), **91** (trimer) and **92** (pentamer) are summarized in Table 4.4. Signals for the chemical shift consistently shifted from monomer to dimer to trimer and to pentamer. There is a high field shift for the signal associated with the meso proton and a low field shift for the N-H proton signal for these dimer, trimer and pentamer compare to OEP and this is most probably because of a decrease in the ring current of macrocycle.

For pentamer **92** the broad signal for ethyl proton and N-H proton can be observed in the ^{1}H NMR spectra. These happen due to the several conformations that existence and can be change from one to other at a rate close to the 'proton relaxation' time.[197]

Beside that, because of substituent on the meso position of the porphyrin arising a strong screening action at the ring current of the substituted group and it is can shows from the upfield shifted of proton signal for CH_2 and CH_3 fragment on the ethyl group

Table 4.4 ^{1}H NMR data of the compounds **2**, **88**, **91** and **92**.

Compounds	*Meso*	*B* (range)	Aromatic (range)	*B* substituted	NH
2	10.14 (4H, s)	-	-	4.14 (16H, q, CH_2) 1.95 (24H, t, CH_3)	-3.72 (2H, s)
88	10.30 (2H, s) 10.00 (1H, s)	10.00 – 8.84	8.84 – 7.82	4.13 (14H, q, CH_2), 3.04 (2H, q, CH_2) 1.95 (20H, m, CH_3), 1.36 (4H, t, CH_3)	-3.05 (2H, d) -2.18 (2H, s)
91	10.00 (2H, s)	9.74 – 8.44	8.24 – 7.82	3.95 (6H, m, CH_2), 2.48 (6H, m, CH_2), 1.87 (4H, m, CH_2) 1.29 (8H, s, CH_3), 0.91 (8H, m, CH_3), 0.66 (8H, m, CH_3)	-2.55 (2H, br) -2.19 (4H, s)
92	-	9.08 – 8.32	8.32 -7.83	2.11 (16H, m, CH_2) 0.25 (24H, m, CH_3)	-2.60 (8H, s)

Overall, the distortion that of the porphyrin increased when the substituent on the *meso* position of the porphyrin increased and sterically hindered making them nonplanar.

4.4 Photophysical studies

The magnitude of electronic interaction between the porphyrin core and the peripheral porphyrin groups can be investigated by electronic absorption spectroscopy. When porphyrins are substituted with other unit porphyrins, normally there will be a red shift in the Soret band region, which corresponds to S_0-S_2 transition, while red shifts of the Q band which corresponds to S_0-S_1 transition are important features since these indicate the coupling between the compounds.

Figure 4.2 shows the comparison spectra between **2**, **88**, **91**, and **92**. **2** showed one Soret band at 398 nm and four Q bands at 497, 531, 566 and 619 nm. Compound **92** with 4 unit porphyrins substituted on the *meso*- position of *β*- substituted porphyrin with phenyl linker show splitting of Soret band at 418 and 484 nm and four Q bands at 554, 590, 648 and 702 nm. Compound **91** with 2 unit porphyrins substituted on *meso*-position of *β*- substituted porphyrin with ethnylbenzene linker showed a broad Soret band at 438 nm and four Q bands at 514, 581, 612 and 671 nm. While compound **88** with one unit porphyrin substituted on *meso*- position of *β*- substituted porphyrin with ethnylbenzene linker showed a broad and low intensity Soret band at 451 nm and three Q bands at 605, 647 and 702 nm.

The Soret and Q bands for all the pentamer, trimer and dimer are significantly red shifted compared to **2**. This indicates that there has a strong exciton coupling between the non planar porphyrin core and porphyrin units. Besides that, it can be shown that, there is an extension of the π-conjugated in the system which can be explained by a decrease of energy gap between HOMO and LUMO.[190,198]
All pentamer, trimer and dimer compounds have similar spectra, the absorption and fluorescence data are summarized in Table 4.5.

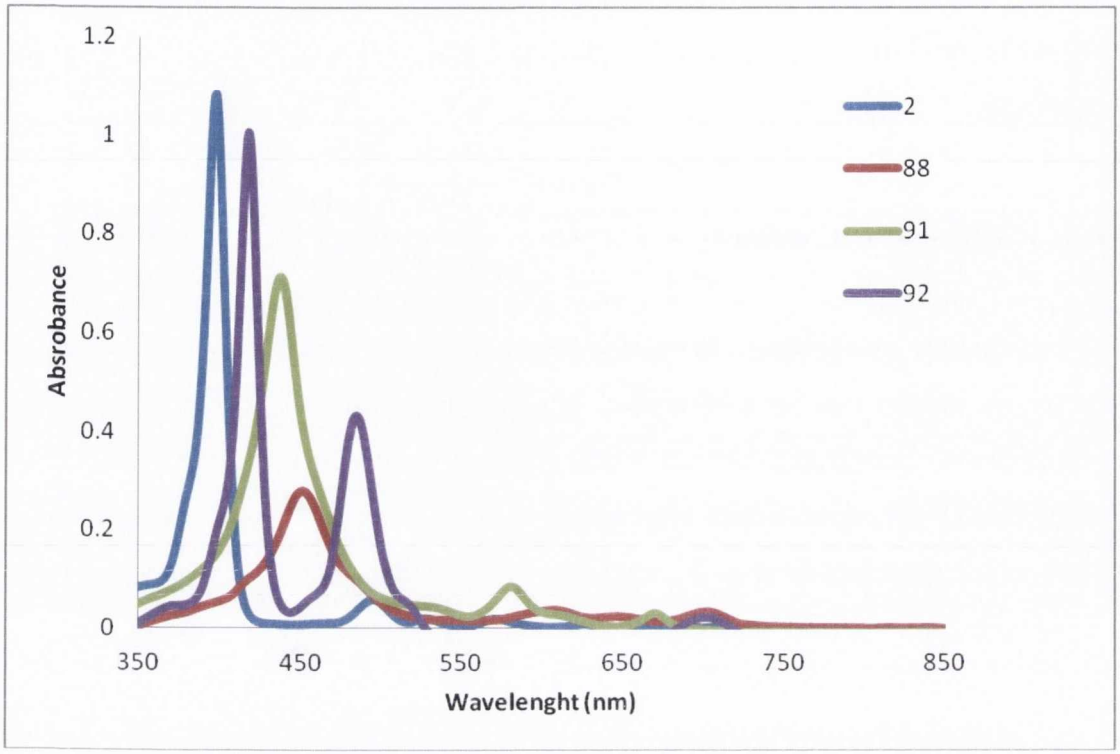


Figure 4.2 Absorption spectra of the porphyrins **2**, **88**, **91** and **92** (1.85×10^{-3}M in DCM).

Table 4.5 UV-visible absorption, fluorescence emission and fluorescence lifetime spectral data of multiporphyrin arrays compounds with **2**.

Compound	[a] Absorption λ_{max}/nm	[b] Emission λ_{em}/nm	[b] Fluorescence lifetime (τ_f, ns)
2	398, 497, 531, 566, 619	635, 700	9.3 ± 0.1
85	409, 434, 505, 533, 571, 661	647, 712	7.8 ± 0.1
86	408, 438, 505, 538, 578, 669	651, 710	7.4 ± 0.1
87	433, 522, 571, 662	653, 719	8.2 ± 0.1
88	451, 605, 647, 702	647, 711	8.3 ± 0.1
89	426, 447, 513, 572, 607, 700	648, 709	7.3 ± 0.1
90	433, 574, 603, 663, 701	653, 717	7.1 ± 0.1
91	438, 514, 581, 612, 671	653, 718	7.6 ± 0.1
92	418, 484, 554, 590, 648, 702	656, 723	7.0 ± 0.1
93	413, 486, 547, 585, 641, 704	654, 720	7.1 ± 0.1

[a] UV-visible measurement was carried out in THF (3.33×10^{-3}M).

[b] Fluorescence lifetime measurements were carried out in THF (5.56×10^{-4}M) and excitation of the porphyrins was performed by 370 nm laser with pulse rate of < 1 ns.

Strong electronic absorption between the porphyrin core and porphyrins peripheral can be demonstrated through emission measurements. Normally free base *β*-substituted porphyrin has week fluorescence and short lifetime when compare to DPP, this has been reported previously by Charlesworth *et al.*[199] When changes in the distortion of the porphyrin macrocycle, huge difference in the electronic properties can be observed. As mentioned before distortion on the porphyrin macrocyle change because of the planarity on the porphyrins. The planarity is inducing by substituent on the *meso* and *β* position on the porphyrin that make the compound become sterically hindered.[199]

Figure 4.3 showed the emission spectra of **2**, **88**, **91**, and **92** in DCM. **2** was excited at 398 nm (Soret band of **2**) and compounds **92**, **91** and **88** were excited at 418

nm (Soret band of **92**), 438 nm (Soret band of **91**) and 451 nm (Soret band of **88**) respectively. Two emission bands at 630-670 nm and 710-740 nm can be observed. Red shifts of the emission spectra as the size of porphyrin array becomes larger showed the π conjugation in the system has been increased.

Additionally, the intensity and the lifetimes of the multi array porphyrins also decreased compared to **2**. This indicates that the faster intersystem crossing and internal conversion, that is of the radiationless deactivation process of the (π, π^*).[200]

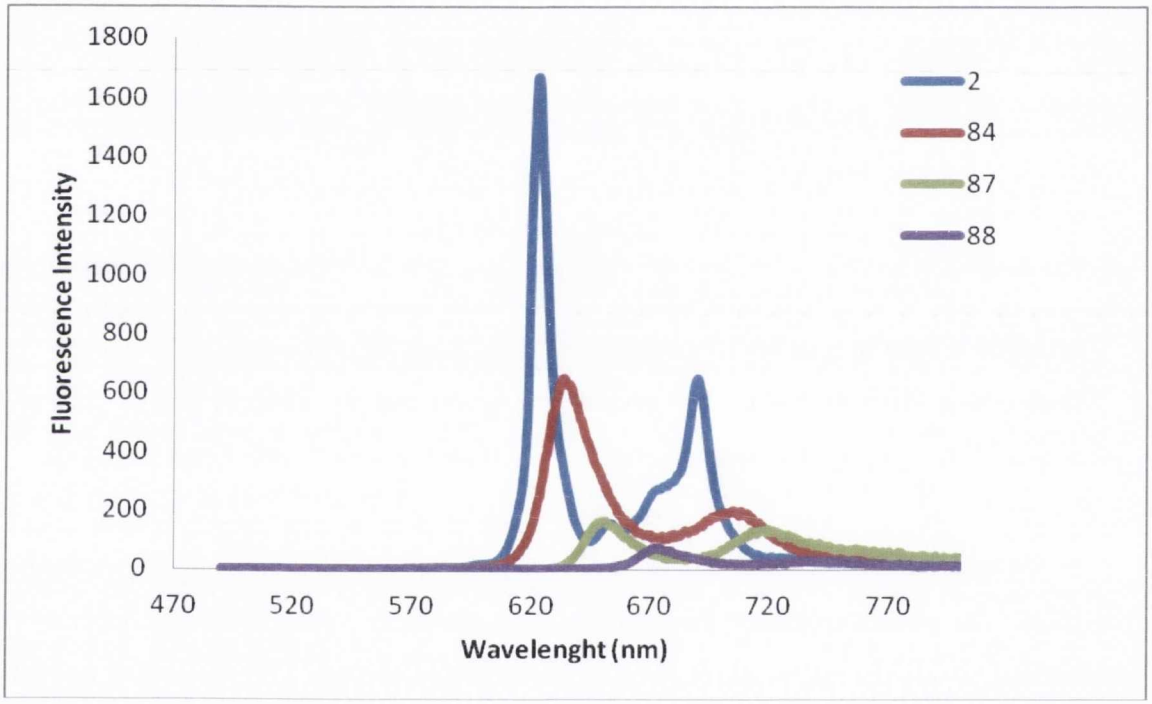
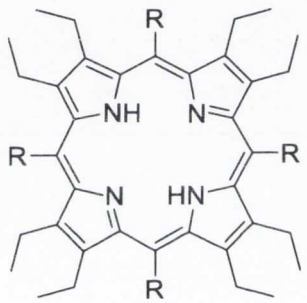


Figure 4.3 Emission spectra at the excitation energies of the Soret bands of the porphyrins **2**, **88**, **91** and **92** (5.56×10^{-4} M in DCM for fluorescence).

4.5 Protonation of multiporphyrin arrays

Introducing substitution on β and meso position of the porphyrin is not only the way to make the compound to show nonplanar properties but substitution on the porphyrin core can also influence the planarity.[201]

This has been discussed by Senge how the protonation on the 5,10,15,20-tetraalkylporphyrins with *n*-butyl, isobutyl, isopropyl, 1-ethyl-propyl or *tert*-butyl showed highly non planar confirmation.[201] This has been proven by the difference of conformation from ruffle to saddle and also from the bathchromic shift on the absorption maxima.



94 R = $CH_2CH_2CH_2CH_3$

95 R = $CH(CH_3)_2$

96 R = $CH(CH_2CH_3)_2$

97 R = $CH_2CH(CH_3)_2$

98 R = $C(CH_3)_3$

The same shifts can be observed, when dimeric, trimeric and pentameric compounds were protonated by adding 0.1% TFA in DCM. Figure 4.4 and Figure 4.5 show the UV spectra for free base multiporphyrin arrays in DCM and dication multiporphyrin arrays in DCM with 0.1% of TFA. As discussed before red shifts have been observed from pentamer to trimer to dimer.

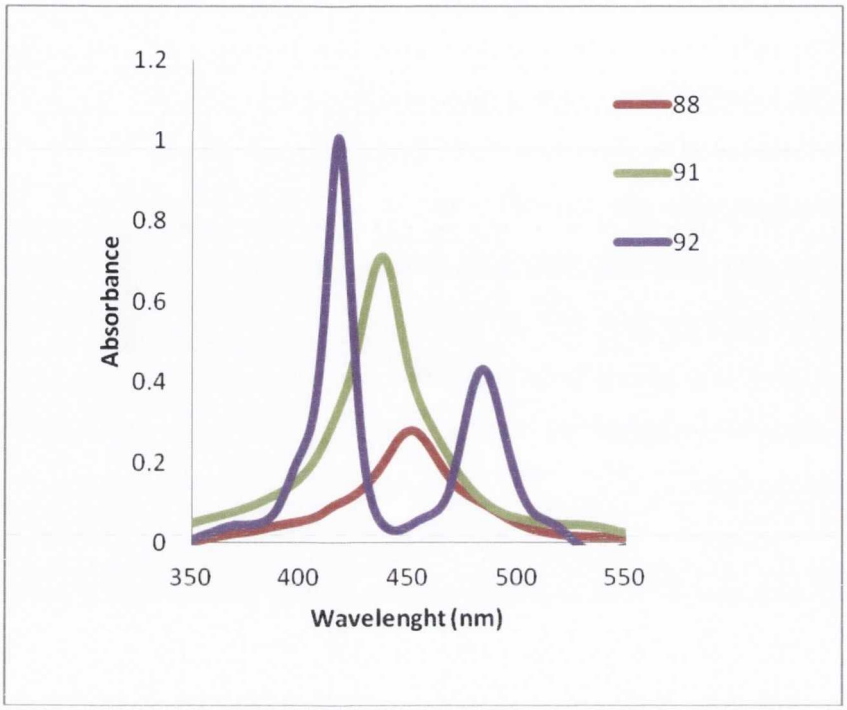


Figure 4.4 UV-vis spectra of free base multiporphyrin arrays in DCM.

Multiporphyrin arrays showed larger bathochromic shifts. Red shifts were observed 21 nm between the pentamer **92** and **2**, 11 nm between the trimer **91** and **2**, and 7 nm between the dimer **88** and **2**,

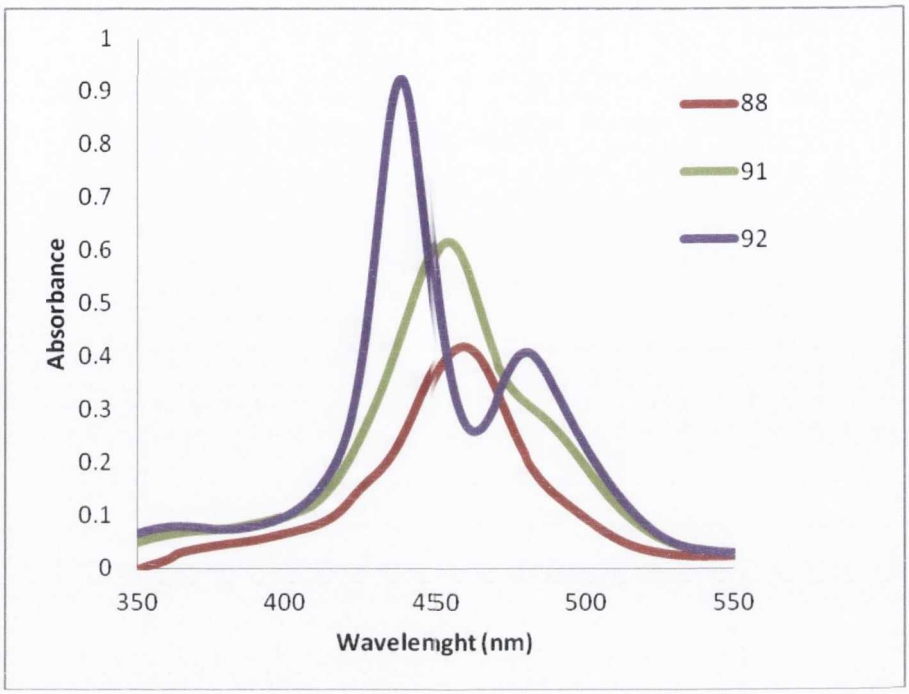


Figure 4.5 UV-vis spectra of multiporphyrin arrays in DCM.

This is a proof that different degrees of distortion occurred on the addition of two hydrogen atoms. Beside addition of two protons to the central pyrolenine nitrogen atoms, the degree of distortion of the macrocycle can depend on axial ligand effects, metal and packing.[58]

4.6 Conclusions

Meso and β functionalised nonplanar porphyrins **69-71** have been synthesized *via* condensation reaction yielded in 16%-19%. These sterically crowded compounds can be used for further reactivity and supramolecular porphyrin assemblies. Dimers and trimers were successfully synthesized in 39%-84% *via* Sonogashira coupling reaction and using palladium as a catalyst. In other hand, pentamers type porphyrins have been synthesized in 33%-57% *via* Suzuki coupling reaction. These multiporphyrin arrays are stable and can be stored in solid form at room temperature.

Photophysical studies indicate great level of electronic coupling among the porphyrin subunits. Emission spectra were recorded in DCM and showed a decreasing in the intensity of multiporphyrins arrays compared to the 2,3,7,8,12,13,17,18-octaethylporphyrin **2** (OEP). The fluorescence lifetime was measured and have shorter lifetimes compared to the OEP. Protonation of multiporphyrins arrays showed a bathchromic shift on the absorption maxima.

CHAPTER 5

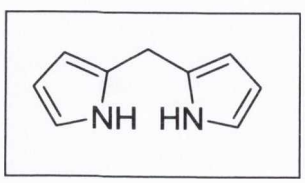
EXPERIMENTAL

5.1 Instrumentation and General Methods

All chemicals were of analytical grade and were purchased from Aldrich Co. unless otherwise stated. NMR spectra were recorded on Bruker DPX 400 (400.13 MHz for ^{1}H NMR, 100.62 MHz for ^{13}C NMR) and/or Bruker AV 600 (600.13 MHz for ^{1}H NMR, 150.2 MHz for ^{13}C NMR). Chemical shifts recorded in ppm refer to tetramethylsilane (TMS) set at 0.00 ppm. Data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, d+d: double doublet, t: triplet, q: quartet, br: broad, m: multiplet), coupling constants (*J* in Hz), integration and assignment. High resolution mass spectrometry was carried out on a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with electrospray source. UV-vis measurements were performed on Shimadzu multiSpec-1505 using dichloromethane as solvent. Melting points were acquired on Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel $60F_{254}$ (Merck) precoated aluminum sheets. Chromatography on silica gel was carried out using a forced flow of the indicated solvent system on Fluka Silica Gel 60 (230-400 mesh). DCM was dried over P_2O_5 followed by distillation and THF was distilled from sodium/benzophenone under argon. Reactions with organolithium reagents were carried out using standard Schlenk techniques and glassware under an atmosphere of argon. All fluorescence spectra were recorded on Perkin-Elmer Precisely LS55 spectrometer. Lifetime measurements were carried out on Fluorolog Horiba Jobin Yvon spectrometer using a laser beam: 370 nm (pulse <1 ns) and 635 nm (<200 ps).

5.2 Synthesis of starting materials

Dipyrromethane 6



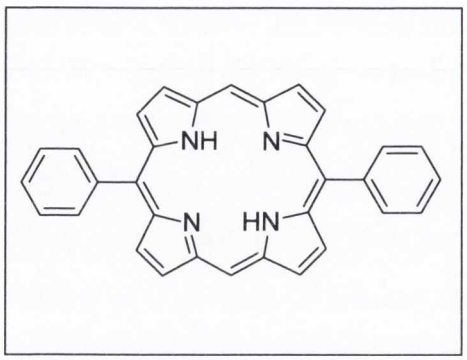
A suspension of **20** (paraformaldehyde) (5 g, 166.50 mmol) in **21** (200 mL, 2.88 mmol) was placed in a 500 mL 3-neck round bottom flask equipped with an internal thermometer and water

condenser in reflux position. The solution was heated to 70 °C and heat source was removed and TFA (0.8 mL) was added immediately. A sharp increased in temperature of solution was observed (to ca 90 °C) and solution became rapidly clear and dark, then the solution was heated at not more than 90 °C for half an hour. KOH (0.80 g in 30 mL H_2O) was added and the reaction mixture left to cool to room temperature. The mixture was filtrated through silica gel and eluted with DCM. The solvents were evaporated and the product was purified by Kugelror (temp 180 °C start at 50 °C increased slowly by 10 °C and pressure must be 6.0×10^2) to yield **6**; 7 g, (0.05 mol, 80 %) as a colorless crystal; mp 72-73 °C, lit mp 74 °C; [202,203] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 6.59 (dd, 2H) 6.14 (dd, 2H), 5.97 (dd, 2H), 3.86 ppm (s, 2H) ppm.

General procedure for the synthesis of 5,15-disubstituted porphyrins

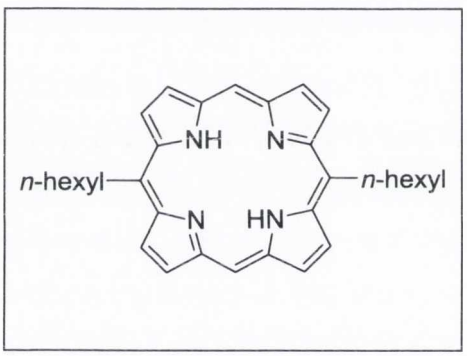
5,15-Disubstituted-phenylporphyrin **9** and 5,15-disubstituted-(*n*-hexyl)-porphyrin **25** were prepared according to a procedure by Lindsey *et al.* [15] Dry DCM (1.5L) was placed in a three-neck 2 L round bottom flask equipped with a magnetic stirrer and gas inlet (argon) and the flask was covered with aluminium foil and 1.2 equiv. of **6** (0.15 mol), 1.2 equiv. aldehyde (0.15 mol) and TFA (1.9 mL, 15 mmol) was added. The reaction was stirred for 18h at room temperature. After this time, 1.2 equiv. of DDQ (0.15 mol) was added and the mixture stirred for a further hour. Then TEA, (12.5 mL) was added before the reaction was filtered through silica with DCM followed by recrystallization from DCM/MeOH.

5,15-Diphenylporphyrin 9



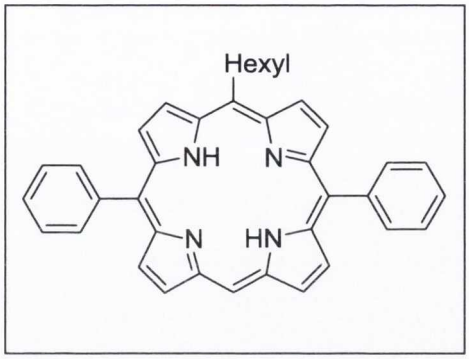
Prepared according to the above procedure using benzaldehyde (2.3 mL) to yield **9**; 1.77 g (9.41 mmol, 40 %) as a violet solid; mp > 250 °C; [204] R_f 0.7 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.08 (s, 2H), 7.85 (m, 6H), 8.32 (m, 4H), 9.13 (d, *J*=4.40 Hz, 4H), 9.43 (d, *J*=4.40 Hz, 4H), 10.36 (s, 2H) ppm.

5,15-Di-(*n*-hexyl)-porphyrin 25



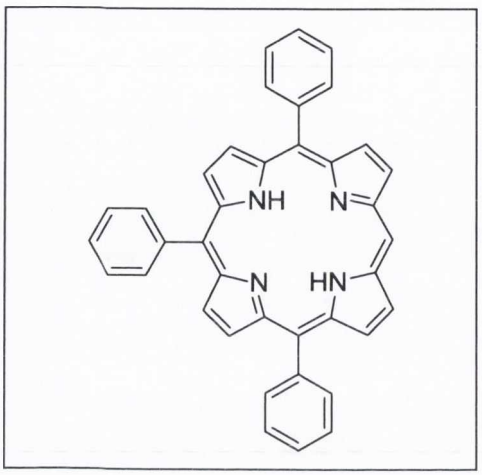
Prepared according to the above procedure using heptanaldehyde (3.4 mL, 0.02 mol) to yield **25**; 0.76 g (1.60 mmol, 16 %); as a violet solid; mp > 260 °C; [112] R_f 0.5 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.91 (s, 2H), 0.96 (t, *J*=7.00 Hz, 6H), 1.42 (q, *J*=7.60 Hz, 4H), 1.52 (t, *J*=7.60 Hz, 4H), 1.82 (q, *J*=7.60 Hz, 4H), 2.50 (q, *J*=8.20 Hz, 4H), 4.94 (t, *J*=8.20 Hz, 4H), 9.31 (d, *J*=4.08 Hz, 2H), 9.50 (d, *J*=4.08 Hz, 4H), 9.81 (d, *J*=4.08 Hz, 2H), 10.02 (d, *J*=4.08 Hz 2H) ppm

5-(*n*-Hexyl)-10,20-diphenylporphyrin 29



A 250 mL Schlenk flask was charged with 1.0 equiv. of **25** (0.10 g, 0.21 mmol) in THF (100 mL) and cooled to -78 °C. Within 20 min. 6.0 equiv. of *n*-hexylLi (0.5 mL, 1.14 mmol, 2.3 M in *n*-hexane) was added drop wise at the same temperature (under Argon) to the solution. The cold bath was removed and the mixture stirred at room temperature for 2.5h (monitored by TLC) and followed by addition of 5 mL of H_2O in 5 mL THF. After stirring for an additional 30 min. 10.0 equiv. of DDQ (0.43 g, 0.06 M) as solution in THF (32 mL) was added. After 1h the reaction mix was filtered through neutral alumina, washed with DCM and concentrated *in vacuo*. Column chromatography by alumina eluting with hexane/DCM (1:1 v/v) yielded **29** (28.50 mg, 0.05 mmol, 24 %) as a violet solid; mp > 250 °C[19] R_f 0.4 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.95 (s, 2H), 0.96 (t, *J*=6.84 Hz, 3H), 1.42 (q, *J*=7.84 Hz, 2H), 1.54 (m, 4H), 1.85 (q, *J*=7.84 Hz, 2H), 2.60 (q, *J*=7.84 Hz, 2H), 7.82 (d, *J*=6.84 Hz, 2H), 8.27 (d, *J*=5.88 Hz, 4H), 9.00 (t, *J*=4.92 Hz, 4H), 9.30 (d, *J*=3.92 Hz, 2H), 9.58 (d, *J*=4.88 Hz, 2H), 10.13 (s, 1H) ppm.

5,10,15-Triphenylporphyrin 42

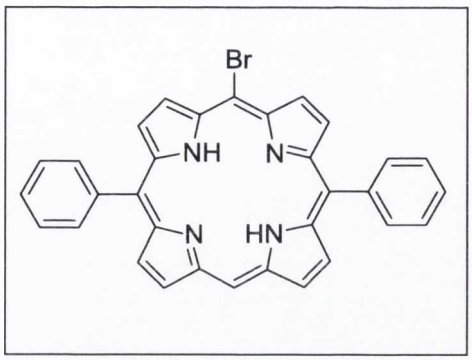


A 500 mL Schlenk flask was charged with 1.0 equiv. of **9** (0.50 g, 1.08 mmol) in dry THF (350 mL) under an argon atmosphere. The solution was cooled to 0 °C and 5.33 equiv. of PhenylLi (3.2 mL, 5.76 mmol, 1.8 M in dibutylether) was added drop wise over 15 min. After removal of the cold bath the reaction mixture was stirred for another hour, followed by addition of 5.0 mL H_2O in 1.0 mL saturated NH_4Cl. After stirring for 30 min. a solution of 4.0 equiv of DDQ in THF (0.06 M as solution) was added and the reaction mixture was stirred for another hour at room temperature. Subsequently, the mixture was filtered through silica gel and purified by flash chromatography on silica gel, followed by recrystallization from DCM/MeOH to yield **42** (0.49 g, 0.92 mmol, 85 %) as purple crystals; mp > 275 °C; [205] R_f 0.5 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.05 (s, 2H), 8.15 (m, 15H), 8.86 (m, 4H), 9.15(d, *J*=5.00 Hz, 4H), 10.25 (s, 1H) ppm.

General procedure for the synthesis of bromoporphyrins

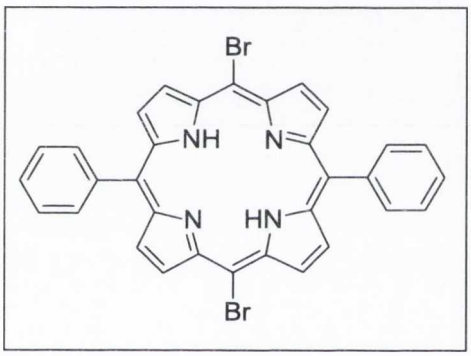
5-Bromo-10,20-diphenylporphyrin **26**, 5,15-Dibromo-10,20-diphenylporphyrin **27**, 5-Bromo-10,20-dihexylporphyrin **28** and 5-Bromo-10,15,20-triphenylporphyrin **43** were prepared according to a procedure by DiMango *et al.* [206] A 500 mL round bottom flask were charged with 1.0 equiv. of porphyrin in $CHCl_3$, 1.0 equiv. of NBS and pyridine (0.6 mL) and the solution stirred at room temperature for 0.5h – 2.0h (monitored by TLC). The reaction was quenched with acetone (2.0 mL). The solution was evaporated and the residue dissolved in $CHCl_3$ and filtered through silica plug and solvent was removed under reduced pressure. The crude was purified by recrystallization from $CHCl_3$/MeOH to yield the desired product.

5-Bromo-10,20-diphenylporphyrin 26



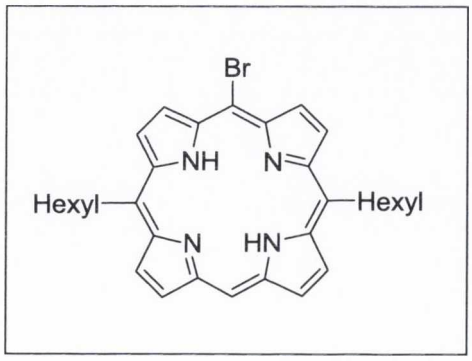
Prepared according to the above procedure using 1.0 equiv. of **9** (1 g, 1.19 mmol) and 1.0 equiv. of NBS (0.28 g, 1.54 mmol) to yield **26**; 0.32 g (0.90 mmol, 76 %) as violet solid; mp > 300 °C; [206] R_f 0.3 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.73 (s, 2H), 7.79 (m, 10H), 8.20 (m, 4H), 8.81 (d, 4H), 8.92 (d, 4H), 9.70 (s, 2H) ppm.

5,15-Dibromo-10,20-diphenylporphyrin 27



Prepared according to the above procedure using 1.0 equiv. of **9** (1 g, 1.19 mmol) and 2.0 equiv. of NBS (0.55 g, 3.09 mmol) to yield **27**; 2.34g (0.18 mmol, 99 %) as a violet solid; mp > 300 °C;[206] R_f 0.6 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.70 (s, 2H), 7.83 (m, 6H), 8.20 (d+d, J=1.16 Hz, 1.76 Hz, 4H), 8.87 (d, J=3.84 Hz, 4H), 9.65 (d, J=5.0 Hz, 4H) ppm.

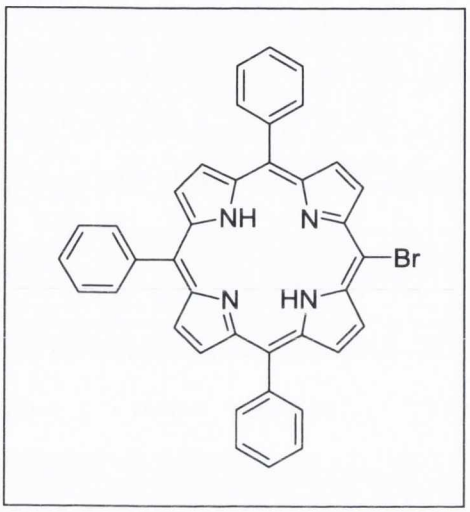
5-Bromo-10,20-dihexylporphyrin 28



Prepared according to the above procedure using 1.0 equiv. of **25** (1 g, 1.19 mmol) and 1.0 equiv. of NBS (0.55 g, 3.09 mmol) to yield **28**; 0.21 g (0.37 mmol, 86 %) as a violet solid; mp > 300 °C; [206] R_f 0.4 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$)) δ -2.91 (s, 2H), 0.96 (t, J=7.00 Hz, 6H), 1.42 (q, J=7.60 Hz, 4H), 1.52 (t, J=7.60 Hz, 4H),

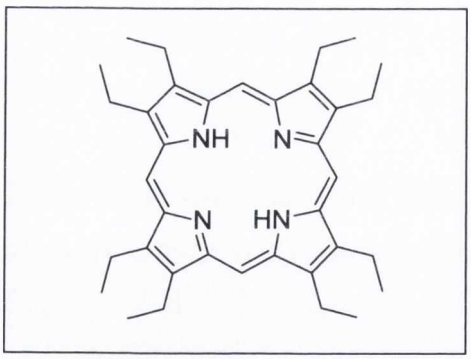
1.82 (q, *J*=7.60 Hz, 4H), 2.50 (q, *J*=8.20 Hz, 4H), 4.94 (t, *J*=8.20 Hz, 4H), 9.31 (d, *J*=4.08 Hz, 2H), 9.50 (d, *J*=4.08 Hz, 4H), 9.81 (d, *J*=4.08 Hz, 2H), 10.02 (s, 1H) ppm.

5-Bromo-10,15,20-triphenylporphyrin 43



Prepared according to the above procedure using 1.0 equiv. of **42** (1 g, 1.19 mmol) 1.0 equiv. of NBS (0.28 g, 1.54 mmol) to yield **43**; 0.68 g (1.14 mmol, 96 %) as a violet solid; mp > 300 °C;[205] R_f 0.3 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.73 (s, 2H), 7.79 (m, 10H), 8.20 (m, 4H), 8.81 (d, 4H), 8.92 (d, 4H), 9.70 (s, 2H) ppm.

2,3,7,8,12,13,17,18-Octaethylporphyrin 2



Step 1 – A 2L three-neck round bottom flask were charged with propionaldehyde (218 mL, 3 mol), isopropyl alcohol (450 mL) and potassium fluoride (25 g, 0.15 mol). The mixture was stirred at 5 °C – 12 °C and within 15 min. 1.0 equiv. of 1-nitropropane (268 mL, 3 mol) was added drop wise at the same temperature to the solution. The ice bath was removed about 30 min after the addition of 1-nitropropane is completed. The mixture was stirred overnight at room temperature. The catalyst was removed by filtration and the filtrate is concentrated under reduced pressure (temp – 88-90 °C, press – 5.0 mbar) to yield **61** (220 g, 55 %) as a light yellow liquid.

Step 2 - Flask from step 1 **61** was added a magnetic stirred egg and H_2SO_4 (0.7 mL). The contents was stirred in an ice bath (to maintain the temperature below 10 ^oC). Acetic anhydride (149 mL, 1.50 mol) was added drop wise and after the addition of Ac_2O was completed, the cooled bath was removed and the mixture was stirred at room temperature for additional 1h. The starting material was evaporated (temperature 43 ^oC and pressure 44) and the residue was distilled (89-92 ^oC and press 5.0 mbar) to yield **62** (230 g, 85 %) as a colourless oil.

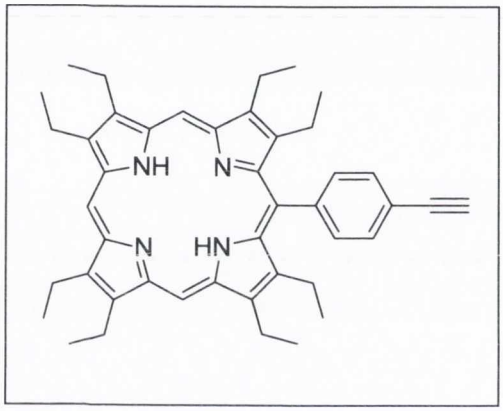
Step 3 – A 1L 3-neck round bottom flask equipped with a magnetic stirrer, dropping funnel, thermometer, and drying tube charged with **62** (103 g, 0.54 mol), ethyl isocyanate **63** (50.70 g, 0.45 mol), dry THF (320 mL) and isopropyl alcohol (130 mL). DBU (152 g, 1 mol) was added dropwise and temperature was maintain at 20 ^oC - 30 ^oC all the times. The orange colour solution was stirred overnight at room temperature. The solvent was completely removed under reduced pressure and the residue poured into 1L beaker and diluted with warm H_2O (300 mL) and extracted with diethyl ether (300 mL × 2). Ether layer was combined and washed with aqueous 10% HCl (300 mL × 2) and dried over with $MgSO_4$. The ether was removed under reduced pressure and yield **64** (75.50 g, 95 %) as a brown colour oil.

Step 4 - The suspension of $LiAlH_4$ (0.41 g, 0.01 mol) in dry THF (15 mL) was stirred at 0-3 ^oC and **64** (0.70 g, 3.60 mol) was added dropwise to the suspension. The mixture was stirred at 0-3 ^oC for 2h. Saturated NH_4Cl (30 mL) and ethyl acetate (5 mL) was then added to the mixture. The solid was filtered off and washed with ethyl acetate (40 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (2×30 mL). The combined organic phase was dry with Na_2SO_4 quickly and the solvent was removed to yield **65** as a light yellow colour oil.

Step 5 - Round bottom flask wrapped with aluminum foil and undried **65**, dimethoxymethane (2.70 g, 0.04 mol) in DCM (15 mL) and PTSA.H_2O (0.11 g, 0.59 mol) was added. The mixture was stirred at room temperature for 24h. One portion of *o*-chloranil (1 g, 4.10 mol) in DCM was added to the red reaction mixture, which was then

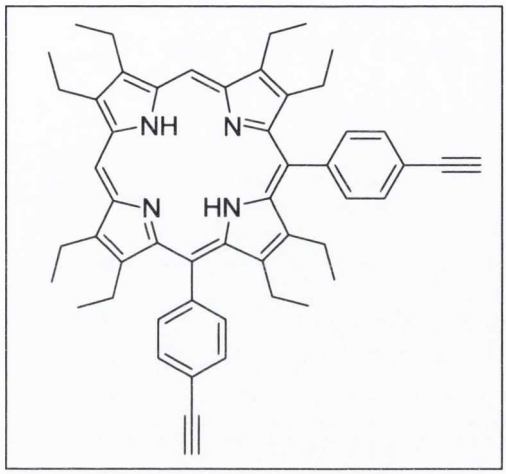
stirred at room temperature for another 24h. The mixture was washed with 1N NaOH (50 mL) and extracted with $CHCl_3$ (3×100 mL). The combined organic phases were rotary-evaporated and chromatographed on alumina using DCM as eluent. The product was recrystallized from $CHCl_3$/MeOH and gave **2**; 1 g (1.87 mmol, 14 %) as a violet solid; mp > 300 °C;[12,182] R_f 0.3 (hexane/DCM, 1:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.72 (s, 2H), 1.95 (t, *J*=7.60 Hz, 24H), 4.14 (q, *J*=7.60 Hz, 16H), 10.13 (s, 4H) ppm.

2,3,7,8,12,13,17,18-Octaethyl-5-(4-ethynyl-phenyl)porphyrin 81



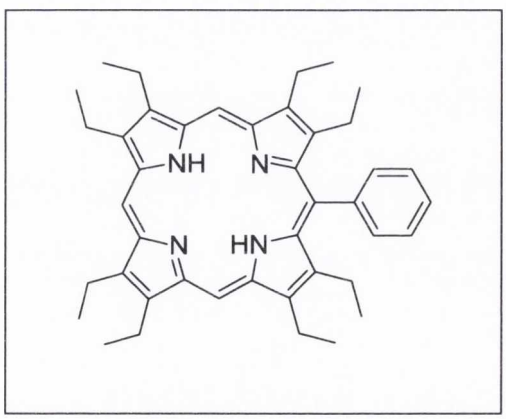
1-Bromo-4-ethynylbenzene (0.50 g, 2.76 mmol) was dissolved in dry diethylether (10 mL) in a 250 mL Schlenk tube. *n*-ButylLi (2.2 mL, 5.52 mmol of a 2.5 M solution in hexane) was added drop wise over 30 min. under argon at -70 °C. The reaction mixture was stirred until the temperature reached to -40 °C and THF (2 mL) was added drop wise until the aryl lithium compound formed a white suspension (light pink to white). After removal of the cold bath the mixture was stirred for 15 min. under argon. A solution of **2** (100 mg, 0.19 mmol) in dry THF (50 mL) was cooled to 0 °C and then added under argon to the vigorously stirred reaction mixture. The cold bath was removed and the mixture stirred for an additional hour (monitored by TLC), followed by addition of saturated NH_4Cl (1 mL). After stirring for an additional 30 min. 10.0 equiv. of DDQ (0.06 M as a solution in THF) was added. After 1h the reaction mixture was filtered through neutral alumina, washed with DCM and concentrated *in vacuo*. Column chromatographic work-up on alumina eluting with DCM/hexane (1:20, v/v), yielded **81** (0.10 g, 0.16 mmol, 85%) as purple crystals, mp 260 °C; [207] R_f 0.20 (DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.15, -3.02 (s, 2H), 1.18 (t, *J*=7.6, 6H), 1.88 (t, *J*=7.6, 6H), 1.94 (t, *J*=7.6, 12H), 2.81 (q, *J*=7.6, 12H), 3.37 (s, 1H), 4.09 (m, 12H), 7.84 (d, *J*=8.2, 2H), 8.22 (d, *J*=8.2, 2H), 9.96 (s, 1H), 10.20 (s, 2H) ppm.

2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(4-ethynyl-phenyl)-porphyrin 82



A solution of **81** (100 mg, 0.16 mmol) in THF (50 mL) was cooled to 0 °C and added to a vigorously stirred solution of 4-lithioethynylphenyl lithium. Subsequent steps followed the procedure given for the synthesis **81**. The reaction mixture was purified by column chromatography on neutral alumina eluting with DCM/hexane (3:2 v/v). Recrystallization from DCM/MeOH gave **82** as purple crystals (96 mg, 0.12 mmol, 76 %); Mp 220 °C;[207] R_f 0.5 (DCM/hexane 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.85 (s (br), 2H), 1.50 (t, *J*=7.5 Hz, 24H), 2.40 (m, 8H), 3.27 (s, 2H), 3.85 (q, *J*=7.5 Hz, 8H), 7.59 (d, *J*=4.7, 4H), 7.64 (d, *J*=4.7, 4H), 9.60 (s, 2H) ppm.

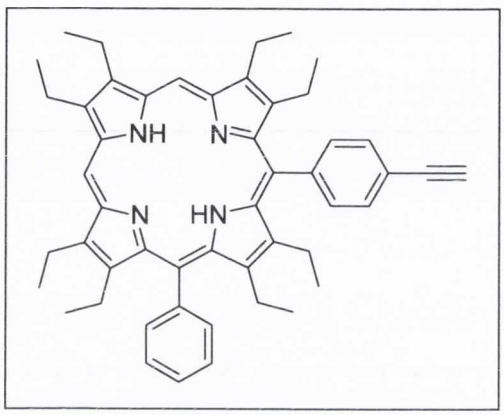
2,3,7,8,12,13,17,18-Octaethyl-5-phenylporphyrin 83



A solution of **2** (100 mg, 0.19 mmol) in dry THF (50 mL) was cooled to 0 °C and PhenylLi (0.5 mL, 0.98 mmol, 1.8 M in dibutylether) was added drop wise under argon over 15 min. After removal of the cold bath the reaction mixture was stirred for another 1h, followed by addition of 5 mL H_2O in 1 mL saturated NH_4Cl. After stirring for 30 min. a solution of 4.0 equiv. of DDQ in THF (0.06 M as solution) was added and the reaction mixture was stirred for another hour at room temperature. Subsequently, the mixture was filtered through neutral alumina and purified by flash chromatography on alumina, followed by recrystallization from DCM/MeOH to yield **83** (93 g, 0.15 mmol, 80 %) as a purple

crystals; Mp 225 °C;[19] R_f 0.5 (DCM/hexane 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.10, -2.96 (s (br), 2H), 1.20 (t, *J*=6.8 Hz, 6H), 1.91 (t, *J*=7.8 Hz, 6H), 1.97 (t, *J*=7.8 Hz, 12H), 2.80 (q, *J*=7.8 Hz, 4H), 4.11 (m, 12H), 7.71 (t, *J*=7.8 Hz, 2H), 7.85 (t, *J*=7.8, 1H), 8.26 (d, *J*=6.8, 2H), 9.98 (s, 1H), 10.23 (s, 2H) ppm.

2,3,7,8,12,13,17,18-Octaethyl-5-(4-ethynyl-phenyl)-10-phenylporphyrin 84



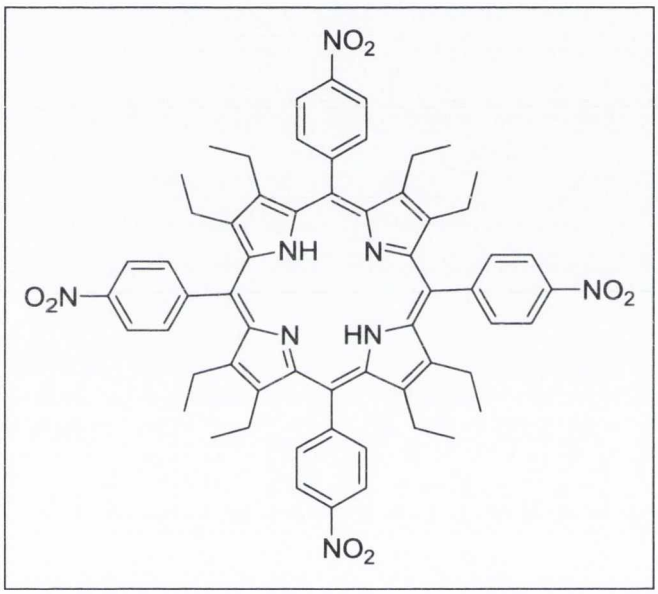
The organo-lithium reagent was prepared as described for the synthesis of **81**, using 0.50 g 1-bromo 4-ethynylbenzene (2.76 mmol) and reacted with 100 mg 2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrin (0.16 mmol) in THF (50 mL) at 0 °C. Purification by column chromatography on neutral alumina eluting with DCM/hexane (1:1, v/v) and recrystallization from DCM/MeOH gave **84** as purple crystals (82.00 mg, 0.12 mmol, 76 %), mp 265 °C;[207] R_f 0.2 (DCM/hexane: 3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.82 (s, 2H), 1.11 (t, *J*=7.5 Hz, 12H), 1.57 (t, *J*=7.3 Hz, 6H), 1.79 (t, *J*=7.3 Hz, 6H), 2.69 (m, 8H), 3.37 (s, 1H), 3.80 (m, 4H), 3.91 (m, 4H), 7.67 (m, 2H), 7.77 (m, 1H), 7.83 (d, *J*=4.3 Hz, 2H), 8.27 (d, *J*=4.3 Hz, 4H), 9.65 (s, 2H) ppm.

General procedure for the synthesis of nonplanar highly substituted porphyrins

2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-nitrophenyl)-porphyrin **69**, 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(pentafluorophenyl)-porphyrin **70** and 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-bromophenyl)-porphyrin **71** were prepared according to a procedure by Senge *et al.*[186] Dry DCM (1.5 L) was placed in a 2L three-neck round bottom flask equipped with a magnetic stirrer and gas inlet (argon) and the flask was covered with aluminium foil. The flask was charged with 1.2 equiv. of

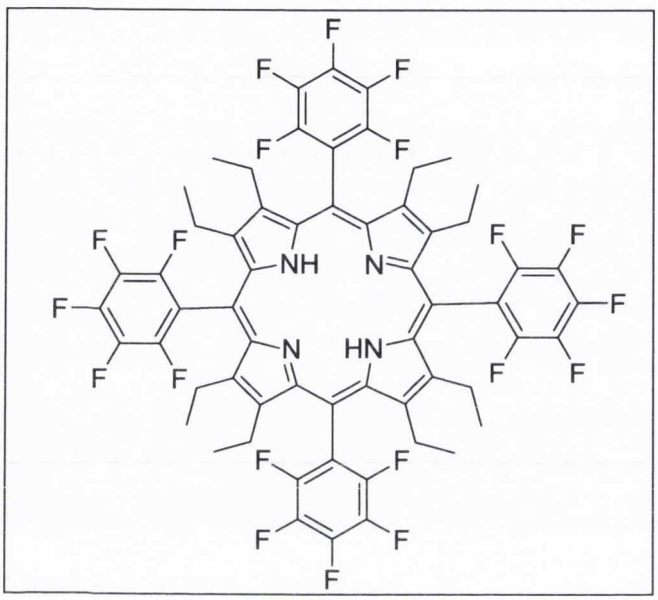
65 (10.5 mL, 0.15 mol), 1.2 equiv. of aldehyde (0.15 mol) and TFA (1.9 mL, 15.00 mmol) was added. The reaction was stirred for 18h at room temperature. After this time, 1.2 equiv. of DDQ (27.70 g, 0.12 mol) was added and the mixture stirred for a further hour. Then TEA (12.5 mL) was added before the reaction was filtered through neutral alumina with DCM followed by purification *via* column chromatography eluting with hexane/DCM 4:1 and finally recrystallization from DCM/MeOH.

2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-nitrophenyl)porphyrin 69



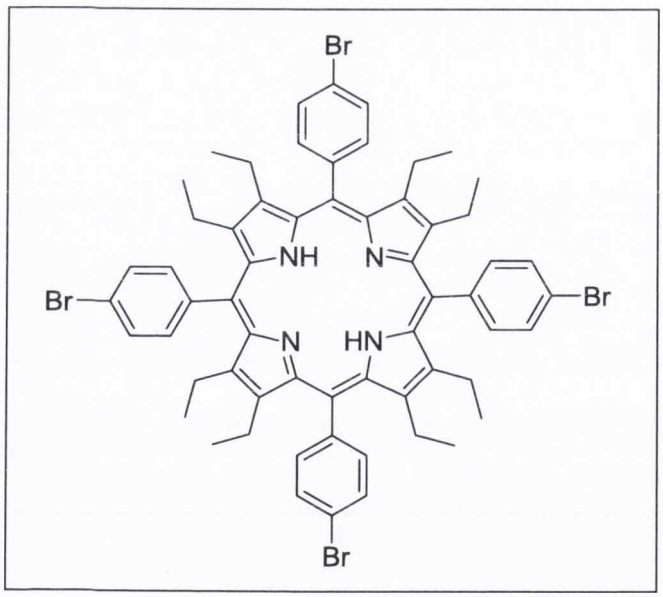
Prepared according to the above procedure using 4-nitrobenzaldehyde (1.63 g) to yield **69** as green coloured crystals (409.50 mg, 0.40 mmol, 16 %); mp > 300° C;[208] R_f 0.5 (DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ -1.92 (s (br), 2H), 0.50 (s (br), 24H), 1.42 (m, 6H), 2.55 (m,10H), 8.58 (d, *J*=8.2 Hz, 7H), 8.65 (d, *J*=8.2 Hz, 9H) ppm.

2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(pentafluorophenyl)porphyrin 70



Prepared according to the above procedure using pentafluorobenzaldehyde (1.06 g) to yield **70** as violet colour crystal (281.60 mg, 0.23 mmol, 19 %); mp > 300° C;[209] R_f 0.5 (hexane/DCM, 3:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -1.75 (s (br), 2H), 0.71 (s, 24H), 2.21 (s (br), 8H), 2.84 (s (br),8H) ppm.

5,10,15,20-Tetra(4-bromophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 71

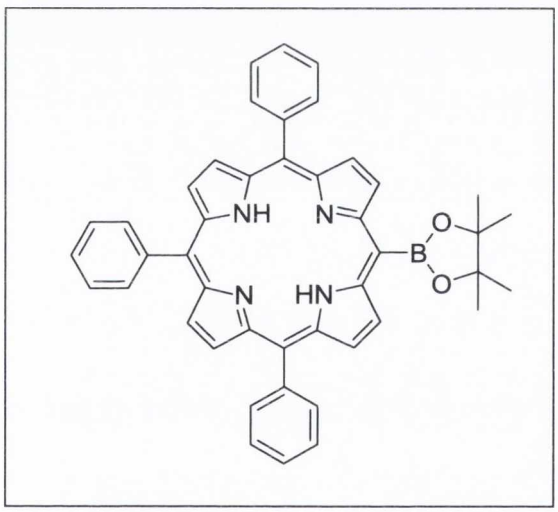


Prepared according to the above procedure using 4-bromobenzaldehyde (1.06 g) to yield **71** as green coloured solid (175.10 mg, 0.21 mmol, 16 %); mp > 300 °C; R_f 0.2 (hexane/DCM, 1:4, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (t, *J*=7.0 Hz, 24H), 2.11 (m, 8H), 2.40 (m, 8H), 8.04 (d, *J*=8.0 Hz, 8H), 8.39 (d, *J*=8.0 Hz, 8H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.4, 18.3, 116.6, 124.7, 131.2, 136.3, 137.7, 143.8 ppm; UV-vis (DCM) λ_{max} (log ε) 483 (2.6), 588 (0.9), 638 (1.2), 701 (1.7) nm; MALDI-TOF MS ($C_{60}H_{58}Br_4N_4$): calcd 1155.7453, found: 1155.1433.

General procedure for the synthesis of borylated porphyrins

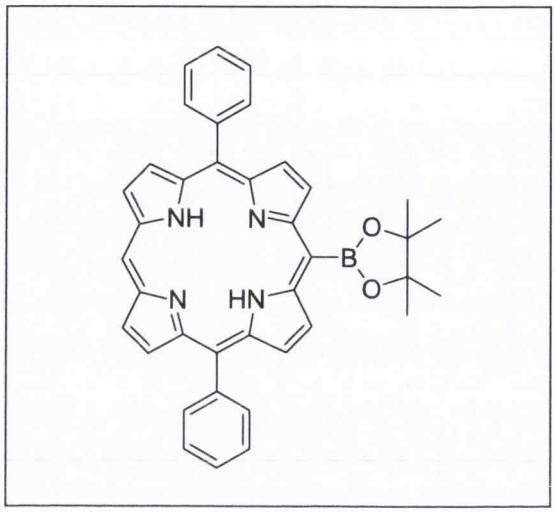
5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-10,15,20-triphenylporphyrin **44**, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-10,20-diphenylporphyrin **45** and 5,10-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-10,20-diphenylporphyrin **46** were prepared according to a procedure by Dahms *et al.*[154] The corresponding bromoporphyrin (222.70 g, 0.36 mmol) was dissolved in dry dichloroethane (23.0 mL) and dry TEA (0.7 mL, 4.69 mmol) under argon, followed by addition of pinacolborane (1.1 mL, 7.20 mmol) and $PdCl_2(PPh_3)_2$. The mixture was stirred at 75 °C and the reaction monitored by TLC. The residue was filtered through silica to remove the catalyst and purified *via* column chromatography on silica gel (hexane:DCM = 1:1 v/v) and finally recrystallization from DCM/MeOH.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane)-10,15,20-triphenylporphyrin 44



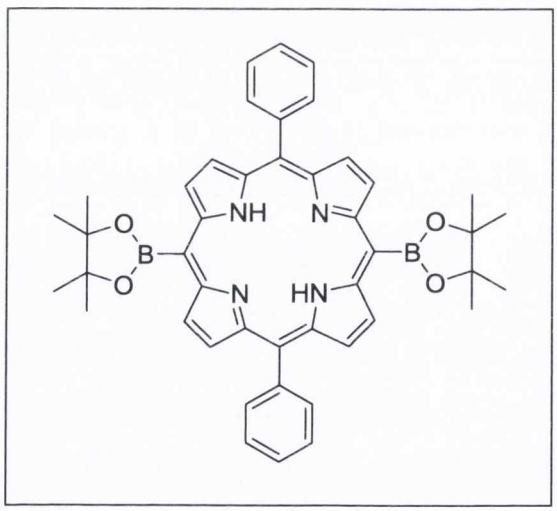
Prepared according to the above procedure using **43** (201.26 mg) to yield **44** as violet colour crystal (175.10 mg, 0.31 mmol, 87 %); mp: 252 °C.[156] R_f 0.2 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.78 (s, 2H), 1.86 (s, 12H), 7.79 (d, J = 7.0 Hz, 9H), 8.23 (d, J = 7.0 Hz, 5H), 8.85 (d+d, J = 4.7 Hz, 4.7 Hz, 4H), 8.99 (d, J = 4.7 Hz, 2H), 9.88 (d, J = 4.7 Hz, 2H) ppm.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane)-10,20-diphenylporphyrin 45



Prepared according to the above procedure using **26** (318.68 mg) to yield **45** as a violet colour crystal (290 mg, 91 %); mp: 230 °C.[156] R_f 0.3 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.14 (br, 2H), 1.88 (s, 12H), 7.83 (m, 6H), 8.58 (d, *J* = 6.4 Hz, 4H), 9.07 (d+d, *J* = 4.7 Hz, 4.7 Hz, 4H), 9.38 (d, *J* = 4.1 Hz, 2H), 9.91 (d, *J* = 4.7 Hz, 2H), 10.32 (s, 1H) ppm.

10,20-Di(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-5,15-diphenylporphyrin 46



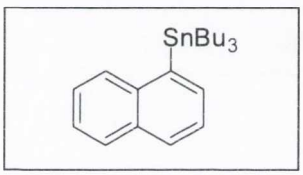
Prepared according to the above procedure using **27** (345 mg) to yield **46** as a violet colour crystal (138 mg, 40 %); mp: 260 °C. [156] R_f 0.1 (hexane/DCM, 1:1, v/v), ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.14 (br, 2H), 1.88 (s, 12H), 7.83 (m, 6H), 8.58 (d, *J* = 6.4 Hz, 4H), 9.07 (d+d, *J* = 4.7 Hz, 4.7 Hz, 4H), 9.38 (d, *J* = 4.1 Hz, 2H), 9.91 (d, *J* = 4.7 Hz, 2H), 10.32 (s, 1H) ppm.

General procedure for the synthesis of tin compounds

Tri-*n*-butylstannephenyl naphthalene **31**, 1,4-Bis(tri-*n*-butylstannyl)benzene **34** and 1,3-Bis(tri-*n*-butylstannyl)benzene **35** were prepared according to a procedure by Sangho *et*

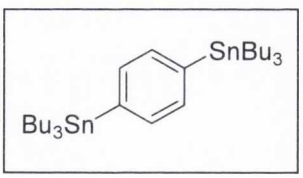
al.[210] The corresponding tinbromide (1.0 equiv.) in THF (37.5 mL) was stirred at 100 °C and 4.0 equiv. of *t*-buLi (12.5 mL, 17.50 mmol, 1.4 M in pentene) was added drop wise. The resulting greenish-brown suspension was stirred vigorously at that room temperature for 1h, followed by adding 3.0 equiv. of *n*-Bu_3SnCl (4 mL, 13.16 mmol). The reaction mixture was stirred at room temperature overnight and then was quenched with saturated aqueous NH_4Cl solution (10 mL). The solution was extracted with diethyl ether (40 mL), washed with brine (saturated NaCl solution, 2×30 mL) and dried over with Na_2SO_4. The mixture was filtered and concentrated under reduced pressure. The crude oil was purified by filtration *via* silica gel and washed with hexane to yield the desired products.

Tri-*n*-butylstannephenyl naphthalene 31



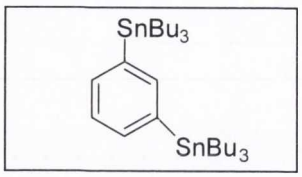
Prepared according to the above procedure using 1.0 equiv. **30** to yield **31**; 2.79g (3.73 mmol, 72 %) as light yellow oil;[211] R_f 0.4 (hexane); ^1H NMR (400 MHz, CD_2Cl_2) δ 0.90 (t, *J*=7.28 Hz, 9H), 1.31 (m, 12H), 1.55 (m, 6H), 7.51 (m, 3H), 7.66 (m, 1H), 7.83 (m, 3H) ppm.

1,4-Bis(tri-*n*-butylstannyl)benzene 34



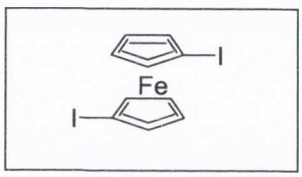
Prepared according to the above procedure using 1.0 equiv. **32** to yield **34**; 1.79g (2.73 mmol, 62 %) as colourless oil;[212] R_f 0.6 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J*=7.52 Hz, 18H), 1.10 (tr, *J*=8.04 Hz, 10H), 1.39 (q, *J*=7.52 Hz, 14H), 1.60 (m, 12H), 7.47 (s, 4H) ppm.

1,3-Bis(tri-*n*-butylstannyl)benzene 35



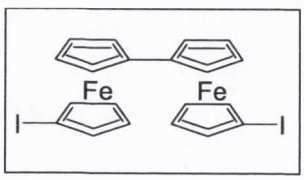
Prepared according to the above procedure using 1.0 equiv. **33** to yield **35**; 1.79g, (2.73 mmol, 62 %) as colourless oil;[212] R_f 0.5 (hexane); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.92 (t, *J*=7.52 Hz, 18H), 1.09 (m, 12H), 1.37 (m, 12H), 1.58 (m, 12H), 7.27 (m, 1H), 7.41 (m, 2H), 7.58 (m, 1H) ppm.

1,1'-Diiodoferrocene 47



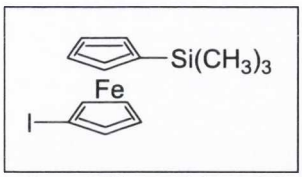
Ferrocene **18** (1.47 g, 7.89 mmol) was placed in a three-neck round bottom flask and then dried under vacuum for 2h. Dry ether (12.6 mL), *n*-BuLi (6.9 mL, 1.6 M in hexane) and TMEDA (2.6 mL, 17.35 mmol) were then added under argon and the mixture was stirred for another 12h. The mixture was cooled to -78 °C and 1,2-diiodoethane (4.89 g, 17.35 mmol) was slowly added over 30 min. The mixture was stirred at -78 °C for 4h and then stirred at room temperature for 2h. H_2O (10 mL) was added and the resulting mixture was extracted with DCM (3×10 mL). The DCM layer was dried over Na_2SO_4, evaporated at reduced pressure and purified *via* column chromatography on silica gel (hexane/DCM 4:1 v/v) to yield **47** (68 %) and **48** (28 %). **47** as a brown oil (2.36 g, 5.38 mmol, 68 %); R_f 0.7 (hexane);[142] ^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.16 (t, 4H), 4.23 (t, 2H), 4.27 (t, 2H) ppm.

1,1'-Diiodo-1,1'-bisferrocene 48



48 orange colour solid (0.50 g, 1.14 mmol, 28 %); mp: 260 °C.[143] R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.93 (t, 2H), 3,98 (t, 2H), 4.16 (t, 4H), 4.23 (t, 2H), 4.27 (t, 2H), 4.35 (t.2H), 4.40 (t, 2H) ppm.

1-Iodo-1'-trimethylsilaneferrocene 49



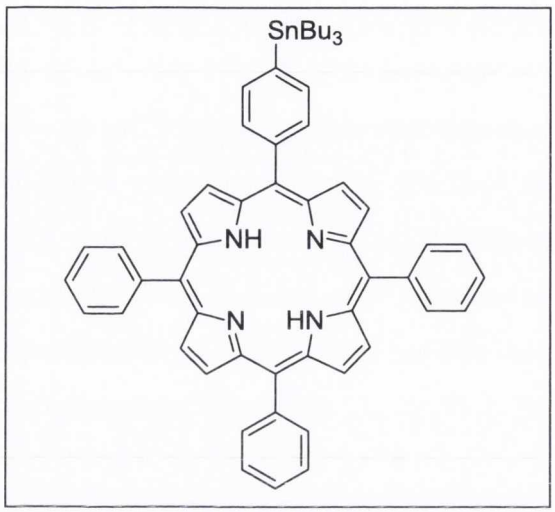
A three-neck round bottom flask were charged with **47** (1.72 g, 5 mmol), dry THF (20 mL) and *n*-BuLi (3.1 mL, 1.6 M in hexane). The resulting solution was stirred at -25 °C for 30 min., followed by chlorotrimethylsilane (5 mmol) and the solution was further stirred at -25 °C for another 25 min. H_2O (20 mL) was added, and the resulting mixture was extracted with ether (2×25 mL). The combined extracts were dried over Na_2SO_4 and evaporated at reduced pressure. The residue was purified on a column of alumina and eluated with hexane/DCM (3:2 v/v) to yield **49** (1.79 g, 2.73 mmol, 62 %) as a brown oil; R_f 0.5 (hexane);[144] ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.93 (t, 2H), 3,98 (t, 2H), 4.23 (t, 2H), 4.27 (t, 2H), 1.29 (t, 9H) ppm.

5.3 Tin porphyrins

General procedure for the synthesis of tin porphyrins *via* Stille coupling reaction

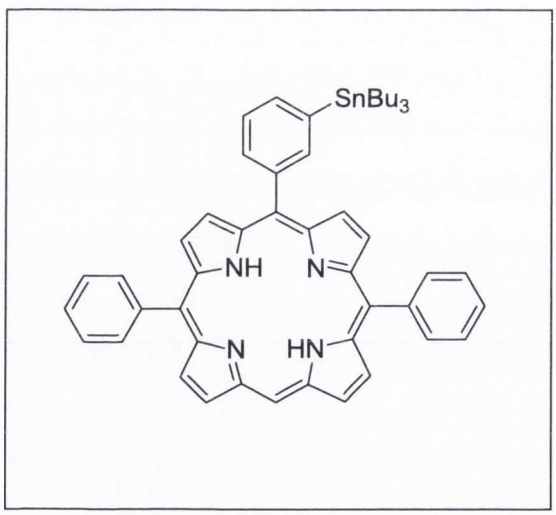
5-[4-(Tri-*n*-butylstannyl)phenyl]-10,15,20-triphenylporphyrin **37**, 5-[3-(Tri-*n*-butylstannyl)phenyl]-10,20-diphenylporphyrin **38**, 5,15-Di-(1-naphthalenyl)-10,20-diphenylporphyrin **39**, (*E*)-5-[2-(Tri-*n*-butylstannyl)vinyl]-10,20-diphenylporphyrin **40** and 1,3-Bis[5-(10,20-diphenylporphyrinyl)benzene **41** were prepared according to a procedure by Frampton *et al.*[104] A heterogeneous solution of a bromoporphyrin (1.0 equiv.), $Pd(PPh_3)_4$ (0.25 equiv.) and tin reagent (2.1 equiv.) in toluene (20 mL) was heated under argon at100 °C for 24-72 h (monitored by TLC). The reaction mixture was filtered through a plug of neutral alumina and washed with ethyl acetate. After removal of the solvents under reduced pressure the residue was chromotographed on neutral alumina using hexane/DCM (1:1 v/v) as a eluent and recrystallized from DCM/MeOH to gave the desired products.

5-[4-(Tri-*n*-butylstannyl)phenyl]-10,15,20-triphenylporphyrin 37



Prepared according to the above procedure using 1.0 equiv. of **27** and 2.1 equiv. of **34** to yield **37** (57.5 mg, 0.06 mmol, 53 %) as violet solid; mp > 300 °C;[101] R_f 0.6 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.59 (br, 2H), 1.05 (tr, *J*=7.3 Hz, 9H), 1.35 (m, 6H), 1.53 (m, 6H), 1.80 (m, 6H), 7.87 (m, 9H), 8.24 (d, *J*=7.8 Hz, 2H), 8.34 (m, 4H), 8.67 (m, 2H), 8.95 (m, 4H), 9.08 (br, 2H), 9.34 (br, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) 9.9, 13.9, 27.5, 29.3, 119.7, 120.3, 120.7, 126.8 (m), 127.8, 131.1 (br), 133.0, 134.3, 134.7 (m), 141.4, 141.7, 142.3 ppm; UV-Vis (THF) λ_{max} (log ε) 421 (4.9), 514 (4.1), 549 (4.0), 592 (3.9), 647 (3.9). TOF MS ES+ ($C_{56}H_{56}N_4Sn$) calcd for [M+H] 905.3605 found 905.3622.

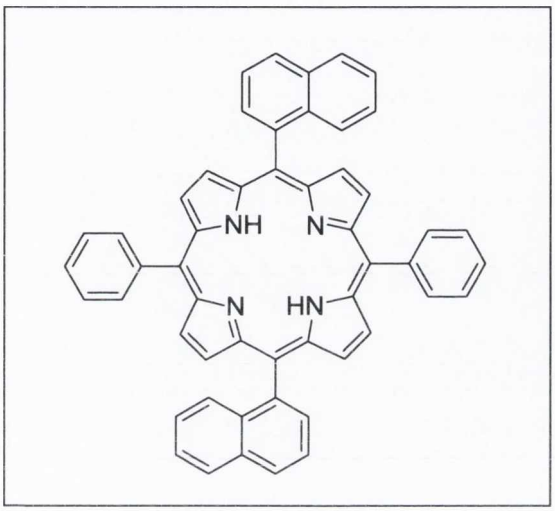
5-[3-(Tri-*n*-butylstannyl)phenyl]-10,20-diphenylporphyrin 38



Prepared according to the above procedure using 1.0 equiv. of **26** and 1.2 equiv. of **35** to yield **38** (25 mg, 0.03 mmol, 21 %) as a violet solid; mp 198 °C;[101] R_f 0.5 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.95 (s, 2H), 0.91 (s, 9H), 1.18 (tr, *J*=7.8 Hz, 6H), 1.37 (q, *J*=7.8 Hz, 6H), 1.65 (m, 6H), 7.83 (m, 8H), 8.18 (d, *J*=6.8 Hz, 1H), 8.29 (m, 5H), 8.94 (br, 4H), 9.06 (d, *J*=4.9 Hz, 2H), 9.37 (d, *J*=4.9 Hz, 2H), 10.25 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.9, 13.8, 27.4, 29.2, 104.7, 119.6, 121.4, 126.0, 126.8, 127.7, 130.6, 131.4, 134.2, 134.7, 135.7, 139.8,

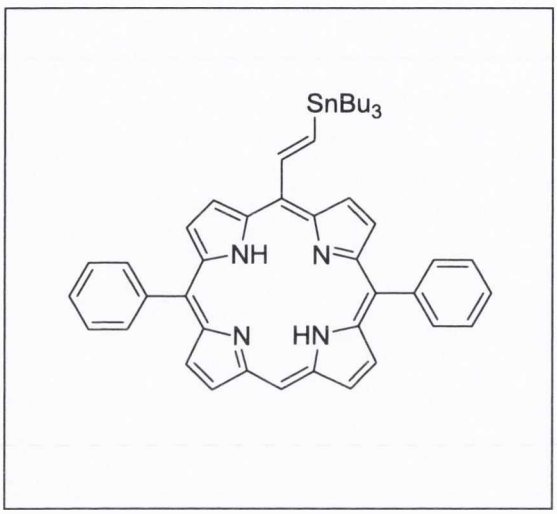
141.8, 141.9, 142.6, 146.4 ppm; UV-Vis (THF) λ_{max} (log ε) 412 (5.4), 440 (5.1), 509 (4.6), 545 (4.5), 585 (4.5), 643 (4.6) nm; TOF MS ES+ ($C_{50}H_{52}N_4Sn$) calcd for [M+H] 829.3292 found 829.3292.

5,15-Di-(1-naphthalenyl)-10,20-diphenylporphyrin 39



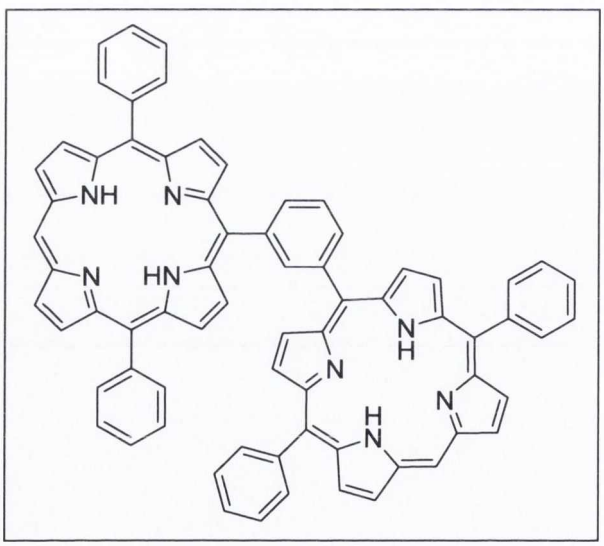
Prepared according to the above procedure using 1.0 equiv. of **27** and 2.6 equiv. of **31** to yield **39** (50.1 mg, 0.07 mmol, 37 %) as a violet solid; mp >300 °C;[101] R_f 0.4 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.48 (s, 2H), 7.15 (m, 4H), 7.52 (m, 2H), 7.74 (m, 6H), 7.90 (m, 2H), 8.20 (m, 6H), 8.32 (m, 4H), 8.61 (d, *J*=3.9 Hz, 4H), 8.77 (d, *J*=3.9 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 117.2, 119.7, 123.8, 125.2, 125.8, 126.2, 127.2, 127.4, 128.2, 130.7 (br), 132.3 (m), 134.0, 136.4, 138.9, 141.5 ppm; UV-Vis (THF) λ_{max} (log ε) 419 (6.0), 514 (5.0), 547 (4.8), 590 (4.8) nm; TOF MS ES+ ($C_{70}H_{46}N_8$) calcd for [M+H] 715.2862 found 715.2862.

(*E*)-5-[2-(Tri-*n*-butylstannyl)vinyl]-10,20-diphenylporphyrin 40



Prepared according to the above procedure using 1.0 equiv. **26** and 1.2 equiv. **36** to yield **40** (51.30 mg, 0.10 mmol, 55 %) as violet solid; mp 240° C;[101] R_f 0.6 (ethyl acetate/hexane, 1:7 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (br, 2H), 1.06 (tr, *J*=7.3 Hz,9H), 1.34 (m, 6H), 1.58 (m, 6H), 1.88 (m, 6H), 7.25 (d, *J*=19.0 Hz, 1H), 7.83 (m, 5H), 8.28 (m, 4H), 8.99 (d+d, *J*=4.6 Hz, 4H), 9.32 (d, *J*=4.6 Hz, 2H), 9.53 (d+d, *J*=4.6 Hz, 19.0 Hz, 3H), 10.17 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.2, 13.9, 27.5, 29.5, 104.5, 119.6, 121.1, 126.8, 129.9, 130.7, 131.1, 131.4, 134.7, 141.9, 146.9, 148.7 ppm; UV-Vis (THF) λ_{max} (log ε) 415 (5.6), 513 (4.7), 549 (4.7), 591 (4.6) nm; HRMS ($C_{46}H_{50}N_4Sn$) calcd for [M+H] 779.3136 found 779.3159.

1,3-Bis[5-(10,20-diphenylporphyrinyl)benzene 41



Prepared according to the above procedure using 1.0 equiv. **26** and 0.5 equiv. **35** to yield **41** (17 mg, 0.02 mmol, 28 %) as a purple colour crystal; mp >300° C;[101] R_f 0.2 (hexane/DCM, 3:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.94 (s, 4H), 7.84 (m, 12H), 8.27 (m, 8H), 8.67 (m, 2H), 9.06 (d+d, *J*=4.9 Hz, 8H), 9.37 (d+d, *J*=3.9 Hz, 8H), 10.24 (s, 2H) ppm; ^{13}C NMR (100.6 MHz,$CDCl_3$)

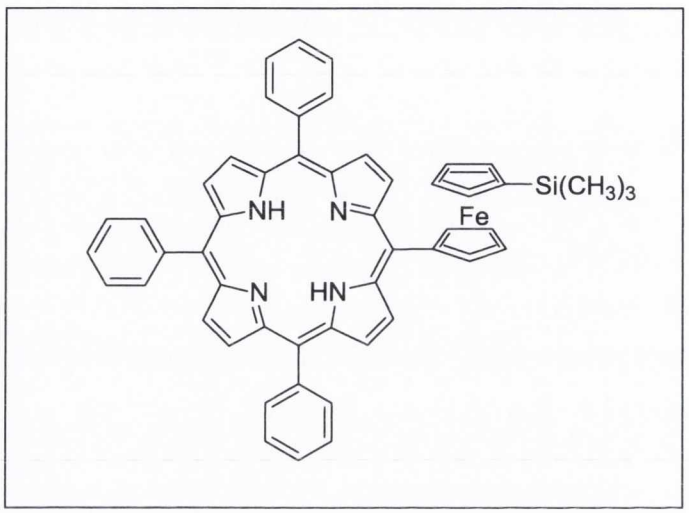
δ 104.5, 119.3, 119.6, 124.3, 126.4, 127.3, 130.7, 130.9 (br), 133.3, 134.2 (m), 139.5, 140.4, 145.7 (br), 146.1 (br) ppm; UV-Vis (THF) λ_{max} (log ε) 408 (5.8), 420 (5.7), 508 (4.9), 540 (4.7), 581 (4.7), 640 (4.5) nm; TOF MS ES+ ($C_{70}H_{46}N_8$) calcd for [M+H] 999.3925 found 999.3924.

5.4 Ferrocene porphyrins

General procedure for the synthesis of ferrocene porphyrins *via* Suzuki coupling reaction

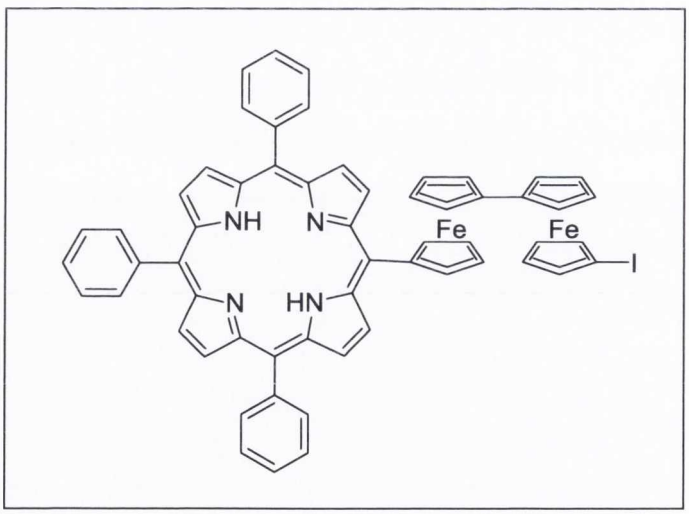
5,10,15-Triphenyl-20-(trimethylsilylferrocenyl)porphyrin **50**, 5-(iodo-1,1'*bis*-ferrocenyl)-10,15,20-triphenylporphyrin **51**, 5-(iodoferrocenyl)-10,15,20-triphenylporphyrin **52**, 5,15-Diphenyl-10-(trimethylsilylferrocenyl)porphyrin **53**, 5-(iodo-1,1'*bis*-ferrocenyl)-10,20-diphenylporphyrin **54**, 5-(iodoferrocenyl)-10,20-diphenylporphyrin **55**, 5-Ferrocenyl-10,20-diphenylporphyrin **56** and 5,15-di(iodoferrocene)-10,20-diphenylporphyrin **57** were prepared according to a procedure by Hyslop *et al.*[190] A 100 mL shlenk tube were charged with borylated porphrins (1.0 equiv.) and ferrocene reagent (1.0 equiv.) and THF (20 mL). The mixture was degasses (freeze-pump-thaw) three time and followed by addition of Cs_2CO_3 (2.0 equiv. total equiv. of reagent and starting material) and the mixture was degassed again. $Pd(PPh_3)_4$ (0.13 equiv) was added and the mixture was refluxed under argon at 77 ^oC for 24-48 h (monitored byTLC). The reaction mixture was filtered through silica gel and washed with DCM. After removal of the solvents under reduced pressure the residue was chromotographed on silica gel (hexane:DCM, 1:1, v/v) and recrystalized from DCM:MeOH.

5,10,15-Triphenyl-20-(trimethylsilylferrocenyl)porphyrin 50



Prepared according to the above procedure using 1.0 equiv. of **44** and 1.0 equiv. of **49** to yield **50** as green solid (18.90 mg, 37 %); mp: > 300 °C;[156] R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.28 (br, 2H), 1.28 (s, 9H), 4.24 (m, 4H), 4.82 (t, J = 1.8 Hz, 2H), 5.56 (t, J = 1.8 Hz, 2H), 7.78 (m, 9H), 8.22 (m, 6H), 8.78 (m, 6H), 10.00 (d, J = 3.5 Hz, 2H) ppm, ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 31.0, 69.5, 74.9, 75.2, 77.5, 118.2, 119.7, 120.2, 122.8, 126.7, 126.8, 127.7, 130.9 (m), 134.5, 134.6, 141.8, 142.5 ppm; UV-vis (THF) λ_{max} (log ε) 420 (5.6), 447 (5.0), 517 (4.7), 595 (4.7), 653 (4.6) nm; MALDI-TOF MS ($C_{51}H_{42}FeN_4Si$) calcd for [M + H] 795.2608, found 795.262.

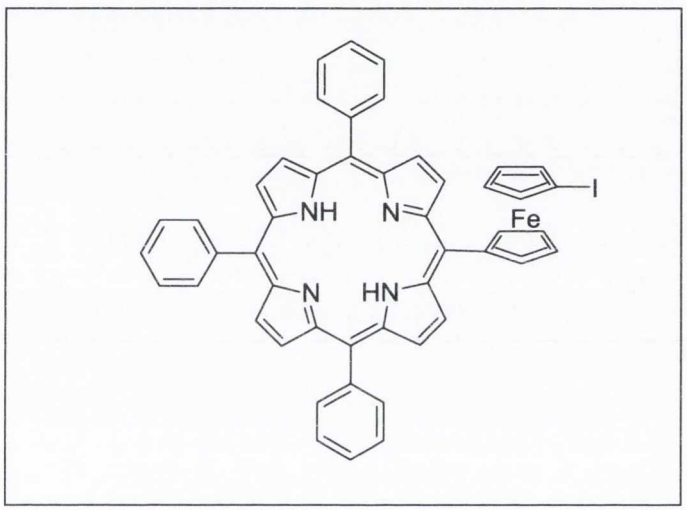
5-(Iodo-1,1'*bis*-ferrocenyl)-10,15,20-triphenylporphyrin 51



Prepared according to the above procedure using 1.0 equiv. of **44** and 1.0 equiv. of **48** to yield **51** as green solid (11.70 mg, 29 %); mp: > 300 °C;[156] R_f 0.3 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.29 (br, 2H), 3.89 (s, 2H), 4.08 (s, 4H), 4.19 (m, 4H), 4.53 (br, 2H), 4.63 (br, 2H), 5.47 (br,

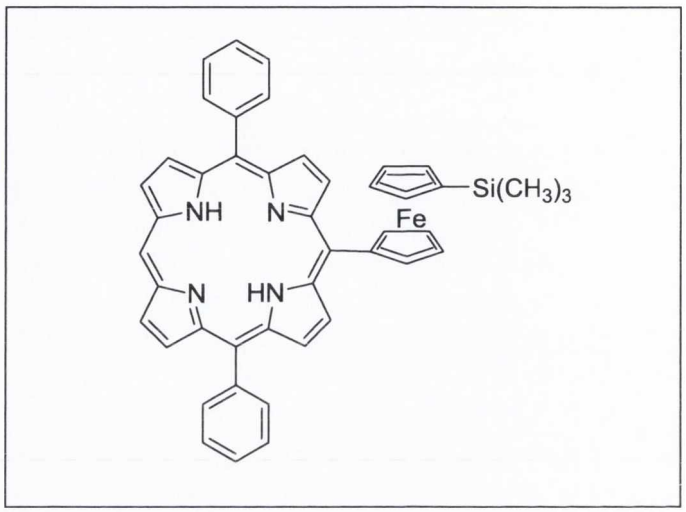
2H), 7.78 (m, 9H), 8.23 (m, 6H), 8.77 (m, 6H), 9.96 (br, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 68.1, 69.0, 69.5, 70.4, 75.2, 77.9, 113.8, 124.8, 126.2, 126.3, 127.2, 127.8, 129.4, 134.0, 138.2, 142.0 ppm; UV-vis (THF) λ_{max} (log ε) 418 (5.6), 515 (4.7), 549 (4.7), 592 (4.6), 649 (4.6) nm; MALDI-TOF MS ($C_{56}H_{41}Fe_2IN_4$) calcd 1032.1078, found 1032.1198.

5-(iodoferrocenyl)-10,15,20-triphenylporphyrin 52



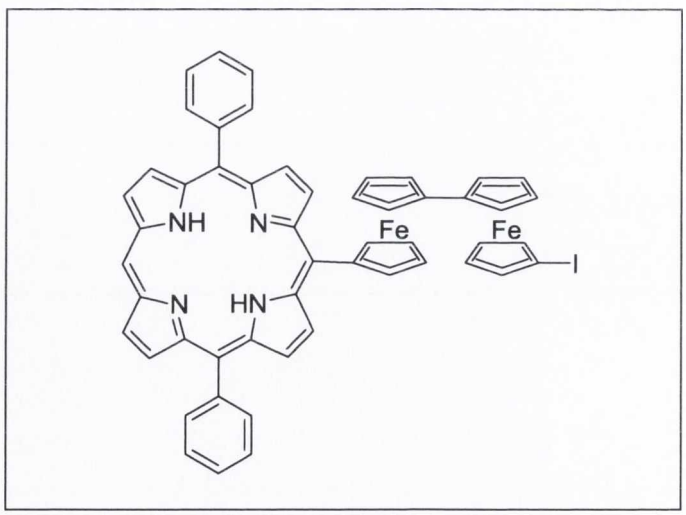
Prepared according to the above procedure using 1.0 equiv. of **44** and 1.0 equiv. of **47** to yield **52** as green solid (15.10 mg, 29 %); mp: > 300 °C;[156] R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.30 (br, 2H), 4.10 (t, *J* = 1.8 Hz, 2H), 4.48 (t, *J* = 1.7 Hz, 2H), 4.84 (t, *J* = 1.7 Hz, 2H), 5.59 (t, *J* = 1.8 Hz, 2H), 7.56 (m, 2H), 8.22 (m, 5H), 8.78 (m, 5H), 7.78 (m, 9H), 10.09 (d, *J* = 7.8 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 67.7, 72.3, 73.3, 79.0, 126.2, 126.4, 127.3, 128.4, 130.4, 134.1, 138.1, 142.0 ppm; UV-vis (THF) λ_{max} (log ε) 419 (5.6), 513 (4.7), 581 (4.7), 669 (4.6) nm; MALDI-TOF MS ($C_{48}H_{33}FeIN_4$) calcd 848.1100, found 848.1074.

5,15-Diphenyl-10-(trimethylsilylferrocenyl)porphyrin 53



Prepared according to the above procedure using 1.0 equiv. of **45** and 1.0 equiv. of **49** to yield **53** as green solid (11.40 mg, 23 %); Mp: > 300 °C;[156] R_f 0.4 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.62 (br, 2H), 1.28 (s, 9H), 4.21 (br, 4H), 4.87 (br, 2H), 5.59 (br, 2H), 7.82 (m, 6H), 8.26 (d+d, *J* = 2.0 Hz, 3.0 Hz, 4H), 8.86 (d, *J* = 4.9 Hz,2H), 8.93 (d, *J* = 3.9 Hz, 2H), 9.27 (d, *J* = 4.9 Hz, 2H), 10.10 (br, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 29.7, 69.0, 70.7, 77.8, 104.3, 118.6, 119.7, 126.7, 127.7, 131.4 (m), 134.6, 142.1 ppm; UV-vis (THF) λ_{max} (log ε) 416 (5.6), 507 (4.7), 588 (4.7), 668 (4.6) nm; MALDI-TOF MS ($C_{45}H_{38}FeN_4Si$) calcd 718.2216, found 718.2234.

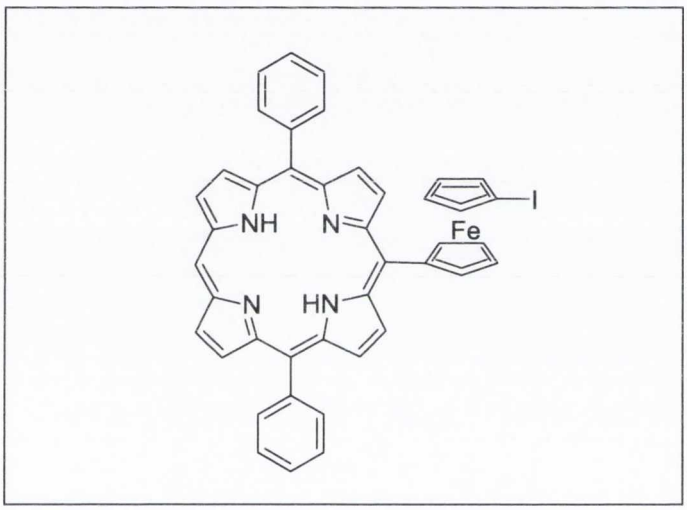
5-(Iodo-1,1'*bis*-ferrocenyl)-10,20-diphenylporphyrin 54



Prepared according to the above procedure using 1.0 equiv. of **45** and 1.0 equiv. of **48** to yield **54** as green solid (15.60 mg, 23 %); mp: > 300 °C;[156] R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.63 (br, 2H), 3.89 (s, 2H), 4.08 (d, *J* = 1.8 Hz, 4H), 4.18(s, 4H), 4.50 (s, 2H), 4.61 (s, 2H), 5.44

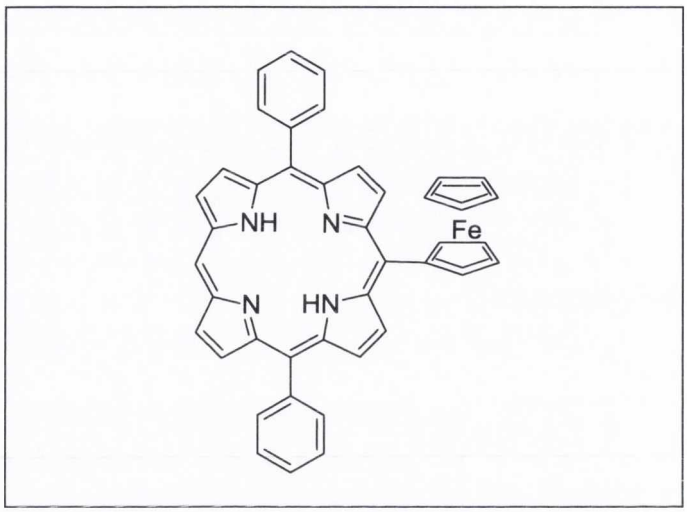
(s, 2H), 7.82 (m, 6H), 8.27 (d, J = 4.7 Hz, 4H), 8.83 (d, J = 4.7 Hz, 2H), 8.93 (d, J = 4.7 Hz, 2H), 9.27 (d, J = 4.6 Hz, 2H), 10.02 (br, 2H), 10.09 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 67.7, 68.1, 69.0, 69.5, 70.4, 71.3, 71.6, 75.3, 78.2, 103.9, 119.2, 126.3, 127.3, 128.4, 130.5, 132.0, 134.2, 141.7 ppm; UV-vis (THF) λ_{max} (log ε) 413 (5.6), 509 (4.7), 542 (4.7), 586 (4.6), 642 (4.6) nm; MALDI-TOF MS ($C_{52}H_{37}Fe_2IN_4$) calcd 956.0764, found 956.0788.

5-(Iodoferrocenyl)-10,20-diphenylporphyrin 55



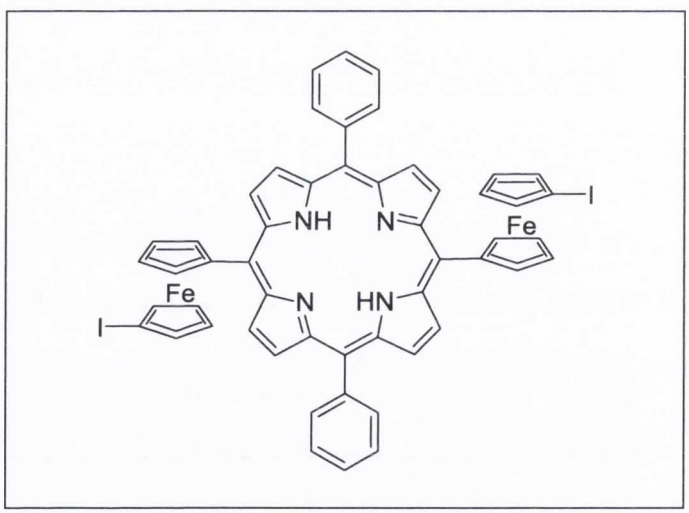
Prepared according to the above procedure using 1.0 equiv. of **45** and 1.0 equiv. of **47** to yield **55** as green solid (48.80 mg, 37 %); mp: > 300 °C;[156] R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.65 (br, 2H), 4.09 (s, 2H), 4.48 (s, 2H), 4.84 (s, 2H), 5.60 (s, 2H), 7.82 (m, 6H), 8.26 (d, J = 5.8 Hz, 4H), 8.89 (d+d, J = 3.9 Hz, 4.9 Hz, 4H), 9.27 (d, J = 4.9 Hz, 2H), 10.03 (br, 2H), 10.12 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 68.8, 70.5, 77.6, 90.0, 104.6, 118.5, 119.8, 126.8, 127.7, 131.0 (m), 134.6, 142.1 ppm; UV-vis (THF) λ_{max} (log ε) 415 (5.6), 509 (4.7), 584 (4.7), 661 (4.6) nm; MALDI-TOF MS ($C_{42}H_{29}FeIN_4$) calcd 772.0787, found 772.0777.

5-Ferrocenyl-10,20-diphenylporphyrin 56



Prepared according to the above procedure using 1.0 equiv. of **45** and 1.0 equiv. of **47** to yield **55** as purple solid (10 mg, 38 %); mp > 200 °C;[132] R_f 0.5 (DCM/hexane: 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.59 (s (br),1H), 4.05 (s, 2H), 4.11 (s, 2H), 4.21 (s, 1H), 4.77 (s, 1H), 4.86 (s, 1H), 5.53 (s, 1H), 5.59 (s, 1H), 7.82 (d, *J*=6.5 Hz, 6H), 8.27 (m, 4H), 8.85 (d, *J*= 4.7 Hz, 2H), 8.94 (d, *J*= 4.7 Hz, 2H), 9.26 (d, *J*= 4.7 Hz, 2H), 10.10 (m, 3H) ppm

5,15-Di(iodoferrocene)-10,20-diphenylporphyrin 57



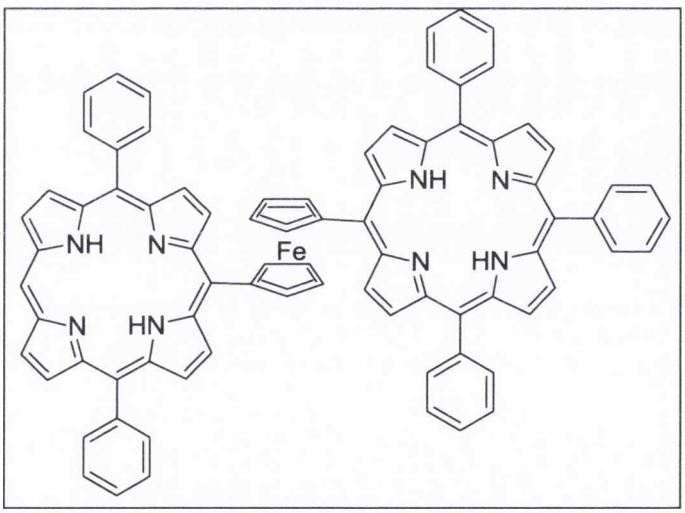
Prepared according to the above procedure using 1.0 equiv. of **46** and 2.0 equiv. of **47** to yield **56** as green solid (9.10 mg, 29 %); mp: > 300 °C;[156] R_f 0.4 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ - 1.66 (br, 2H), 4.02 (t, *J* = 1.8 Hz, 2H), 4.14 (s, 4H), 4.33 (br, 2H), 4.42 (t, *J* = 1.8 Hz, 2H), 4.82 (d+t, *J* = 1.8 Hz, 12.2Hz, 3H), 5.53 (d, *J* = 1.8 Hz, 3H), 7.79 (m, 6H), 8.20 (m, 4H), 8.70 (t, *J* = 4.1 Hz, 4H), 9.82 (d+d, *J* = 4.9 Hz, 5.2 Hz, 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 67.5, 68.4, 70.6, 71.8, 74.0, 77.1, 104.9, 118.7, 126.6, 127.3, 130.6, 131.2, 134.4, 140.9, 144.8, 146.7 ppm; UV-vis (THF) λ_{max} (log ε) 419 (5.6), 516 (4.7),

549 (4.7), 593 (4.6), 651 (4.3), 742 (4.1) nm; MALDI-TOF MS ($C_{52}H_{37}Fe_2I_2N_4$) calcd [M - I] 956.0764, found 956.0826.

General procedure for the synthesis of ferrocene bridged porphyrins *via* Suzuki coupling reaction

1-(5,15-Diphenylporphyrin)-1'-(5,10,15-triphenylporphyrin)ferrocene **58** and 1,1'-*Bis*(5,15-diphenylporphyrin)ferrocene **59** were prepared according to a procedure by Hyslop *et al.*[145] A heterogeneous solution of a compound **47** (0.14 mmol), borylated porphrins (0.14 mmol), Cs_2CO_3 (91.23 mg, 0.28 mmol) and $Pd(PPh_3)_4$ (21.03 mg, 0.02 mmol) in THF (20 mL) was reflux under argon at 77 °C for 24-48 h (monitored by TLC). The reaction mixture was filtered through silica gel and washed with DCM. After removal of the solvents under reduced pressure the residue was chromotographed on silica gel (hexane:DCM, 2:3, v/v) and recrystalized from DCM/MeOH.

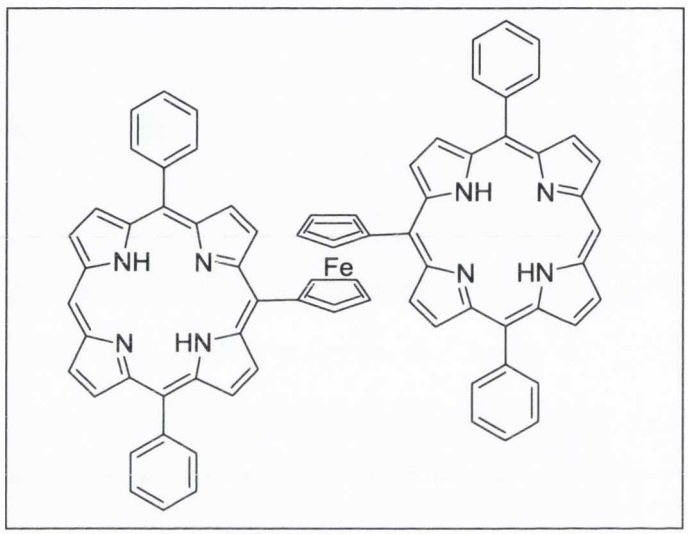
1-(5,15-Diphenylporphyrin)-1'-(5,10,15-triphenylporphyrin)ferrocene 58



Prepared according to the above procedure using 1.0 equiv of **44**, 1.0 equiv. of **45** and 1.0 equiv. of **47** to yield **58** as a green solid (13.20 mg, 28 %); mp: > 300 °C;[156] R_f 0.20 (hexane/DCM, 2:3, v/v); ^1H NMR (400 MHz, $CDCl_3$): δ -3.04 (br, 2H), -2.75 (br, 2H), 4.96 (br, 4H), 5.65 (br, 4H), 7.45 (m, 11H), 7.91 (m, 10H), 8.23 (m, 4H), 8.44 (m, 3H), 8.72 (m, 7H), 9.19 (m, 2H), 9.84 (m, 4H), 10.05 (s,1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 69.9, 70.2, 70.6, 77.4, 78.0,89.4, 90.1, 103.8, 118.6, 119.2, 119.3, 126.3, 127.2, 130.5, 131.2 (m), 134.2,

141.7 ppm; UV-vis (THF) λ_{max} (log ε) 416 (5.6), 513 (4.7), 547 (4.7), 591 (4.7), 647 (4.6), 742 (4.3) nm; MALDI-TOF MS ($C_{80}H_{54}FeN_8$) calcd 1182.3823, found 1182.3801.

1,1'-*Bis*(5,15-diphenylporphyrin)ferrocene 59



Prepared according to the above procedure using 2.0 equiv. of **45** and 1.0 equiv. of **47** to yield **59** as a green solid (13.20 mg, 30 %); Mp: > 300 °C;[156] R_f 0.23 (hexane/DCM, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ -2.96 (br, 4H), 4.86 (s, 4H), 5.59 (s, 4H), 7.39 (m, 8H), 7.56 (m, 12H), 8.03 (d, J = 3.5 Hz, 4H), 8.69 (d, J = 4.0 Hz, 4H), 9.21 (d, J = 4.0 Hz, 4H), 9.90 (br, 4H), 10.07 (s, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 67.7, 70.8, 79.5, 91.8, 104.0, 116.3, 118.7, 124.9, 125.8, 126.8, 127.8, 128.4, 128.6, 130.5, 133.7, 137.4, 141.1 ppm; UV-vis (THF) λ_{max} (log ε) 413 (5.6), 510 (4.7), 551 (4.7), 588 (4.7), 643 (4.6), 741 (4.3) nm; MALDI-TOF MS ($C_{74}H_{50}FeN_8$) calcd 1106.3511, found 1106.3480.

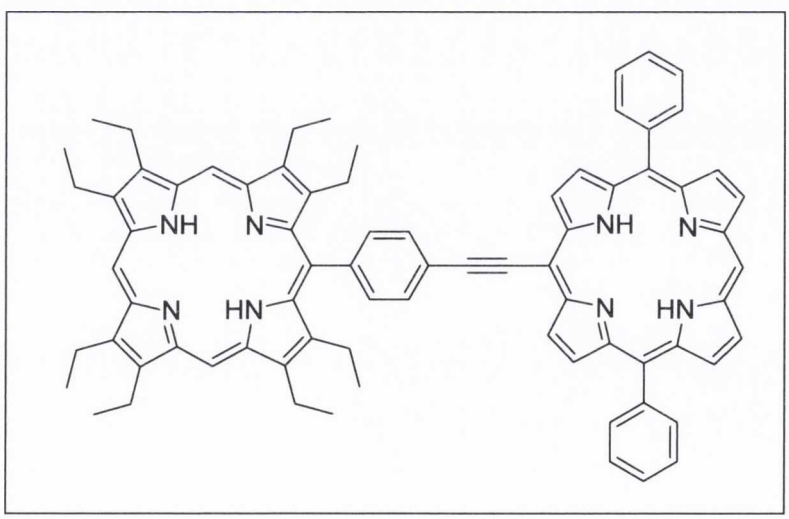
5.5 Non planar multiporphyrin arrays

General procedure for the synthesis of dimers and trimers *via* Sonogashira coupling reaction

2,3,7,8,12,13,17,18-Octaethyl-5-[4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl]porphyrin **85**, 2,3,7,8,12,13,17,18-Octaethyl-5-[4-(10',15',20'-triphenylporphyrin-5-yl)phenylethynyl]porphyrin **86**, 2,3,7,8,12,13,17,18-Octaethyl-5-

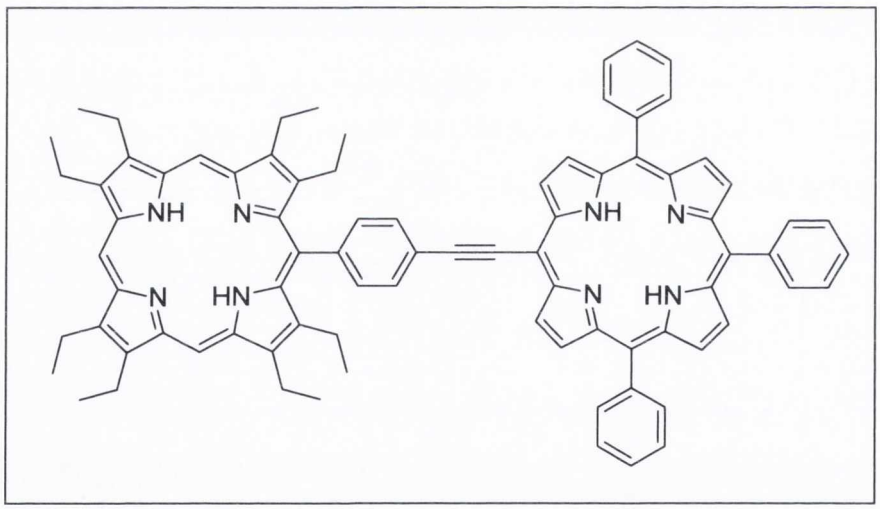
[4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl]-10-phenylporphyrin **87**, 2,3,7,8,12,13,17,18-Octaethyl-5-[4-(10',15',20'-triphenylporphyrin-5-yl)phenylethynyl]-10-phenylporphyrin **88**, 5,15-Bis[4-(2',3',7',8',12',13',17',18'-Octaethylpoprhyrin-5-yl)ethynylphenyl]-10,20-diphenylporphyrin **89**, 2,3,7,8,12,13,17,18-Octaethyl-5,10-bis[4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl]porphyrin **90** and 2,3,7,8,12,13,17,18-Octaethyl-5,10-bis[4-(10',15',20'-triphenylporphyrin-5-yl)phenylethynyl]porphyrin **91** were prepared according to a procedure by Odobel *et al.*[190] A heterogeneous solution of a ethyyl-substituted porphyrin (1equiv.) and bromoporphyrin (1 equiv.) with dry THF (15 mL) and dry TEA (5 mL) and were added to 50 mL Shlenk tube. The mixture was degasses (freeze-pump-thaw) three time and followed by addition of CuI (0.2 equiv.) and the mixture was degasses again. $PdCl_2(PPh_3)_2$ (0.1 equiv.) were added and the mixture was reflux under argon at 60 ^oC in the close system for 24-48 h (monitored byTLC). The reaction mixture was filtered through silica gel and washed with DCM. After removal of the solvents under reduced pressure the residue was chromotographed on silica gel (hexane/DCM 3:2 v/v) and recrystalization from DCM/MeOH.

2,3,7,8,12,13,17,18-Octaethyl-5-[4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl]porphyrin 85



Prepared according to the above procedure using 1.0 equiv. of **81** and 1.0 equiv of **26** to yield **85** as green solid (43.80 mg, 0.04 mmol, 50 %); mp > 300° C; R_f 0.2 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.07, -2.92 (s, 2H), -2.42 (s, 2H), 1.36 (t, *J* = 7.6 Hz, 6H), 1.95 (m, 18H), 3.04 (d, *J* = 7.6 Hz, 4H), 4.13 (m, 12H), 7.87 (s (br), 6H), 8.33 (m, 4H), 8.42 (d, *J* = 7.6 Hz, 2H), 8.49 (d, *J* = 7.6 Hz, 2H), 9.02 (d, *J* = 4.6 Hz, 2H), 9.13 (d, *J* = 4.6 Hz, 2H), 9.34 (d, *J* = 4.6 Hz, 2H), 10.00 (s (br), 1H), 10.10 (d, *J* = 4.6 Hz, 2H), 10.24 (d, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.8, 18.0, 18.1, 18.2, 19.3, 19.4, 20.7, 96.4, 106.2, 120.3, 123.7, 126.6, 127.5, 129.1, 130.8, 133.4, 134.3, 140.6, 140.9, 141.9, 142.1, 144.0 ppm; UV-vis (DCM) λ_{max} (log ε) 409 (2.5), 434 (2.8), 505 (1.6), 533 (1.4), 571 (1.8), 661 (1.2) nm; MALDI-TOF MS ($C_{76}H_{70}N_8$): calcd 1094.5723, found [M+H]: 1095.5786.

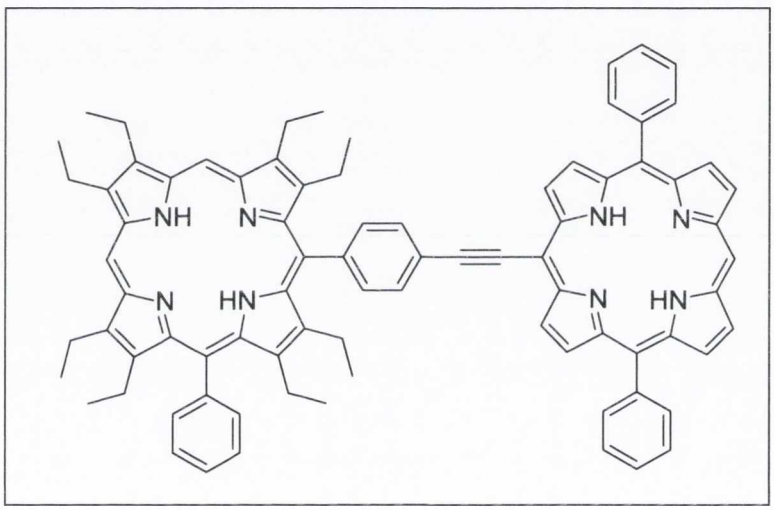
2,3,7,8,12,13,17,18-Octaethyl-5-[4-(10',15',20'-triphenylporphyrin-5-yl)phenylethynyl]porphyrin 86



Prepared according to the above procedure using 1.0 equiv. of **81** and 1.0 equiv. of **43** to yield **86** as green solid (36 mg, 0.03 mmol, 39 %); mp > 300° C; R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.08, -2.92 (s, 2H), -2.18 (s, 2H), 1.35 (t, *J* = 7.0 Hz, 4H), 1.96 (m, 20H), 3.04 (q, *J* = 7.0 Hz, 4H), 4.12 (q, *J* = 7.6 Hz, 14H), 7.82 (m, 9H), 8.24 (d, *J* = 7.6 Hz, 2H), 8.30 (d, *J* = 7.0 Hz, 4H), 8.41 (d, *J* = 7.6 Hz, 2H), 8.49

(d, J = 7.6 Hz, 2H), 8.84 (s, 4H), 9.06 (d, J = 4.0 Hz, 2H), 10.00 (s, 3H), 10.30 (s, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.8, 18.0. 18.1, 18.2, 19.3, 19.4, 20.7, 92.7, 95.1, 96.4, 96.9, 99.0, 117.6, 120.8, 121.6, 123.7, 126.3, 126.4, 127.5, 129.1, 133.4, 134.0, 134.1, 140.6, 141.3, 141.5, 141.9, 142.1, 142.4, 142.9, 144.0, 145.4 ppm; UV-vis (DCM) λ_{max} (log ε) 408 (2.4), 438 (2.7), 505 (1.5), 538 (1.3), 578 (1.3), 669 (1.3) nm; MALDI-TOF MS ($C_{82}H_{74}N_8$): calcd 1170.6036, found [M+H]: 1171.6046.

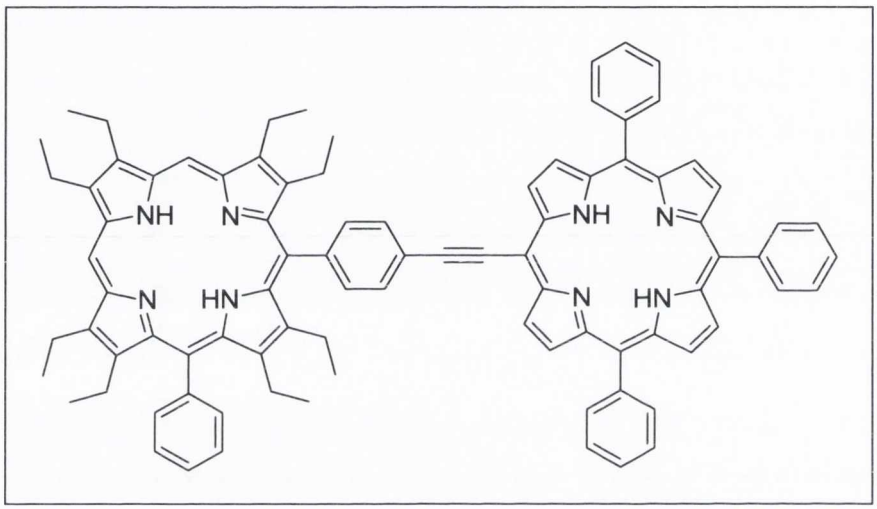
2,3,7,8,12,13,17,18-Octaethyl-5-[4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl]-10-phenylporphyrin 87



Prepared according to the above procedure using 1.0 equiv. of **84** and 1.0 equiv. of **26** to yield **87** as green solid (41 mg, 0.04 mmol, 50 %); mp > 300° C; R_f 0.2 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.61 (s (br) 2H), -2.43 (s (br), 2H), 1.29 (s (br), 12H), 1.86 (m, 12H), 2.34 (m, 3H), 2.71 (m, 3H), 3.89 (m, 10H), 7.88 (m, 8H), 8.33 (m, 4H), 8.41 (dd, J = 7.6 Hz, 8.2 Hz, 4H), 8.59 (d, J = 7.6 Hz, 2H), 9.02 (d, J = 5.0 Hz, 2H), 9.11 (d, J = 4.0 Hz, 2H), 9.34 (d, J = 4.0 Hz, 2H), 9.70 (d, J = 5.0 Hz, 2H), 10.08 (d, J = 5.0 Hz, 2H), 10.23 (s (br), 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.8, 18.0. 18.1, 18.2, 19.3, 19.4, 20.7, 92.7, 95.1, 96.4, 96.9, 99.0, 117.6, 120.8, 121.6, 123.7, 126.3, 126.4, 127.5, 129.1, 133.4, 134.0, 134.1, 140.6, 140.9, 147.1, 147.4 ppm;

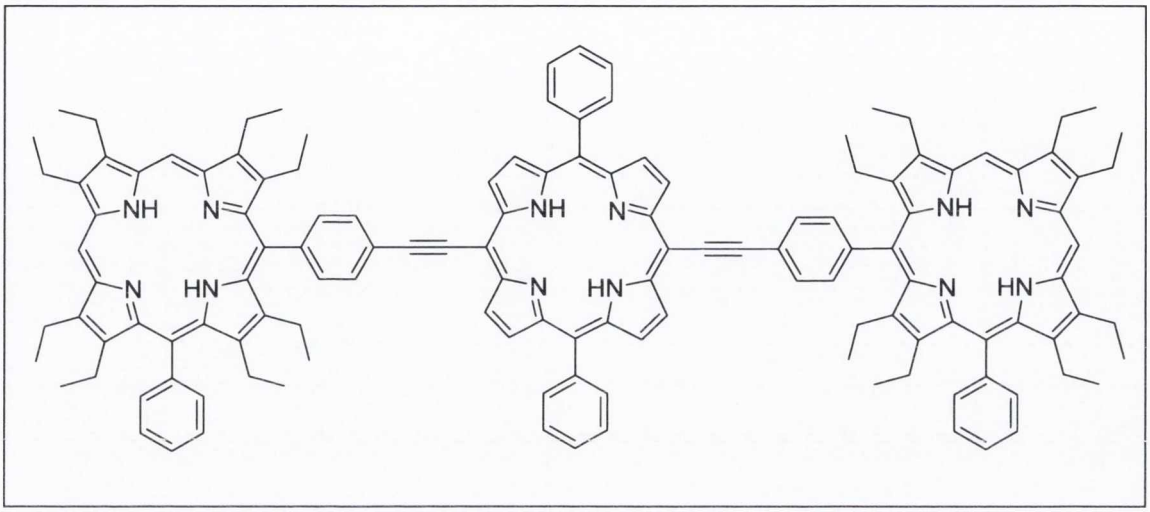
UV-vis (DCM) λ_{max} (log ε) 433 (2.5), 522 (1.5), 571 (1.5), 662 (1.2) nm; MALDI-TOF MS ($C_{132}H_{126}N_{12}$): calcd 1170.6036, found: [M+H] 1171.5989.

2,3,7,8,12,13,17,18-Octaethyl-5-[4-(10',15',20'-triphenylporphyrin-5-yl)phenylethynyl]-10-phenylporphyrin 88



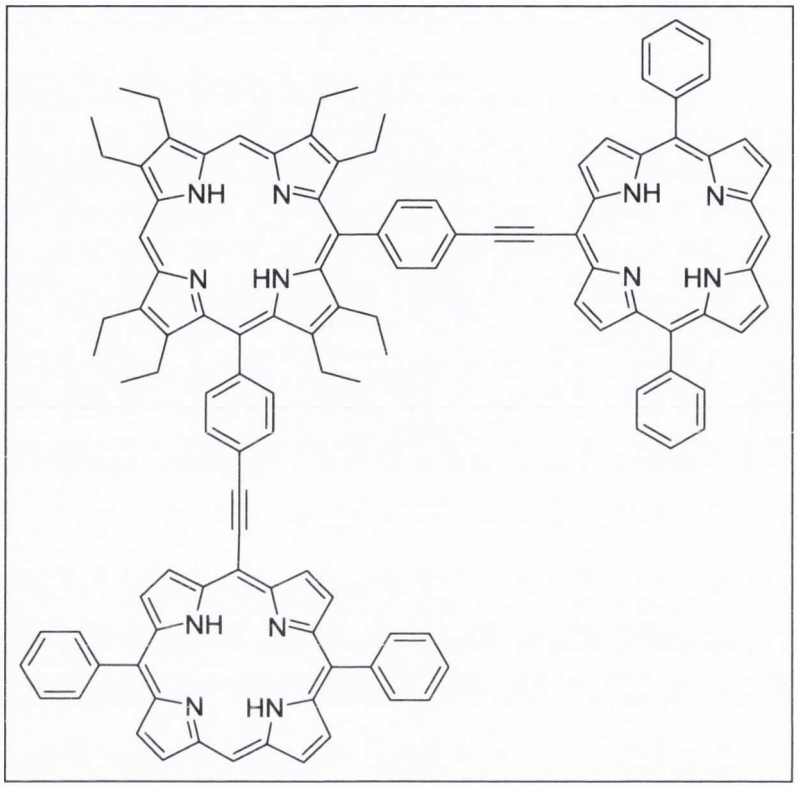
Prepared according to the above procedure using 1.0 equiv. of **84** and 1.0 equiv. of **43** to yield **88** as green solid (58.60 mg, 0.05 mmol, 47 %); mp > 300° C; R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.62 (s (br) 2H), -2.19 (s, 2H), 1.28 (s (br), 12H), 1.85 (m, 12H), 2.33 (m, 3H), 2.70 (m, 3H), 3.89 (m, 10H), 7.82 (m, 12H), 8.26 (dd, *J* = 7.6 Hz, 7.0 Hz, 8H), 8.40 (m, 4H), 8.58 (d, *J* = 7.6 Hz, 2H), 8.82 (s (br), 4H), 9.05 (d, *J* = 4.0 Hz, 2H), 9.70 (d, *J* = 5.8 Hz, 1H), 9.99 (d, *J* = 4.0 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.8, 18.0. 18.1, 18.2, 19.3, 19.4, 20.7, 92.7, 95.1, 96.4, 96.9, 99.0, 117.6, 120.8, 121.6, 123.7, 126.3, 126.4, 127.5, 129.1, 133.4, 134.0, 134.1, 140.6, 141.3, 141.5, 141.9, 142.1, 142.4, 142.9, 144.0, 145.4 ppm; UV-vis (DCM) λ_{max} (log ε) 451 (2,2), 605 (1.3), 647 (1.1), 702 (1.2) nm; MALDI-TOF MS ($C_{88}H_{78}N_8$): calcd 1246.6349, found: [M+H] 1247.6395.

5,15-Bis[4-(2',3',7',8',12',13',17',18'-Octaethylpoprhyrin-5-yl)ethynylphenyl]-10,20-diphenylporphyrin 89



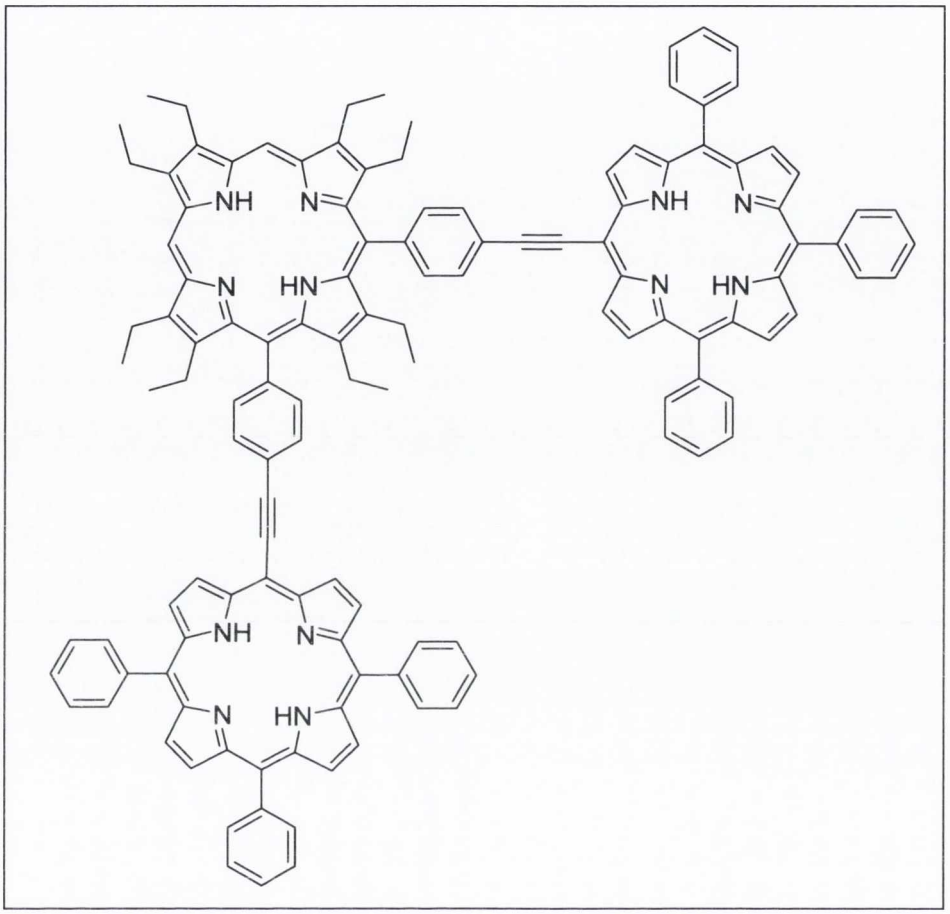
Prepared according to the above procedure using 2.0 equiv. of **84** and 1.0 equiv. of **27** to yield **89** as green solid (29.30 mg, 0.02 mmol, 39 %); mp > 300° C; R_f 0.2 (hexane/DCM, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.62 (s (br) 4H), -1.72 (s, 2H), 1.29 (s (br), 24H), 1.86 (m, 24H), 2.35 (m, 6H), 2.71 (m, 6H), 3.92 (m, 20H), 7.74 (m, 8H), 7.86 (m, 10H), 8.40 (m, 10H), 8.59 (m, 4H), 9.00 (d, J = 4.0 Hz, 2H), 9.71 (d, J = 5.0 Hz, 4H), 9.96 (d, J = 4.0 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.7, 17.1, 17.5, 17.7, 17.8, 19.2, 20.5, 29.3, 106.2, 120.3, 126.6, 127.5, 129.5, 130.3, 130.9, 131.1, 134.3, 135.4, 140.9, 147.1, 147.4 ppm; UV-vis (DCM) λ_{max} (log ε) 426 (2.4), 447 (2.5), 513 (1.6), 572 (1.6), 607 (1.7), 700 (1.5) nm; MALDI-TOF MS ($C_{132}H_{126}N_{12}$): calcd 1880.4932, found: [M+H] 1881.0201.

2,3,7,8,12,13,17,18-Octaethyl-5,10-bis[4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl]porphyrin 90



Prepared according to the above procedure using 1.0 equiv. of **82** and 1.0 equiv. of **26** to yield **90** as green solid (50 mg, 0.03 mmol, 74 %); mp > 300° C; R_f 0.5 (hexane/DCM, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.52, -2.44 (br, 6H), 0.65 (m, 6H), 0.87 (m, 11H), 1.29 (s (br), 7H), 1.89 (t, J = 6.4 Hz, 4H), 2.59 (s (br), 6H), 4.00 (m, 6H), 7.87 (s (br), 16H), 7.87 (s (br), 16H), 8.32 (d, J = 3.0 Hz, 9H), 8.47 (d, J = 8.0 Hz, 3H), 8.84 (d, J = 8.0 Hz, 3H), 9.01 (d, J = 4.6 Hz, 5H), 9.11 (d, J = 4.6 Hz, 3H), 9.33 (d, J = 3.0 Hz, 4H), 10.08 (m, 3H), 10.22 (s (br), 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.7, 17.1, 17.5, 17.7, 17.8, 19.2, 20.5, 29.3, 106.2, 120.3, 126.6, 127.5, 129.5, 130.3, 130.9, 131.1, 134.3, 135.4, 140.9, 147.1, 147.4 ppm; UV-vis (DCM) λ_{max} (log ε) 433 (2.6), 574 (1.7), 603 (1.4), 663 (1.4), 701 (1.2) nm; MALDI-TOF MS ($C_{116}H_{94}N_{12}$): calcd 1656.0680, found: 1656.7773.

2,3,7,8,12,13,17,18-Octaethyl-5,10-bis[4-(10',15',20'-triphenylporphyrin-5-yl)phenylethynyl]porphyrin 91

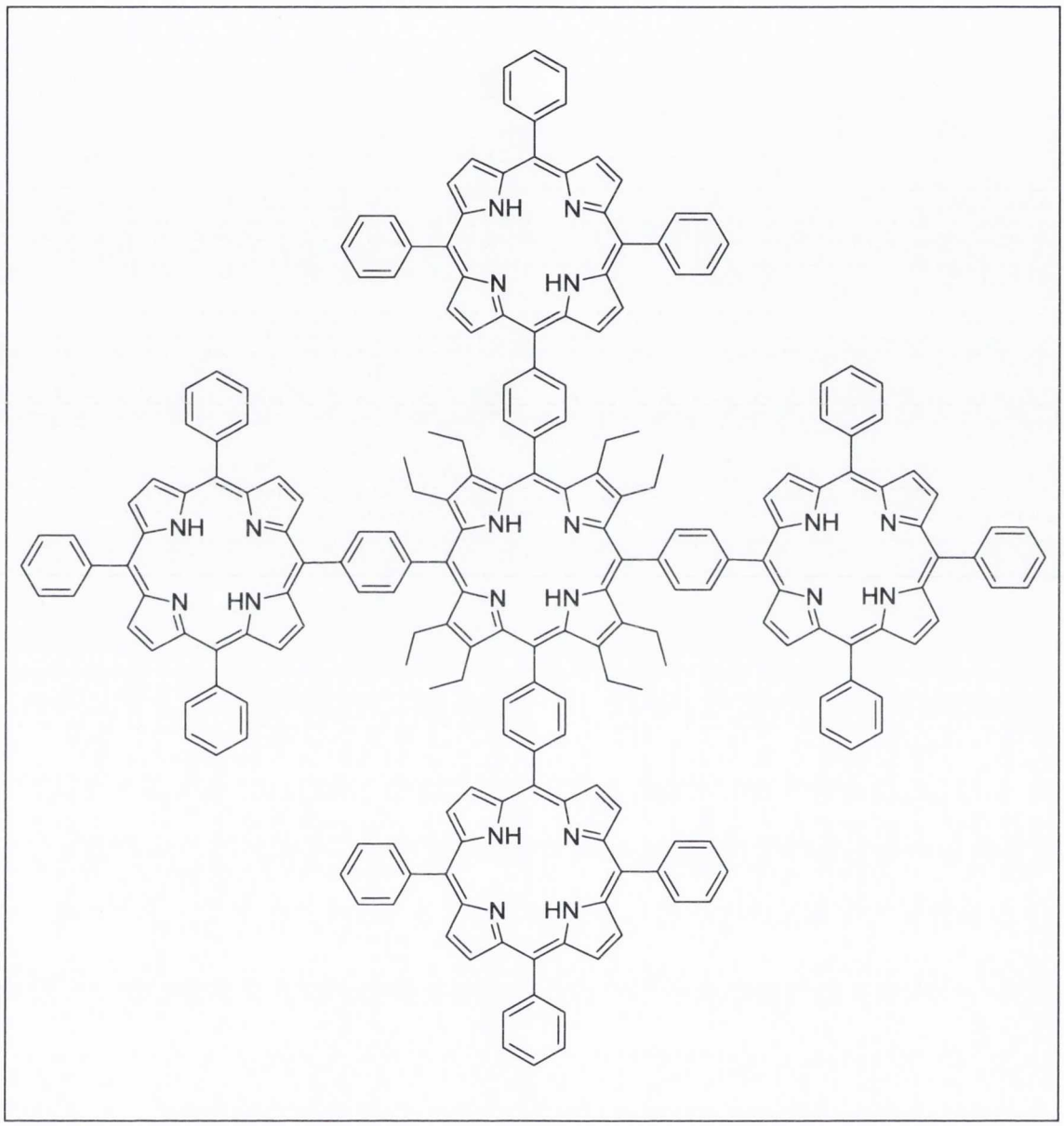


Prepared according to the above procedure using 1.0 equiv. of **82** and 1.0 equiv of **43** to yield **91** as green solid (70 mg, 0.04 mmol, 84 %); mp > 300° C; R_f 0.5 (hexane/DCM, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.55 (br, 2H), , -2.19 (s, 4H), 0.66 (m, 8H), 0.91 (m, 8H), 1.29 (s (br), 8H), 1.87 (m, 4H), 2.48 (m, 6H), 3.95 (m, 6H), 7.82 (m, 25H), 8.24 (m, 13H), 8.44 (m, 3H), 8.63 (m, 2H), 8.83 (s (br), 7H), 9.06 (s (br), 3H), 9.74 (s, 1H), 9.33 (d, J = 3.0 Hz, 4H), 10.00 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.5, 17.1, 17.7, 17.8, 18.2, 19.2, 20.3, 29.3, 120.8, 126.3, 126.4, 127.5, 129.5, 130.4, 134.0, 134.1, 141.3, 141.5 ppm; UV-vis (DCM) λ_{max} (log ε) 438 (2.6), 514 (1.4), 581 (1.7), 612 (1.1), 671 (1.2) nm; MALDI-TOF MS ($C_{128}H_{102}N_{12}$): calcd 1808.2599, found: 1808.8462.

General procedure for the synthesis of pentamers *via* Suzuki coupling reaction

2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraakis(5',10',15',20'-tetraphenylporphyrin)porphyrin **92** and 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraakis(5',10',15'-triphenylporphyrin)porphyrin **93** were prepared according to a procedure by Hyslop *et al.*[190] A 100 mL shlenk tube were charged with borylated porphrins (4.0 equiv.) and bromoporphyrin (1.0 equiv.) and THF (20 mL). The mixture was degasses (freeze-pump-thaw) three time and followed by addition of Cs_2CO_3 (5.0 equiv.) and the mixture was degassed again. $Pd(PPh_3)_4$ (0.13 equiv) was added and the mixture was refluxed under argon at 77 ^{o}C for 72h (monitored byTLC). The reaction mixture was filtered through silica gel and washed with DCM. After removal of the solvents under reduced pressure the residue was chromotographed on silica gel (hexane:DCM, 1:4, v/v) and recrystalized from DCM:MeOH.

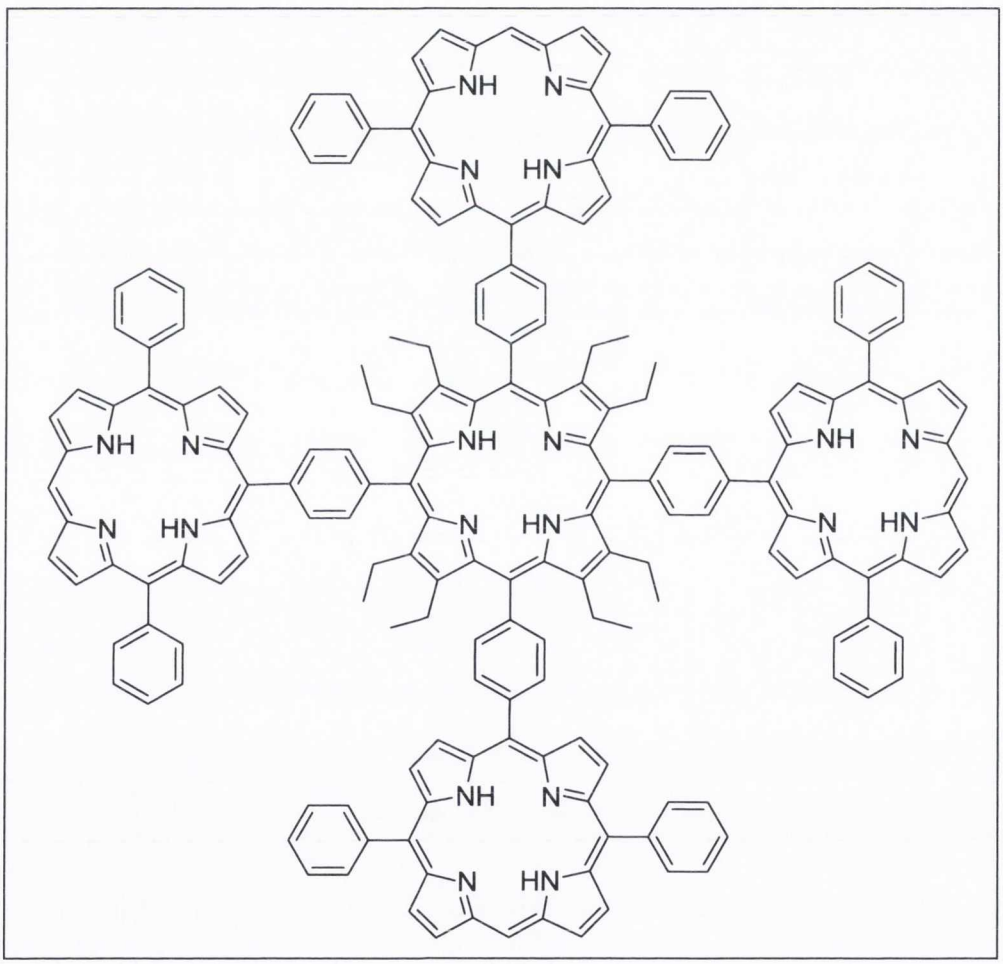
2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraakis(5',10',15',20'-tetraphenylporphyrin)porphyrin 92



Prepared according to the above procedure using 1.0 equiv. of **71** and 4.0 equiv. of **44** to yield **92** as green solid (50 mg, 0.02 mmol, 33 %); mp > 300° C; R_f 0.5 (DCM/ethyl acetate, 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.60 (s, 8H), 1.31 (m, 24H), 2.11 (m, 16H), 7.83 (s (br), 42H), 8.08 (m, 12H), 8.32 (m, 26H), 8.95 (s (br), 20H), 9.08 (m, 8H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2, 15.2, 15.5, 22.8, 25.0, 26.4, 27.0, 29.9,

30.3, 31.1, 31.8, 31.9, 32.0, 32.8, 33.3, 34.9, 66.3, 67.4, 96.4, 99.4, 102.3, 112.9, 113.6, 115.7, 116.7, 119.7, 124.2, 126.9, 132.6, 133.2, 136.0, 136.1, 137.6, 138.2, 138.7, 139.3, 139.4, 139.5, 140.3, 140.7, 141.4, 141.5, 143.5, 143.5, 143.9, 144.0, 145.0, 151.5, 159.3, 159.5, 173.2 ppm; UV-vis (DCM) λ_{max} (log ε) 418 (2.7), 484 (2.4), 554 (1.4), 590 (1.2), 648 (1.2), 702 (1.6) nm; MALDI-TOF MS ($C_{212}H_{158}N_{20}$): calcd 2985.6559, found: 2985.3506.

2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraakis(5',10',15'-triphenylporphyrin)porphyrin 93



Prepared according to the above procedure using 1.0 equiv. of **71** and 4.0 equiv. of **45** to yield **93** as green solid (80 mg, 0.03 mmol, 57 %); mp > 300° C; R_f 0.5 (DCM/ethyl

acetate, 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.83 (s, 8H), 0.94 (m, 14H), 1.02 (m, 8H), 1.30 (m, 16H), 7.86 (s (br), 30H), 8.09 (m, 6H), 8.35 (s (br), 20H), 8.82 (m, 8H), 9.13 (m, 16H), 9.43 (s (br), 8H), 10.32 (s (br), 4H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 15.0, 15.2, 22.8, 24.8, 26.6, 29.9, 30.1, 30.2, 30.9, 31.8, 32.0, 33.3, 34.9, 66.3, 67.3, 97.3, 99.3, 112.9, 118.3, 119.5, 119.6, 124.2, 126.9, 132.7, 133.3, 135.8, 137.5, 137.6, 138.2, 140.6, 141.4, 141.5, 143.0, 143.3, 143.4, 145.0, 146.1, 146.2, 147.4, 147.9, 151.4, 159.5, 173.1 ppm; UV-vis (DCM) λ_{max} (log ε) 413 (2.8), 486 (2.4), 547 (1.4), 585 (1.3), 641 (1.2), 704 (1.6) nm; MALDI-TOF MS ($C_{188}H_{142}N_{20}$): calcd 2681.2731, found: 2681.1184.

General procedure for the synthesis of metallated porphyrins

72, **73**, **75**, **76**, **78** and **79** were prepared according to a procedure by Buchler *et al.*[185] An excess of $Zn(OAc)_2$ or $Cu(OAc)_2$ (4.0 equiv.) was added to a solution of porphyrin (1.0 equiv.) in DCM/MeOH (22 mL 10:1 v/v) and mixture was stirred at room temperature for 2h. The conversion was monitored by TLC. The reaction was stopped when no more starting material appear on the TLC. The mixture was filtered by neutral alumina and washed with DCM and recrystalization with DCM/MeOH.

74, **77** and **80** were prepared according to a procedure by Buchler *et al.*[185] An excess of $Ni(OAc)_2.4H_2O$ (4.0 equiv.) was added to a solution of porphyrin (1.0 equiv) in DCM/toluene (20 mL 1:4 v/v) and mixture was reflux overnight at 130 °C. The conversion was monitored by TLC. The reaction was stopped when no more starting material appear on the TLC. The mixture was cooled it down to room temperature before filtered off through neutral alumina and eluted with DCM followed by recrystalization with DCM/MeOH.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-nitrophenyl)-porphyrin]copper 72

Prepared according to the above procedure using 1.0 equiv. of **69** and 4.0 equiv. of $Cu(OAc)_2$ to yield **72** as violet colour solid (42.70 mg, 0.04 mmol, 81 %); mp: > 300 °C; R_f 0.5 (hexane/DCM, 1:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (m, 40H), 8.96 (s (br), 16H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.2, 19.1. 116.4, 121.9, 136.0, 145.7, 147.5 ppm; UV-vis (THF) λ_{max} (log ε) 450 (2.4), 473 (2.4), 584 (1.6) nm; MALDI-TOF MS ($C_{60}H_{56}CuN_8O_8$): calcd 1079.3517, found: 1079.3507.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-nitrophenyl)-porphyrin]zinc 73

Prepared according to the above procedure using 1.0 equiv. of **69** and 4.0 equiv. of $Zn(OAc)_2$ to yield **73** as a green colour solid (50.70 mg, 0.05 mmol, 95 %); mp: > 300 °C;[208] R_f 0.5 (hexane/DCM, 1:4, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 0.54 (t, J = 7.0 Hz, 24H), 1.93 (q, J = 7.6 Hz, 8H), 2.66 (q, J = 7.6 Hz, 8H), 8.57 (d, J = 8.2 Hz, 8H), 8.65 (d, J = 8.2 Hz, 2H) ppm.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-nitrophenyl)-porphyrin]nickel 74

Prepared according to the above procedure using 1.0 equiv. of **69** and 4.0 equiv. of $Ni(OAc)_2$ to yield **74** as a green colour crystal (43 mg, 0.04 mmol, 82 %); mp: > 300 °C;[213] R_f 0.5 (DCM); ^1H NMR (400 MHz, $CDCl_3$) δ 0.37 (t, J = 7.0 Hz, 24H), 4.14 (q, J = 7.0 Hz, 16H), 8.77 (m,16H) ppm.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(pentafluorophenyl)-porphyrin]copper 75

Prepared according to the above procedure using 1.0 equiv. of **70** and 4.0 equiv. of $Cu(OAc)_2$ to yield **75** as a violet colour crystal (48.90 mg, 0.04 mmol, 93 %); mp: > 300 °C; R_f 0.3 (hexane/DCM, 4:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 0.72 (t, J = 7.6 Hz, 24H), 2.77 (m,16H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.5, 19.2, 99.4, 114.3, 136.1,

138.6, 140.7, 143.3, 145.5, 148.0; UV-vis (THF) λ_{max} (log ε) 431 (2.5), 571 (1.3), 609 (1.4) nm; MALDI-TOF MS ($C_{60}H_{40}F_{20}N_4Cu$): calcd 1259.2230, found: 1259.2209.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(pentafluorophenyl)-porphyrin]zinc 76

Prepared according to the above procedure using 1.0 equiv. of **70** and 4.0 equiv. of $Zn(OAc)_2$ to yield **76** as a violet colour solid (45.90 mg, 0.04 mmol, 80 %); mp: > 300 °C; R_f 0.5 (hexane/DCM, 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, J = 7.6 Hz, 24H), 2.25 (br, 6H), 2.73 (br, 10H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.8, 19.6, 29.3, 143.3, 146.5; UV-vis (THF) λ_{max} (log ε) 451 (2.3), 585 (0.8), 678 (1.3) nm; MALDI-TOF MS ($C_{60}H_{40}F_{20}N_4Zn$): calcd 1260.2225, found: 1260.2173

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(pentafluorophenyl)-porphyrin]nickel 77

Prepared according to the above procedure using 1.0 equiv. of **70** and 4.0 equiv. of $Ni(OAc)_2$ to yield **77** as a violet colour crystal (46.40 mg, 0.04 mmol, 88 %); mp: > 300 °C;[214] R_f 0.6 (hexane/DCM, 3:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (t, J = 7.0 Hz, 24H), 2.25 (br, 16H) ppm.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-bromophenyl)-porphyrin]copper 78

Prepared according to the above procedure using 1.0 equiv. of **71** and 4.0 equiv. of $Cu(OAc)_2$ to yield **78** as a violet colour crystal (44.10 mg, 0.04 mmol, 84 %); mp: > 300 °C; R_f 0.5 (hexane/DCM, 3:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (m, 24H), 1.58 (br, 16H), 8.20 (br,16H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.7, 19.0, 114.5, 123.3, 129.4, 135.0, 137.3, 142.1, 145.4; UV-vis (THF) λ_{max} (log ε) 435 (2.4), 573 (1.3) nm; MALDI-TOF MS ($C_{60}H_{56}Br_4N_4Cu$): calcd 1211.0534, found: 1211.0540.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-bromophenyl)-porphyrin]zinc 79

Prepared according to the above procedure using 1.0 equiv. of **71** and 4.0 equiv. of $Zn(OAc)_2$ to yield **79** as a violet colour crystal (34.10 mg, 0.04 mmol, 64 %); mp: > 300 °C; R_f 0.4 (hexane/DCM, 3:2, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 0.67 (m, 24H), 1.44 (br, 16H), 8.25 (br,16H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.5, 20.2, 114.5, 121.3, 130.8, 133.2, 138.0, 144.1, 144.9; UV-vis (THF) λ_{max} (log ε) 481 (2.5), 640 (0.6), 696 (1.5) nm; MALDI-TOF MS ($C_{60}H_{56}Br_4N_4Cu$): calcd 1212.0530, found [M-Br+H_2O]: 1151.1452.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra(4-bromophenyl)-porphyrin]nickel 80

Prepared according to the above procedure using 1.0 equiv. of **71** and 4.0 equiv. of $Ni(OAc)_2$ to yield **80** as a violet colour crystal (50 mg, 0.04 mmol, 46 %); mp: > 300 °C; R_f 0.5 (hexane/DCM, 3:2, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 0.54 (t, J = 7.6 Hz, 24H), 2.25 (br, 16H), 7.77 (d, J = 8.2 Hz, 8H), 7.96 (d, J = 8.2 Hz, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.5, 19.2, 115.5, 122.3, 129.8, 135.2, 138.3, 144.1, 145.0; UV-vis (THF) λ_{max} (log ε) 435 (2.5), 555 (1.2), 592 (1.1) nm; MALDI-TOF MS ($C_{60}H_{56}Br_4N_4Ni$): calcd 1206.0592, found: 1206.0540.

CHAPTER 6

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